CHAPTER 1

HISTORICAL BACKGROUND AND INTRODUCTORY CONCEPTS

1.1. Brownian motion

The first detailed account of Brownian motion was given by the eminent botanist Robert Brown in 1827 [1, 2] while studying the plant life of the South Seas. In this study, he dealt with the transfer of pollen into the ovulum of a plant. He examined aqueous suspensions of pollen grains of several species under a microscope and invariably found that the pollen grains were in "*rapid oscillatory motion.*"

Initially, he thought that the movement was not only "vital" (in the sense of not having a physical cause), but peculiar to the male sexual cells of plants. He quickly disembarrassed himself of this explanation on observing that the motion was exhibited by grains, which he called irritable particles, of both *organic* and *inorganic* matter in suspension. We describe the evolution of Brown's reasoning in his own words [1]:

> "...having found, as I believed, a peculiar character in the motion of the particles of pollen in water, it occurred to me to appeal to this peculiarity as a test in certain cryptogamous plants, namely Mosses and the genus *Equisetum*, in which the existence of sex organs had not been universally admitted ... But I at the same time observed, that on bruising the ovula or seeds of *Equisetum*, which at first happened accidentally, I so greatly increased the number of moving particles, that the source of the added quantity could not be doubted. I found also that on bruising first the floral leaves of Mosses, and then all other parts of those plants, that I readily obtained similar particles not in equal quantity indeed, but equally in motion. My supposed test of the male organ was therefore necessarily abandoned. ... Reflecting on all the facts with which I had now become acquainted, I was disposed to believe that the minute spherical particles or Molecules of apparently uniform size, ... were in reality the supposed constituent or elementary molecules of organic bodies, first so considered by Buffon and Needham ..."

Brown investigated whether the motion was limited to organic bodies:

> "...a minute portion of silicified wood, which exhibited the structure of *Coniferae*, was bruised, and spherical particles, or molecules in all respects like those so frequently mentioned, were readily obtained from it; in such quantity,

> however, that the whole substance of the petrification seemed to be formed of them. But hence I inferred that these molecules were not limited to organic bodies, nor even to their products."

Later, he writes:

> "Rocks of all ages, including those in which organic remains have never been found, yielded the molecules in abundance. Their existence was ascertained in each of the constituent minerals of granite, a fragment of the Sphinx being one of the specimens examined."

Brown finally describes the motion as "matter is composed of small particles which he called *active molecules* that exhibit a rapid irregular motion having its origin in the particles themselves and not in the surrounding fluid" [1]. Following Brown's work there were many years of speculation [1, 2, 3] about the cause of the phenomenon, before Einstein made conclusive mathematical predictions of a diffusive effect arising from the random thermal motions of particles in suspension. Most of the hypotheses advanced in the nineteenth century could be dismissed by considering an experiment described by Brown in which a drop of water of microscopic size, immersed in oil and containing just one particle, unceasingly exhibited the motion. According to Nelson [1], the first investigator to express a notion close to the modern theory of Brownian movement (i.e., that the perpetual haphazard motion or Brownian *Schwankung* is caused by bombardment of the Brownian particle by the particles of the surrounding medium) was C. Weiner in 1863 [3].

We mention the very detailed experimental investigation made by Gouy, which strongly supported the kinetic-theory explanation. Gouy's conclusions may be summarized by the following seven points [1, 2, 3].

(1) The motion is very irregular, composed of translations and rotations, and the trajectory appears to have no tangent.
(2) Two particles appear to move independently, even when they approach one another to within a distance less than their diameter.
(3) The smaller the particles, the more active the motion.
(4) The composition and density of the particles have no effect on the motion.
(5) The less viscous the fluid, the more active the motion.
(6) The higher the temperature, the more active the motion.
(7) The motion never ceases.

Point 1 is of profound interest in view of the later work of N. Wiener [1], who proved in 1923 that the sample points of the Brownian-motion trajectory

are almost everywhere continuous, but nowhere differentiable. Despite these careful observations in favor of kinetic theory, however, several arguments always seemed to militate against it. We give below two of the most prominent.

An early attempt to explain Brownian motion in terms of collisions was made by von Nägeli. We consider the *conservation of momentum* during an atomic collision with a macroscopic Brownian particle of mass M and velocity $\dot{s}$. If the surrounding molecules each have mass m and velocity v, the velocity change Δv of the molecule on a *single* impact is $(m/M)\,v$. Now if v is calculated from the kinetic-theory equation

$$m\langle v^2\rangle / 2 = 3kT / 2$$

(where $k = 1.38 \times 10^{-23}\ \mathrm{J\,K^{-1}}$ is the Boltzmann constant and T is the absolute temperature), and then the principle of conservation of momentum is applied, Δv for a typical Brownian particle (10^{-6} m in diameter) in water at 300 K is about $5 \times 10^{-8}\ \mathrm{m\,s^{-1}}$. The observed Brownian movement for this system, however, is *greater* than this by two orders of magnitude. Von Nägeli was aware of this discrepancy; however, he could not explain it in terms of collisions because he assumed that these would produce *zero net effect*. Thus, he effectively calculated only the velocity change as a result of a *single* collision. His error lay in regarding the random collisions as occurring in regularly alternating directions that would keep bringing the target molecule back to its starting position. This assumption is invalid, because if n random collisions occur (see the discussion of the random-walk problem in Ref. [4]), the displacement (root-mean-square value) will be proportional to $n^{1/2}$. Now, if the time interval between successive observations of the particle is τ, n will be proportional to τ. Thus the root-mean-square value of the displacement is proportional to $\tau^{1/2}$, and *not zero* as assumed by von Nägeli.

Many investigators assumed (correctly) that the macroscopic Brownian particle could be treated simply as an enormous "atom" of mass M. This would also allow a test of the kinetic theory, because the law of equipartition of energy implied that the kinetic energy of translation of a Brownian particle and of a molecule should be equal. Thus, the velocity $\dot{s}$ of a Brownian particle should be given by that of a molecule:

$$\frac{1}{2}M\langle \dot{s}^2\rangle = \frac{3}{2}kT. \tag{1.1.1}$$

For the system described above, $\langle \dot{s}^2\rangle$ predicted by Eq. (1.1.1) is much greater than the visually observed value. The explanation is that the equipartition formula above holds only when the *time between observations* is of the order of

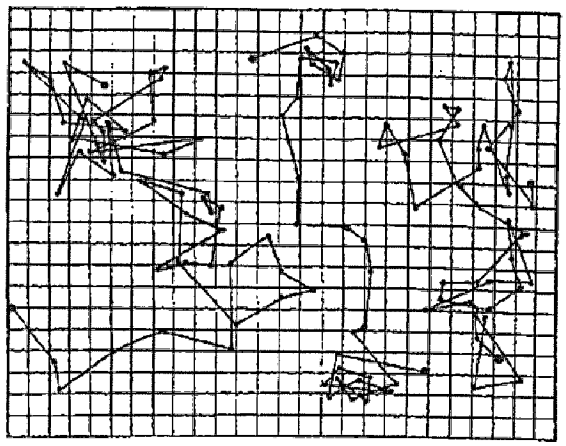


Figure 1.1.1. Trajectory of a Brownian particle: three drawings obtained by tracing the segments which join the consecutive positions of the particle at intervals of 30 s. After J. Perrin, *Brownian movement and molecular reality*, London, Taylor & Francis, 1910.

the *time between collisions*. In practice, we cannot make observations to such a fine degree.

To aid our argument let us consider $\langle \dot{s}^2 \rangle$ more closely. Suppose we observe at 30 s intervals the motion of a Brownian particle and plot its two-dimensional "random walk." Its trajectory looks like that shown in Fig. 1.1.1. Suppose the same random walk had been observed at intervals τ of 10 s. There would then be three times as many points, and the overall impression would be that the particle is moving $\sqrt{3}$ times as fast. During a time interval τ the particle undergoes millions of collisions, so as the time interval between observations is decreased still further, the apparent velocity continues to increase, and only when τ is of the order of the time between collisions will Eq. (1.1.1) hold true. We note that the trajectory that we will observe is in no sense the actual path of the particle; consider the following remarks of Fowler [5, 6]:

> "We can never follow the details of the movement of the grain [(Brownian particle)], which has a kink at every molecular collision—about 10^{21} times a second in an ordinary liquid... What we observe as displacements are of the nature of residual fluctuations about a mean value zero, and have little direct connection with the actual detailed path of the grain. To our senses (pushed to their farthest limit in the form of [the best cine camera] taking 10^5 pictures a second) the details of the path are impossibly fine. The path may fairly be compared in a crude way to the graph of a continuous function with no [derivative]." (We shall say more of this later)

The above remarks of Fowler have been beautifully reinforced and added to by Schroeder [7] – see his Fig. 1, p. 142 – where Brownian motion is cited as the supreme example of a *random fractal phenomenon*. Fractals are, in general

(as defined by Mandelbrot [8]), exceedingly fine-grained structures that exhibit *self-similarity* with respect to *multiplicative changes in scale*. In other words, a self-similar object appears [7] unchanged after increasing or decreasing its size. Self-similar objects typify many laws of nature which are independent, or nearly so, of a scaling factor, examples of scale factors being [7] Planck's constant or the speed of light. Perhaps a useful working definition for physicists of a fractal is that attributed to Mandelbrot by Feder [9]:

> "A fractal is a shape made of parts similar to the whole in some way."

For the purposes of this book, fractals may be considered [9] as sets of points embedded in a space. (A detailed account of Brownian paths considered as fractals is available in the book of Mazo [10].)

In the context of a record of Brownian motion as a random fractal object, the *statistically* self-similar nature of the observations (realizations) of Brownian motion (that is, the Brownian record looks "the same" [9]) constitutes *scale invariance* or *symmetry* of the Brownian record. In Brownian motion, the range of lengths over which statistical self-similarity prevails may run from macroscopic sizes almost down to the mean free path of a molecule.

1.2. Einstein's explanation of Brownian movement

It was left to Einstein in 1905 to explain Brownian movement, essentially by combining (in the sense that the velocity, but not the displacement, distribution is in equilibrium) the elementary stochastic process known as the random walk with the Maxwell–Boltzmann distribution [3]. His ideas may be summarized thus: If a particle in a fluid without friction receives a blow due to a collision with a molecule, then the *velocity* of the particle changes. However, if the fluid is very viscous, the change in velocity is quickly dissipated and the net result of an impact is a change in the displacement of the particle. Thus, Einstein assumed that the cumulative effect of collisions is to produce random jumps in the *position* of a Brownian particle; that is, the particle performs a kind of random walk. Taking the jumps in the walk as small, he obtained a partial differential equation for the probability density function of the displacement in one dimension [3]. This equation is a diffusion equation similar to that for unsteady heat conduction. It is the simplest case of a class of equations (probability density diffusion equations) that have become known as the *Fokker–Planck equations*. Einstein obtained its solution, from which he was able to show that the mean-square displacement of a Brownian particle should increase linearly with time. By using the fact that at equilibrium the Maxwellian distribution of

velocities must hold, he was able to express the constants in the solution in terms of the temperature and the viscosity of the fluid. Einstein's formula for the mean-square displacement was verified experimentally by Perrin in 1908 [1, 2, 6]. He obtained from Einstein's formula a value of Avogadro's number that agreed to within 19% with the accepted value. This provided powerful evidence for the molecular structure of matter.

It is interesting to recall that Einstein formulated his theory without having observed Brownian movement, but predicted that such a movement should occur from the standpoint of the kinetic theory of matter. We quote from his paper [3]:

> "...according to the molecular-kinetic theory of heat, bodies of microscopically-visible size suspended in a liquid will perform movements of such magnitude that they can be easily observed in a microscope, on account of the molecular motions of heat. It is possible that the movements to be discussed here are identical with the so-called "Brownian molecular motion": however, the information available to me regarding the latter is so lacking in precision, that I can form no judgment in the matter... If the movement discussed here can actually be observed (together with the laws relating to it that one would expect to find), then classical thermodynamics can no longer be looked upon as applicable with precision to bodies even of dimensions distinguishable in a microscope: an exact determination of actual atomic dimensions is then possible. On the other hand, had the prediction of this movement proved to be incorrect, a weighty argument would be provided against the molecular-kinetic conception of heat."

and later:

> "...from the standpoint of the molecular kinetic theory of heat... a dissolved molecule is differentiated from a suspended body *solely* by its dimensions, and it is not apparent why a number of suspended particles should not produce the same osmotic pressure as the same number of molecules. We must assume that the suspended particles perform an irregular movement—even if a very slow one—in the liquid, on account of the molecular movement of the liquid."

We remark, by way of historical background, that Laplace [11] in 1812 obtained a partial differential equation similar to the Fokker–Planck equation, in a discussion of the mixing of balls drawn and replaced at random from two urns, and that a similar equation was obtained by in 1894 by Rayleigh [12], who wished to find the probability distribution function of a sum of n sinusoidal motions all having the same period and amplitude with a *random* distribution of phases. For $n \to \infty$, Rayleigh [12] obtained a diffusion equation similar to that of Einstein. Both of the previous examples are forms of the random walk problem which is discussed at length in [4, 13, 14, 15, 16] in the context of Brownian movement. The first clear statement of the random walk problem seems to have been made by Karl Pearson in 1905 [4, 5].

> "A man starts from a point O and walks l yards in a straight line; he then turns through any angle whatever and walks another l yards in a second straight line. He repeats this process n times. I require the probability that after these n stretches he is at a distance between r and $r + \delta r$ from his starting point, O."

The phrase "turns through any angle whatever and walks another l yards in a second straight line" constitutes a *Stosszahlansatz* or *mechanism* of the random walk process.

Bachelier in 1900 made a mathematical model of the French Stock Exchange and obtained a diffusion equation similar to that of Einstein [2, 5, 17, 18, 19, 20]. Later [5] (1911, 1912), he studied the related problem of the Gambler's Ruin, which is in effect a type of random walk problem. He showed that, when the sequence of bets placed by the gambler is large, it is simpler to formulate a continuous model of the process. He was again led to a type of Fokker–Planck equation. More examples are given by Gardiner [14], and further applications to financial problems are given in [18, 19, 20]. A rudimentary, but nonetheless useful intuitive derivation of the specialized form of the Fokker–Planck equation, known as the Smoluchowski equation, may be given as follows.

Suppose that we have f Brownian grains per unit volume suspended in a liquid per unit volume between $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$ at time t. Suppose further that these particles are subject to an external force which is the negative gradient of a potential $V(\mathbf{r})$, so that

$$\mathbf{K} = -\text{grad}V(\mathbf{r}) = -\nabla_{\mathbf{r}}V(\mathbf{r}). \tag{1.2.1}$$

Now consider a volume υ in the liquid bounded by a closed surface S, and calculate the (drift) current of particles crossing S due to the action of $\mathbf{K}$. We have by Gauss's divergence theorem

$$\frac{\partial}{\partial t}\int_{\upsilon} f(\mathbf{r},t)\,d\upsilon = -\int_{S}\mathbf{J}_{\mathrm{d}}\cdot\mathbf{n}dS = -\int_{\upsilon}\text{div}\mathbf{J}_{\mathrm{d}}\,d\upsilon, \tag{1.2.2}$$

where $\mathbf{J}_{\mathrm{d}}$ is the current density of particles and $\mathbf{n}$ is the unit normal to S. Thus, we have the continuity equation

$$\dot{f} + \text{div}\mathbf{J}_{\mathrm{d}} = 0, \tag{1.2.3}$$

which is the law of conservation of representative points. Now, the drift current is $\mathbf{J}_{\mathrm{d}} = f\mathbf{v}$. Here $\mathbf{v}$ is the drift velocity of a particle moving in the liquid. On supposing that $\mathbf{K} - \zeta\mathbf{v} = 0$, where $-\zeta\mathbf{v}$ is the viscous drag and ζ is the drag coefficient of a particle, the drift current is

$$\mathbf{J}_{\mathrm{d}} = -\frac{f}{\zeta}\nabla_{\mathbf{r}}V. \tag{1.2.4}$$

The analysis so far takes no account of the thermal agitation of the particles (the Brownian movement). In order to take account of this let us now add to $\mathbf{J}_d$ a diffusive term

$$\mathbf{J}_{\text{diff}} = -D\nabla_{\mathbf{r}} f, \tag{1.2.5}$$

where D is the diffusion coefficient, in this instance, kT/ζ. The addition of this diffusive term makes the distribution $f(\mathbf{r}, t)$ more nearly uniform. The continuity equation, Eq. (1.2.3), then becomes

$$\frac{\partial f}{\partial t} = D\text{div}\left(\nabla_{\mathbf{r}} f + \frac{f}{kT}\nabla_{\mathbf{r}} V\right), \tag{1.2.6}$$

which is the specialized form of the Fokker–Planck equation known as the *Smoluchowski equation*, which describes approximately the evolution of f in configuration space. (For a detailed account of Smoluchowski's method of derivation of this equation, which was based on a specific detailed kinetic model, namely collisions of hard spheres, see Mazo [10]). Equation (1.2.6) was first [5] given by Einstein in 1905 for the special case of $V = 0$. In general, direct justification of the inclusion of thermal agitation by adding the diffusive term of Eq. (1.2.5) is difficult; nevertheless, it yields the same results (with very much less labor) as the detailed methods of derivation of the Fokker–Planck equation presented below. The *stationary* solution of the Fokker–Planck equation is the solution with $\dot{f} = 0$. The diffusion coefficient D is found by requiring that, in general, the stationary solution should be the Boltzmann distribution (with certain restrictions, such as the case of a particle moving in a tilted cosine potential, which are discussed in [21]; see Chapter 5). The approximate Smoluchowski equation assumes that the velocity distribution has reached statistical equilibrium, i.e., that it has the Maxwellian distribution.

Another form of the Fokker–Planck equation which we shall be referring to later is the *Klein–Kramers equation* [5] (originally derived by Klein in 1921 [4]) which describes the evolution of the density $f(\mathbf{r}, \mathbf{v}, t)$ of representative points in phase space $(\mathbf{r}, \mathbf{v})$, viz.,

$$\frac{\partial f}{\partial t} + \mathbf{v}\cdot\nabla_{\mathbf{r}} f - \frac{1}{m}\nabla_{\mathbf{v}} f \cdot \nabla_{\mathbf{r}} V = \frac{\zeta}{m}\left[\text{div}_{\mathbf{v}}\left(\mathbf{v}f\right) + \frac{kT}{m}\nabla_{\mathbf{v}}^2 f\right]. \tag{1.2.7}$$

The Fokker–Planck equation is a partial differential equation of parabolic type. In the mathematical literature, it is called a *forward Kolmogorov equation*. It may be described in general terms as a diffusion equation with an additional first-order derivative $\nabla_{\mathbf{r}}$ with respect to position (i.e., a convective or

hydrodynamical derivative). The rigorous derivation of the Fokker–Planck equation is given in Section 1.9.

The detailed derivation of Einstein's formula for the mean-square displacement of a Brownian particle and the associated Fokker–Planck equation will be given in Section 1.4 below. We shall first, however, give the calculation of the mean-square displacement using the method based on the equation of motion of the random variable proposed by Langevin [22] in 1908; it is the extension of this method to treat nonlinear dynamical systems without recourse to the Fokker–Planck equation which is the principal concern of this book.

More specifically, the method of calculation of the average properties of a dynamical system (e.g., mean-square displacement, velocity correlation function, etc.) which has hitherto been used is to construct the Fokker–Planck equation in phase space from the Langevin equation for random variables representing, say, the position and velocity of a Brownian particle. The distribution function is then expanded where possible into a product of a set of orthogonal functions in the position, and an orthogonal set in the velocities, corresponding directly to the averages of the dynamical quantities which one wishes to calculate. For example, for rotational Brownian motion about a fixed axis, one will obtain a Fourier–Hermite series (see Chapter 10). The above procedure leads to a set of differential-recurrence relations for the coefficients of the generalized Fourier series, which govern the time behavior of the averages of the desired dynamical quantities (observables). The same is true for the Smoluchowski equation, which supposes that equilibrium of the velocities has been attained (here the configuration space distribution is expanded in a set of orthogonal functions in the configuration variables), and which is approximately valid if inertial effects are small. Our main objective is to show (by suitable transformation of, and averaging of, the Langevin equation interpreted as an integral equation according to the Stratonovich rule; see Chapter 2, Section 2.3) how the set of differential-recurrence relations may be generated directly from the Langevin equation. The Fokker–Planck equation is then bypassed entirely.

The advantages of this formulation of the theory are that:

(a) In general, Langevin's method is far easier to comprehend than that based on the Fokker–Planck equation, as it directly utilizes the concept of the time evolution of the random variable describing the process, rather than the time evolution of the underlying probability distribution. Indeed, to quote Wang and Uhlenbeck [13], the Langevin equation is "the real basis of the theory of the Brownian motion," since the drift and

diffusion coefficients in the Fokker–Planck equation must be calculated from it *a priori*.

(b) The need to construct the Fokker–Planck equation from the Langevin equation is dispensed with.

(c) It is often very difficult to separate the variables in the Fokker–Planck equation by expanding in the orthogonal sets of functions corresponding to the observables, Langevin's method avoids such a procedure, all that is required is the interpretation of his equation as an integral equation (see Section 1.10 and Chapter 2).

For ease of comparison with the work of the early investigators, we shall adhere to their notation as far as possible in Sections 1.3–1.6; these sections constitute a detailed account of the work of Einstein and Langevin including a brief summary of those parts of statistical mechanics which are essential to our discussion. Thus, in these sections, no distinction is made between a random variable $\xi(t)$ and one of its realizations $x(t)$, as is often done in theoretical physics. We will also, in these sections, use the notation $f(x, t)$ for the probability density function (PDF) in configuration space adopted by Einstein, rather than $W(x, t)$ (which is used in the rest of the book) or $\rho(\mathbf{q}, \mathbf{p}, t)$ (when treating the Liouville equation in Section 1.5). Section 1.6 constitutes an introduction to those parts of the theory of probability which are needed; hence, in accordance with standard textbooks in statistics, the letter $\xi(t)$ is used to denote a time-dependent random variable, and lower case roman letters, e.g., $x(t)$, are realizations. Elsewhere, unless evident from the context, we shall always use $\xi(t)$ to denote a random (stochastic) variable.

1.3. The Langevin equation

The theory of Brownian movement as formulated by Einstein [3] and Smoluchowski [4], although in agreement with experiment, seemed far removed from the Newtonian dynamics of particles [1], as it appeared to rely on the concept of the PDF of Brownian particles and the Fokker–Planck equation for the time evolution of that PDF. It was Langevin who, in 1908, by introducing the concept of the equation of motion of a random variable (in this case the position of a Brownian particle), initiated, to quote Nelson [1], "a new train of thought culminating in a truly dynamical theory of Brownian motion" (*inter alia* conceiving the idea of a stochastic differential equation). Notwithstanding this, it must be emphasized that the reduction of Brownian motion to Newtonian

particle dynamics is still incomplete, as the problem (or one formulation of it [1]) is to deduce each of the following theories from the one below it:

- Einstein–Smoluchowski
- Ornstein–Uhlenbeck
- Maxwell–Boltzmann
- Hamilton–Jacobi

The reader is referred to Section 4 of [4], Chapter VI of [23], [5], and [15] for further discussions of this problem. The Ornstein–Uhlenbeck theory which, with its subsequent additions, is itself a rigorous formulation of Langevin's ideas, is discussed in detail later.

Langevin [5, 22] began by simply writing down the equation of motion of the Brownian particle according to Newton's laws, assuming that it experiences two forces arising from the heat bath, namely: (i) A systematic force (viscous drag) $-\zeta \dot{x}(t)$, which represents a dynamical friction experienced by the particle encouraging collapse to a "dead" state [24] ($\dot{x}$ is the velocity and ζ is the coefficient of friction). (ii) A rapidly fluctuating force $F(t)$, which is due to the impacts of the molecules of the liquid on the particle, now called white noise. This is the residual force exerted by the surroundings or heat bath when the frictional force has been subtracted and which keeps the motion "alive" [24].

Thus, Langevin's stochastic differential equation of motion, according to Newton's second law, is, for a particle of mass m,

$$m\ddot{x}(t) = -\zeta \dot{x}(t) + F(t). \tag{1.3.1}$$

The friction term $\zeta \dot{x}$ is assumed to be governed by Stokes' law, which states that the frictional force decelerating a spherical particle of radius a is

$$\zeta \dot{x} = 6\pi\eta a\dot{x}, \tag{1.3.2}$$

where η is the viscosity of the surrounding fluid. The following assumptions are made about the fluctuating part $F(t)$ [5]: (i) $F(t)$ is independent of x, (ii) $F(t)$ varies extremely rapidly compared to the variation of $x(t)$, and (iii) $F(t)$ is so irregular that the average

$$\overline{F(t)} = 0. \tag{1.3.3}$$

The overbar in Eq. (1.3.3) means the statistical average over an ensemble of particles, each particle in the ensemble starting with the *same* (sharp) initial conditions. Assumption (ii) above implies that each collision is practically instantaneous. This rapid variation can be expressed by [5]

$$\overline{F(t)F(t')} = 2\zeta kT\delta(t-t'), \tag{1.3.4}$$

where $\delta(t)$ is the Dirac delta function, t and t' are distinct times, and $2\zeta kT$ is called the *spectral density*; this is flat, i.e., independent of frequency ω, so that we have *white noise* (Section 1.7 and Chapter 3). Formally speaking,

$$\overline{F(t)F(t')} = \overline{F(t)F(t+\tau)} = \lim_{T'\to\infty} \frac{1}{T'} \int_{-T'/2}^{T'/2} F(t)F(t+\tau)dt,$$

which is the time average of a two-time product over an arbitrary range time T' which is allowed to become infinite [14]. In reality, the *autocorrelation function* (ACF), Eq. (1.3.4), starting from $2\zeta kT$, does not drop instantaneously to zero, so that the spectral density $\Phi_F(\omega)$ does not have the constant value $2\zeta kT$ at very high frequencies (colored noise). Consequently, the situation where $\Phi_F(\omega)$ is constant for all ω (white noise), corresponding in the time domain to the delta function ACF of Eq. (1.3.4), is the limiting case of a purely random process (i.e., a process without a memory) which will never [25] occur in practice. It will become apparent later (see Section 1.6.3) that $F(t)$ is a *centered Gaussian* random variable and that $F(t)$ obeys *Isserlis's theorem* [13, 26]

$$\overline{F_1F_2\cdots F_{2n}} = \overline{F(t_1)F(t_2)\cdots F(t_{2n})} = \sum\prod\nolimits_{k_i<k_j} \overline{F(t_{k_i})F(t_{k_j})}, \qquad (1.3.5)$$

where the sum is over all distinct products of expectation value pairs, each of which is formed by selecting n pairs of subscripts from $2n$ subscripts. For example, when $n=2$, we have

$$\overline{F_1F_2F_3F_4} = \overline{F_1F_2}\ \overline{F_3F_4} + \overline{F_1F_3}\ \overline{F_2F_4} + \overline{F_1F_4}\ \overline{F_2F_3}. \qquad (1.3.6)$$

In general, there will be $(2n)!/(2^n n!)$ such distinct pairs. We also have, for an odd number of observations,

$$\overline{F(t_1)F(t_2)\cdots F(t_{2n+1})} = 0.$$

By transforming Eq. (1.3.1) into a *stochastic differential equation corresponding to the desired observable*, Langevin [5] derived the formula for the *mean-square displacement* of the Brownian particle as follows. On multiplying Eq. (1.3.1) by $x(t)$, since

$$\dot{x}x = \frac{1}{2}\frac{d}{dt}x^2 \quad \text{and} \quad \ddot{x}x = \frac{1}{2}\frac{d}{dt}\left(\frac{d}{dt}x^2\right) - \dot{x}^2,$$

we have

$$\frac{m}{2}\frac{d}{dt}\left(\frac{d}{dt}x^2(t)\right) - m\dot{x}^2(t) = -\frac{\zeta}{2}\frac{d}{dt}x^2(t) + F(t)x(t). \qquad (1.3.7)$$

Equation (1.3.7) refers to only one selected Brownian particle. The complete solution of the motion of a macroscopic system would consist of solving all the

microscopic equations of the system. Because we cannot do this, we instead use the averaged equation of motion, i.e.,

$$\frac{m}{2}\frac{d}{dt}\left(\frac{d}{dt}\overline{x^2}\right)-m\overline{\dot{x}^2}=-\frac{\zeta}{2}\frac{d}{dt}\overline{x^2}+\overline{Fx}. \tag{1.3.8}$$

In Eq. (1.3.8), it is assumed that $\overline{Fx}$ vanishes because of the irregular variation of the force F, i.e., the random force F and the displacement x are completely *uncorrelated*. From statistical mechanics, once the velocity process reaches equilibrium, the Maxwellian distribution sets in [5], so that the mean kinetic energy of the particle becomes

$$m\overline{\dot{x}^2}/2=kT/2. \tag{1.3.9}$$

Thus, Eq. (1.3.8) becomes

$$\frac{m}{2}\frac{d}{dt}\left(\frac{d\overline{x^2}}{dt}\right)+\frac{\zeta}{2}\frac{d\overline{x^2}}{dt}=kT. \tag{1.3.10}$$

The solution of Eq. (1.3.10) is

$$\frac{d\overline{x^2}}{dt}=Ce^{-\zeta t/m}+\frac{2kT}{\zeta}, \tag{1.3.11}$$

where C is a constant of integration. For very large times t compared to m/ζ, which is of the order of 10^{-8} s, we have

$$\frac{d}{dt}\overline{x^2}=\frac{2kT}{\zeta}. \tag{1.3.12}$$

Neglecting the exponential term in Eq. (1.3.11) implies ignoring the effect of the inertia of the particle. Integrating Eq. (1.3.12) from $t=0$ and writing $\overline{(\Delta x)^2}$ for the mean-square displacement instead of $\overline{x^2}$, we have Einstein's formula [3]

$$\overline{(\Delta x)^2}=\frac{2kT}{\zeta}t, \tag{1.3.13}$$

which has a meaning described remarkably well by Sears [27]:

> "We observe a Brownian grain at time 0 and at time t. During the time interval $(0, t)$ it has undergone a displacement Δs, whose projection on the x-axis is Δx. The same grain is observed at later times $2t$, $3t$, ..., and Δx is determined for each interval. These values are squared and their mean value is calculated; which is $\overline{(\Delta x)^2}$. We emphasize that these displacements which we observe are not in any sense the *detailed* path of the grain, nor is $\Delta x/t$ its velocity. For example, in a time interval $t = 1$ second the particle makes millions of collisions and what we see are simply its initial and final positions, which we connect by a

straight line, while the true path is a confused zigzag of linear segments. What we observe is already a greatly simplified "path" [an example of which is given in Fig 1.1.1]. If one imagines each of the linear elements in this figure to be composed of millions of straight lines, one will begin to approximate the actual path. It is impossible to analyze this complicated motion in all of its details and we must therefore be satisfied to observe, in a certain time interval t, the corresponding magnitude of $\overline{(\Delta x)^2}$ which is only loosely related to the true path".

The noise force $F(t)$ in the Langevin equation may be related to the drag coefficient ζ as follows (i.e., the *fluctuation–dissipation theorem*)

$$\int_0^\infty \overline{F(t)F(t+\tau)}\,d\tau = \frac{1}{2}\int_{-\infty}^{\infty} \overline{F(t)F(t+\tau)}\,d\tau = \zeta kT \int_{-\infty}^{\infty} \delta(\tau)\,d\tau = \zeta kT, \qquad (1.3.14)$$

hence

$$\zeta = \frac{1}{kT}\int_0^\infty \overline{F(t)F(t+\tau)}\,d\tau, \qquad (1.3.15)$$

thereby relating the *systematic* frictional force driving the system towards a "dead" state and the *random* force keeping it "alive" [24].

In summary, the essence of Langevin's method is to rewrite his Newtonian-like equation of motion of the random variable describing the dynamics of a representative point in phase space $(x,\dot{x})$ in variables corresponding to the desired observable(s); cf. Eq. (1.3.7). Then one averages the new equation over its realizations, yielding the deterministic evolution equation for the observable(s). Once a potential is involved [30], the Langevin equation generates coupled stochastic differential-recurrence equations which, when averaged using the properties of Gaussian white noise, become a deterministic hierarchy of coupled equations for the observables.

1.3.1. *Calculation of Avogadro's number*

We have seen that, according to Stokes' law, the friction coefficient ζ of a spherical particle moving in a viscous liquid is $\zeta = 6\pi\eta a$, where a is the radius of the particle and η is the viscosity of the liquid. If we combine this formula with the Einstein equation, Eq. (1.3.14), we obtain

$$\overline{(\Delta x)^2} = 2tRT/(N\zeta), \qquad (1.3.1.1)$$

where $N = R/k$ is the Avogadro number and R is the gas constant. If the gas constant R is known (8.314 J K^{-1} mol^{-1}), all the other variables in Eq. (1.3.1.1)

except N may be determined in a suitable experiment. Thus, one may use Einstein's formula to estimate N. In 1908, Perrin computed the Avogadro number N from observations of Brownian movement, obtaining $N = 6.85 \times 10^{23}$ mol^{-1} [2, 5]. He also confirmed the relation between t, η, and T predicted by the Einstein equation, for which he was awarded the Nobel prize in 1926. A detailed account of his research is given by Fowler [6], who has succinctly summarized the work of the early investigators (see also [2, 4, 10, 18] and Fig. 1.3.1.1):

> "(1) We can see the manifestations of the molecular motions going on before our eyes.
> (2) We can check the assumptions of statistical mechanics in a rather detailed way by proving that the characteristics of the Brownian movement agree with the demands of the theory.
> (3) We obtain a direct, though not very accurate method of measuring molecular magnitudes."

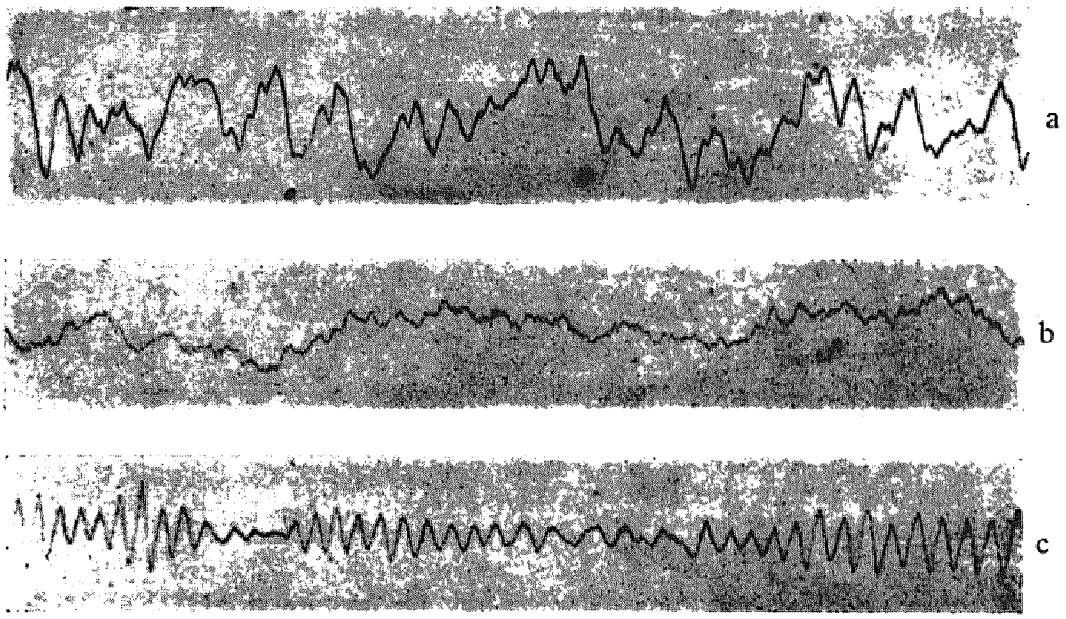


Figure 1.3.1.1. Brownian fluctuation of a very light mirror suspended upon a fine quartz fiber of torsion constant A. (a) Pressure 4×10^{-3} mm Hg. (b) Atmospheric pressure. (c) Pressure 10^{-4} mm Hg. The motion of the system is characterized by the angle φ through which the mirror has rotated from its position of equilibrium. One may expect that the system will perform Brownian motion of such magnitude that $A\overline{\varphi^2}/2 = kT/2$. Measurements of A and $\overline{\varphi^2}$ [28] permit one to obtain a value of the Boltzmann constant k as well as the Avogadro number N. At low pressures (c), the motion approaches the sinusoidal natural mode of oscillation of the system and tends to lose its random character. All of the curves, in spite of the difference in their forms, yield identical values of $\overline{\varphi^2}$. (Taken from R. Barnes and S. Silverman [29]; see detailed discussion in [1]).

1.4. Einstein's method

Einstein derived his expression for the mean-square displacement of a Brownian particle by means of a diffusion (Fokker–Planck) equation, which he constructed using the following assumptions [3]: (i) Each individual particle executes a motion which is independent of the motion of all other particles in the system. (ii) The motion of a particle at one particular instant is independent of the motion of that particle at any other instant provided the time interval is large enough. (This is essentially another way of stating the assumption that $\overline{Fx} = 0$ in the Langevin equation.)

Einstein's method may be described as follows: we introduce a time interval τ, which is *large enough* that, according to assumption (ii) above, the motion of a particle at time t is *independent* of its motion at time $t \pm \tau$, but *small* compared to the time intervals between observations. Suppose that there are f particles per unit volume in a liquid between x and $x + dx$ at time t (we shall consider only the one-dimensional case since there is no loss of generality in doing so). After a time τ has elapsed, we consider a volume element of the same size at point x'. Each particle has a different (positive or negative) value. We suppose that [5] the *probability* of a particle entering from a *neighboring* element to x' is a function of $\Delta = x' - x$ and τ (a brief description of the relevant probability theory is given in Section 1.6). We denote this probability by $\phi(\Delta, \tau)$. Since the particle must come from *some* volume element, the density at time τ is [5]

$$f(x, t+\tau) = \int_{-\infty}^{\infty} f(x+\Delta, t)\phi(\Delta, \tau)d\Delta. \tag{1.4.1}$$

Now positive and negative displacements are equiprobable, so we have an *unbiased random walk*. Thus the function $\phi(\Delta, \tau)$ satisfies

$$\phi(\Delta, \tau) = \phi(-\Delta, \tau). \tag{1.4.2}$$

Now suppose that τ is very small, so we can expand the left-hand side of Eq. (1.4.1) in powers of τ, i.e.,

$$f(x, t+\tau) = f(x, t) + \tau \frac{\partial f}{\partial t} + \cdots. \tag{1.4.3}$$

Furthermore, we develop $f(x+\Delta, t)$ in the right-hand side of Eq. (1.4.1) in powers of the small displacement Δ, thereby obtaining

$$f(x+\Delta, t) = f(x, t) + \Delta \frac{\partial}{\partial x} f(x, t) + \frac{\Delta^2}{2} \frac{\partial^2}{\partial x^2} f(x, t) + \cdots. \tag{1.4.4}$$

The integral equation (1.4.1) therefore becomes

$$f+\tau\frac{\partial f}{\partial t}=f\int_{-\infty}^{\infty}\phi d\Delta+\frac{\partial f}{\partial x}\int_{-\infty}^{\infty}\Delta\phi d\Delta+\frac{\partial^2 f}{\partial x^2}\int_{-\infty}^{\infty}\frac{\Delta^2}{2!}\phi d\Delta+\cdots. \tag{1.4.5}$$

Since ϕ is a PDF and $\phi(\Delta,\tau)=\phi(-\Delta,\tau)$, we have

$$\int_{-\infty}^{\infty}\phi(\Delta,\tau)d\Delta=1,\quad \int_{-\infty}^{\infty}\Delta\phi(\Delta,\tau)d\Delta=\overline{\Delta}=0,\quad \int_{-\infty}^{\infty}\Delta^2\phi(\Delta,\tau)d\Delta=\overline{\Delta^2}, \tag{1.4.6}$$

where the overbar denotes the mean over the displacements for each particle. Now all higher order terms such as $\overline{\Delta^4}$ in Eq. (1.4.5) are at least of order τ^2. Hence, Eq. (1.4.5) simplifies to

$$\tau\frac{\partial f}{\partial t}=\frac{\overline{\Delta^2}}{2}\frac{\partial^2 f}{\partial x^2}. \tag{1.4.7}$$

If we set $D=\overline{\Delta^2}/(2\tau)$, then Eq. (1.4.7) can be written as

$$\frac{\partial f}{\partial t}=D\frac{\partial^2 f}{\partial x^2}. \tag{1.4.8}$$

Equation (1.4.8) is a diffusion equation in one dimension derived for small Δ from the integral equation (1.4.1) with D the translational diffusion coefficient. The solution of Eq. (1.4.8) may be found by assuming that all the Brownian particles are initially placed near the point $x=0$ at time $t=0$ (sharp initial conditions) [5]. This corresponds to finding the point-source solution of the diffusion equation that is Green's function (the transition probability or propagator). The conditions to be imposed on the solution are

$$f(x,0)=\delta(x), \tag{1.4.9}$$

where $\delta(x)$ is the Dirac delta function. Since f is a PDF, we also have

$$\int_{-\infty}^{\infty}f(x,t)dx=1 \tag{1.4.10}$$

(see Section 1.6). The solution of Eq. (1.4.8) subject to these conditions is given by [5]

$$f(x,t)=\frac{1}{\sqrt{4\pi Dt}}e^{-x^2/(4Dt)},\quad -\infty<x<\infty. \tag{1.4.11}$$

Equation (1.4.11) determines the root-mean-square displacement of the particle in the x direction. We have

$$\sqrt{\overline{x^2}}=\sqrt{2Dt}. \tag{1.4.12}$$

We emphasize (with Wang and Uhlenbeck [13] and Kac [15]; see also [5]) that one may only obtain the diffusion equation, Eq. (1.4.8), when in *small* times τ, the space coordinate Δ can only change by a *small* amount. In the general case, the process will always be governed by an integro-differential equation which is of the same type as the Boltzmann equation of the kinetic theory of gases [13, 21, 31], of which Eq. (1.4.1) is an example with $\phi(\Delta,\tau)=\phi(-\Delta,\tau)$ as the *Stosszahlansatz*. In addition, if r is the total displacement of the particle in space, i.e., $\overline{r^2}=\overline{x^2}+\overline{y^2}+\overline{z^2}$ so that $\overline{r^2}=3\overline{x^2}$ [3].

Einstein determined the diffusion coefficient D in terms of molecular quantities by imagining that the Brownian particles are placed in a field of force $\mathbf{K}(x)$ so that the Boltzmann distribution for the configuration of the particles must eventually set in, meaning that

$$f=f_0e^{-V/(kT)}. \tag{1.4.13}$$

If the force is constant, as would be true when gravity acts on the Brownian particles, the potential energy V is

$$V=-Kx, \tag{1.4.14}$$

where we suppose that the particles are so few that their mutual interactions may be neglected (we have an "atmosphere" of Brownian particles). We may imagine the Boltzmann distribution to be set up as a result of the motion of the Brownian particles due to the *force together with a diffusion current* that seeks to satisfy Eq. (1.4.8). Now, the velocity of a spherical particle that is in equilibrium under the action of the applied force and viscosity is given by Stokes' law, Eq. (1.3.2), viz.,

$$v=K/(6\pi\eta a).$$

The number of particles crossing unit area in unit time $J_d=vf$ (current density of particles) is then $J_d=fK/(6\pi\eta a)$; *however, in order to preserve equilibrium under the action of the force*, a diffusion current of equal strength flows in the opposite direction so that, by inspection of Eqs. (1.2.4) and (1.2.5),

$$D\frac{\partial f}{\partial x}=\frac{fK}{6\pi\eta a}. \tag{1.4.15}$$

This is the mathematical statement of the fact that, at equilibrium, the rate of diffusion under the concentration gradient must just balance the directed effect of the field of force. However, from Eqs. (1.4.13) and (1.4.14), we also have (i.e., the overall current must vanish)

$$\frac{1}{f}\frac{\partial f}{\partial x}=\frac{K}{kT}. \tag{1.4.16}$$

Thus, on comparing Eqs. (1.4.15) and (1.4.16), we obtain Einstein's formula for the translational diffusion coefficient $D = kT/(6\pi\eta a)$.

The arguments used to establish the formula for the mean-square displacement may be extended to rotational Brownian motion about a diameter of a particle in suspension. If θ is an angular coordinate and if $\overline{\theta^2}$ is the mean-square angular displacement in time τ due to molecular agitation, then according to Eq. (1.4.8), the PDF of the orientations satisfies

$$\frac{\partial f}{\partial t} = D_{\mathrm{R}} \frac{\partial^2 f}{\partial \theta^2}, \tag{1.4.17}$$

where $D_{\mathrm{R}} = \overline{\theta^2}/(2\tau)$ is the rotational diffusion coefficient. Suppose that an external torque of potential $V(\theta)$ acts on the body. In equilibrium we would then have $f = f_0 e^{-V(\theta)/(kT)}$, and thus

$$\frac{1}{f}\frac{\partial f}{\partial \theta} = -\frac{1}{kT}\frac{\partial V}{\partial \theta}. \tag{1.4.18}$$

For a particular particle under a torque $-\partial V/\partial\theta$, we have a steady angular velocity $\varsigma\dot{\theta} = -\partial V/\partial\theta$, where the drag coefficient ς for a sphere rotating about a fixed axis in a viscous liquid is $\varsigma = 8\pi a^3\eta$ [32]. The number of particles diffusing across a given value θ of the coordinate in unit time is

$$J_{\mathrm{d}} = -\frac{f}{\varsigma}\frac{\partial V}{\partial \theta} = D_{\mathrm{R}}\frac{\partial f}{\partial \theta},$$

and hence $D_{\mathrm{R}} = kT/\varsigma$. Thus, we have Einstein's formula for the mean-square angular displacement $\overline{\theta^2} = kT\tau/\varsigma = kT\tau/(4\pi a^3\eta)$. However, this formula cannot be applied for any *arbitrarily small time*. We give the original argument of Einstein that illustrates this [3]. The *mean* rate of change of θ as a result of thermal agitation is

$$\sqrt{\overline{\theta^2}}/t = \sqrt{2\varsigma kT/(tI)}. \tag{1.4.19}$$

This becomes infinitely great for indefinitely small intervals of time t. This is impossible, since each suspended particle would move with an infinitely great instantaneous angular velocity. The reason for this difficulty is that we have implicitly assumed in our development that events occurring *during* the interval t are *completely independent* of events in the time *immediately* preceding it. This is not true if t is chosen small enough because *inertial effects* will come into play so inducing *memory* of previous events.

Einstein established a range of validity for his formula using the following argument. Suppose that the instantaneous rate of change of θ at an initial time

$t_0 = 0$ is $\dot{\theta}(t = t_0) = \omega_0$. Suppose further that the angular velocity $\omega(t)$ at some later time t is not affected by the irregular thermal processes that occur in the time interval (t_0, t), but that the change in ω is determined *solely by the viscous drag* $\varsigma\omega$. Then we have

$$I\dot{\omega} = -\varsigma\omega. \tag{1.4.20}$$

The moment of inertia I is defined by the condition that $I\omega^2/2$ must be the rotational kinetic energy corresponding to the angular velocity $\omega(t)$. This is evidently the moment of inertia of the sphere about a diameter. By integration of Eq. (1.4.20), we obtain

$$\dot{\theta}(t) = \omega(t) = \omega_0 e^{-\varsigma t/I}.$$

This is negligible only when the time interval between observations is large compared with the friction time I/ς, i.e, $t >> I/\varsigma$. If this condition is not satisfied, inertial effects must be taken into account. Einstein calculated that, for bodies of 1 μm diameter and unit density in water at room temperature (300 K) the lower limit of applicability of the formula for $\overline{\theta^2}$ is of the order of 10^{-7} s; this lower limit for the interval between observations increases in proportion to the *square of the radius* of the body. The same considerations hold for translational as for rotational motion of the grain. For practical purposes, inertial effects will only start to become prominent when Brownian movement is used to model high-frequency relaxation processes.

Einstein also showed how his theory may be applied to conduction processes in a conductor. The charge carriers are regarded as charged Brownian particles; thus, if ζ is replaced by the electrical resistance R of the conductor and the charge q replaces the displacement x of the Brownian particle, then Einstein's formula gives, for the mean-square charge that has flowed across a section of the conductor at time t,

$$\overline{q^2} = (2kT/R)t. \tag{1.4.21}$$

De Haas-Lorentz, in her book *Die Brownsche-Bewegung*, published in 1913 [4] (which contains a very thorough account of the history of the phenomenon to that date), lists six electrical systems in which fluctuations are treated by means of Brownian movement. In the above example, the ACF of the voltage $e(t)$ across the conductor due to thermal fluctuations is

$$\overline{e(t_1)e(t_2)} = 2RkT\delta(t_1 - t_2). \tag{1.4.22}$$

Equation (1.4.22) is related to the work of Johnson [33] and Nyquist [34] (see also Refs. [29] and [35]). In particular, the result for the spectral density, namely

$$\Phi_e(\omega) = 2RkT, \tag{1.4.23}$$

is known as Nyquist's theorem. $\Phi_e(\omega)$ has the following meaning. Suppose that, by using a filter, we measure $\tilde{e}(\omega)\Delta\omega$, which is the voltage across the conductor in the angular frequency range $(\omega, \omega+\Delta\omega)$, where $\tilde{e}(\omega)$ is the Fourier transform of $e(t)$. Then

$$\Phi_e(\omega)\Delta\omega / R = 2kT\Delta\omega \tag{1.4.24}$$

is the mean power dissipated in the conductor in the frequency band $\Delta\omega$ [25].

To assist the reader, the following Sections 1.5 and 1.6 will illustrate the basic concepts of statistical mechanics and probability theory, which will be needed throughout the rest of the book. The reader familiar with these concepts may skip these sections if so desired.

1.5. Essential concepts in statistical mechanics

The development of statistical mechanics and the introduction of stochastic processes into physics began in the nineteenth century [11, 31], when physicists were attempting to show that heat in a medium is due to the random motion of the constituent molecules. Excellent historical summaries are given by Jeans [36], in the first and second editions of Chapman and Cowling [37], and by Born [38]. We briefly summarize the work of Maxwell who, in 1859 [11, 31, 36], considered gases as if they were made up of small rigid spheres distributed randomly but with uniform average density in a vessel [5]. In his model, the molecules are assumed to have random velocities and to collide in a perfectly random fashion with each other and with the walls of the vessel. The process is also assumed to have been going on for a long time, so that equilibrium conditions will have been attained. The position of the molecule is represented by Cartesian coordinates x, y, z and its velocity by coordinates u, v, w, so that $\dot{x} = u$, $\dot{y} = v$, $\dot{z} = w$. Maxwell wanted to know the steady state probability $f(u, v, w)\, du\, dv\, dw$ that the velocity components lie in small ranges between u and $u + du$, v and $v + dv$, and w and $w + dw$. His original argument, although now not regarded as completely satisfactory, is of interest both for its simplicity and for its historical importance.

The derivation we give here is essentially that of Maxwell [5, 31, 36], with a few slight changes in nomenclature.

> "Let N_0 be the whole number of particles. Let u, v, and w be the components of the velocity of each particle in three rectangular directions, and let the number of particles for which u lies between u and $u + du$ be $N_0 f(u)\, du$, where $f(u)$ is a function of u to be determined. The number of

particles for which v lies between v and $v+dv$ will be $N_0 f(v)\,dv$, and the number for which w lies between w and $w+dw$ will be $N_0 f(w)\,dw$, where f always stands for the same function. Now the existence of the velocity u does not in any way affect that of the velocities v or w, since these are all at right angles to each other and independent, so that the number of particles whose velocity lies between u and $u+du$, and also between v and $v+dv$ and also between w and $w+dw$ is

$$N_0 f(u) f(v) f(w) du dv dw.$$

If we suppose the N_0 particles to start from the origin at the same instant, then this will be the number in the element of volume $du\,dv\,dw$ after unit of time, and the number referred to unit of volume will be $N_0 f(u) f(v) f(w)$. But the directions of the velocities are perfectly arbitrary, and therefore this number must depend on the distance from the origin alone, that is

$$f(u) f(v) f(w) = \phi(u^2 + v^2 + w^2).$$

Solving this functional equation, we find

$$f(u) = Ce^{Au^2}, \quad \phi(u^2 + v^2 + w^2) = C^3 e^{A(u^2+v^2+w^2)}.$$ "

This proof, although attractive because of its simplicity, is deemed unsatisfactory because it assumes *a priori* the three velocity components to be independent. The distribution may, however, be justified from rigorous considerations. The constant C^3 is chosen so as to satisfy the condition:

$$\frac{1}{C^3} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{A\left(u^2+v^2+w^2\right)} du\,dv\,dw.$$

The constant A is $-m/(2kT)$, where m is the mass of a gas molecule.

In 1868, Boltzmann [31, 36, 37, 39] generalized Maxwell's results by supposing that the molecules are also subjected to a conservative field of force $\mathbf{K}(x,y,z) = -\text{grad}V(x,y,z)$, where $V(x,y,z)$ is the potential energy, so that the total energy E of a molecule is $E(x,y,z,u,v,w) = V(x,y,z) + m(u^2+v^2+w^2)/2$. He then found that

$$f(x,y,z,u,v,w) = C' e^{-E(x,y,z,u,v,w)/(kT)}, \tag{1.5.1}$$

where C' is a constant. Such a gas is said to have the Maxwell–Boltzmann probability distribution. Hence the mean kinetic energy for each degree of freedom of the gas molecules is the same

$$\overline{mu^2}/2 = m\langle u^2\rangle/2 = m\langle v^2\rangle/2 = m\langle w^2\rangle/2 = kT/2.$$

This property, which applies also when there are several different kinds of molecule in the gas, is known as the *equipartition of energy*. If we interpret the mean kinetic energy as temperature, the equipartition theorem implies that gases

in contact reach a common temperature, which is in agreement with experiment. In Sections 1.5.1–1.5.4, we shall follow closely the discussion of Tolman [23].

1.5.1. *Ensemble of systems*

In classical mechanics, we consider the behavior of any given mechanical system of interest as it changes in time from one *precisely* defined state to another. In statistical mechanics, we have *some* knowledge of the system but *not enough for a complete specification of the precise state.* For this purpose, we shall consider the average behavior of a *collection* of systems of the *same structure* as the one of actual interest, but distributed over a range of *different* possible states. We speak of such a collection as an *ensemble of systems*. Here we picture an ensemble as consisting [40] of the system in question and a very large number of copies of it with which it is in thermal equilibrium. By *ensemble average*, we understand an average over the ensemble at a given instant in time; we denote such averages by angular braces $\langle\ \rangle$.

1.5.2. *Phase space*

In order to investigate the behavior of ensembles, it is convenient to have a quasi-geometric language [23, 41] which can be used to specify the state of each system in the ensemble and to describe the condition of the ensemble as a whole. Thus, corresponding to any system of N degrees of freedom, we construct a conceptual Euclidian space Ω of $2N$ dimensions with $2N$ rectangular axes, one for each of the coordinates $\mathbf{q} = (q_1, ..., q_N)$ and one for each of the momenta $\mathbf{p} = (p_1, ..., p_N)$, where these values would determine the *instantaneous state* or *phase* $(\mathbf{q}, \mathbf{p})$ of the system. We speak [42] of such a conceptual space as a *phase space* for the particular system (Fig. 1.5.2.1). For example, the phase (state or representation) space of the system treated in Section 1.5 is (x, y, z, u, v, w).

1.5.3. *Representative point*

The instantaneous state of any system in an ensemble can be regarded as being specified by the position of a *representative point* in the phase space, and the condition of the ensemble as a whole can be described by a "cloud" of density $\rho[\mathbf{q}(t), \mathbf{p}(t), t]$ of such representative points, one for each system in the ensemble. The behavior of the ensemble over time can then be associated with the "streaming" motion of the representative points as they describe trajectories in the phase space, in accordance with the laws of mechanics. The representative

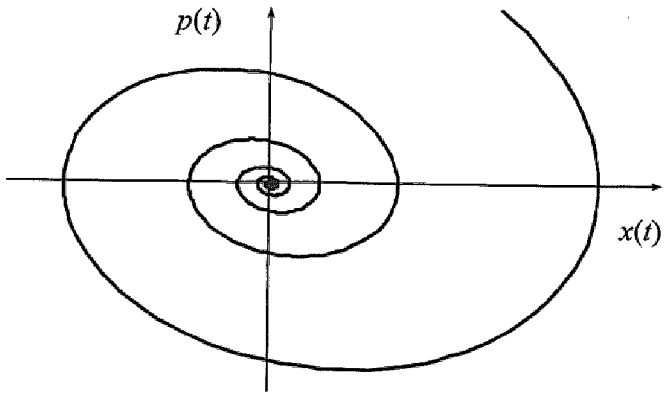


Figure 1.5.2.1. Phase plane trajectories $\{x(t), p(t) = m\dot{x}(t)\}$ of a damped harmonic oscillator with the equation of motion $\ddot{x}(t) + \gamma\dot{x}(t) + \omega_0^2 x(t) = 0$.

points for the different systems are often spoken of as *phase points*. In Section 1.5, the coordinates of a representative point (state variables) are (x, y, z, u, v, w). Excellent accounts of phase space and ensembles are given in Refs. [23], [41], and [42].

1.5.4. *Ergodic hypothesis*

Maxwell and Boltzmann [31] hoped to justify the methods of statistical mechanics by showing that the *time average* [25] of any quantity pertaining to any *single* system of interest would actually agree with the *ensemble average* for that quantity calculated from statistical mechanics. The postulate leading to this conclusion was called by Boltzmann the *ergodic* (Greek, *έργον* – work – and *όδος* – path) *hypothesis*, and by Maxwell the assumption of *continuity in phase*. It states that the phase point for any isolated system should pass in succession through every point compatible with the energy of the system before finally returning to its original position in phase space. This is not strictly true in the form postulated by the founders of statistical mechanics (see [23], pages 63–70); thus in calculating average values one has, *in general*, to distinguish between an *ensemble average* and a *time average* [25]. However, for a *stationary* process in which all time dependent averages are functions only of time differences, i.e., invariant under time transformations, these two methods of averaging will always give the same result. A graphic example using random function generators is given in Ref. [25]. For example, we have defined the autocorrelation function as the time average of a two-time product over an arbitrary range time T', viz., [14]

$$C_x(\tau) = \overline{x(t)x(t+\tau)} = \lim_{T'\to\infty} \frac{1}{T'} \int_{-T'/2}^{T'/2} x(t)x(t+\tau)dt, \qquad (1.5.4.1)$$

where in all cases τ for negative values is to be interpreted as $|\tau|$. Thus ergodicity means that, for a stationary process, where

$$\overline{x(t)x(t+\tau)} = \overline{x(t)x(t-\tau)}, \qquad (1.5.4.2)$$

we may also consider *ensemble averages* in which we *simultaneously* repeat the same measurement for a huge number of copies of the system [14] and calculate averages yielding a result identical to Eq. (1.5.4.1), i.e.,

$$\langle x(t)x(t+\tau)\rangle = \overline{x(t)x(t+\tau)}. \qquad (1.5.4.3)$$

1.5.5. *Calculation of averages*

It is convenient to summarize how the averages of dynamical quantities may be calculated. Following Gibbs [5, 23, 41], we will describe the state of a given system in terms of coordinates $\mathbf{q} = (q_1, q_2, \ldots, q_N)$ and conjugate momenta $\mathbf{p} = (p_1, p_2, \ldots, p_N)$ (rather than velocities), the number of each being equal to the number of degrees of freedom of the system. We also suppose that the system is in thermodynamic equilibrium at temperature T. Then, in the notation of Gibbs [5], the Maxwell–Boltzmann law (i.e., the probability of finding the state of the system in the range $d\Omega = dq_1 dp_1 \cdots dq_N dp_N$) is

$$\rho d\Omega = Ce^{-\frac{E(p_1\cdots p_N, q_1\cdots q_N)}{kT}} dq_1 dp_1 \cdots dq_N dp_N,$$

where E is the Hamiltonian or total energy of the system. As before, the coefficient C is chosen to satisfy the normalization condition

$$\int_\Omega \rho d\Omega = 1,$$

where the integration extends over all possible values of the variables. In calculating the resulting averages for a system, it is convenient to introduce the *partition function* Z defined by

$$Z = \int_\Omega e^{-\frac{E}{kT}} d\Omega,$$

so that $C = Z^{-1}$. Thus the average value of any function of the p's and q's, $A(\mathbf{p}, \mathbf{q})$, is then given by

$$\langle A(\mathbf{p},\mathbf{q})\rangle = \frac{1}{Z}\int_\Omega Ae^{-\frac{E}{kT}} d\Omega.$$

We shall use overbars and angle brackets to denote averages; overbars will denote time averages, and angle brackets will denote ensemble averages. It is a fundamental tenet of statistical mechanics (see Section 1.5.4) that, for a stationary process, *the time-averaged behavior of a system is equal to the ensemble-averaged behavior.* In particular, the average total energy is given by

$$\langle E \rangle = \frac{1}{Z}\int_{\Omega} E e^{-\frac{E}{kT}} d\Omega.$$

Suppose that the coordinates are chosen such that the kinetic energy is expressed as a sum of squares of the momenta with constant coefficients, that is, $\sum_i p_i^2/(2m_i)$, and the Hamiltonian is thus

$$E = \sum_i \frac{1}{2m_i} p_i^2 + V(\mathbf{q}).$$

Then, in calculating Z, or the average of any function of the coordinates only, the integrals that occur are the *products* of integrals over the position and momentum coordinates, respectively. For example, in evaluating $\langle E \rangle$,

$$\frac{1}{2m_i}\langle p_i^2 \rangle = \frac{1}{2m_i}\int_{-\infty}^{\infty} p_i^2 e^{-\frac{p_i^2}{2m_i kT}} dp_i \Big/ \int_{-\infty}^{\infty} e^{-\frac{p_i^2}{2m_i kT}} dp_i = \frac{1}{2}kT.$$

Thus, we have the equipartition theorem as described above: the mean value of the *kinetic energy* in any coordinate (one degree of freedom) is $kT/2$. The same is true for potential energy terms, which are simply of the form $K_i q_i^2/2$ (a harmonic oscillator), assuming that q_i does not enter the Hamiltonian in any other form. If the coordinate q_i enters the Hamiltonian as $p_i^2/(2m_i) + K_i q_i^2/2$, however, the particle cannot come into thermal equilibrium with the remainder of the system; thus there must be some kind of interaction between it and the rest of the system. This interaction is generally provided by a mechanism such as the collision of gas molecules with the particle, which constitutes the oscillator. In general, if the *interaction energy depends solely on the coordinates,* and not on the momenta, then the equipartition theorem holds.

According to the theorem, each degree of freedom has associated with it a mean kinetic energy $kT/2$. Hence, one may calculate the fluctuations due to this thermal energy in perfect generality from the laws of statistical mechanics. This is possible because the average energy of these random motions will be exactly the same for all systems at the same temperature (so long as each is in thermodynamic equilibrium with its surroundings), and will be entirely independent of the nature of the systems and the mechanisms that produce them. The energy distribution will be a function of the particular system in question.

Barnes and Silverman [29] show how the equipartition theorem may be used to set a natural limit on the ultimate sensitivity of all measuring devices.

1.5.6. *Liouville equation*

In Section 1.2 above, we very briefly alluded to the Klein–Kramers equation for the evolution of the PDF f in the phase space (x, v); unlike the (approximate) Smoluchowski equation, Eq. (1.2.6), used by Einstein, this includes exactly the effect of the inertia of the Brownian particles. We remark that the Smoluchowski equation is an approximate equation for the evolution of the PDF in configuration space (x), which assumes that the velocities are already in equilibrium. In the Langevin picture, this assumption is contained in the steps in going from the exact Eq. (1.3.8) to the approximate Eq. (1.3.12). Consequently, the Smoluchowski equation describes the evolution of the PDF in configuration space in the limit of very high friction or small inertial effects. Returning again to the Klein–Kramers equation and the question of a plausible derivation of that equation along the lines of that presented for the Smoluchowski equation in Eqs. (1.2.1)–(1.2.6) above, it is first necessary to refer to a *purely dynamical* theorem due to Liouville [23]. This theorem provides an ideal basis for the discussion of the effect of a heat bath on a dynamical system. For convenience, we will use Hamilton's canonical variables, namely position q and momentum p. Here, we shall also follow [23] and use the symbol ρ for the density of representative points in the phase space (q, p).

The dynamical evolution of a conservative system is, in general, described by the Liouville equation (see Tolman [23]), which, for a system of N particles, which have $3N$ degrees of freedom, with Hamiltonian

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} + V(q_1, q_2, \ldots, q_{3N}), \tag{1.5.6.1}$$

is

$$\frac{D\rho}{Dt} = 0, \tag{1.5.6.2}$$

where D/Dt is the total or hydrodynamical (convective) derivative operator defined by

$$D/Dt = \partial/\partial t + \mathbf{u} \cdot \text{grad} \tag{1.5.6.3}$$

and $\mathbf{u} = (\dot{\mathbf{q}}, \dot{\mathbf{p}})$ is the $6N$-dimensional vector, which is the flow vector in phase space. Equation (1.5.6.2) follows from the continuity equation $\dot{\rho} + \text{div}\mathbf{u}\rho = 0$ since $\text{div}\mathbf{u} = 0$, because Hamiltonian's equations are obeyed. A very detailed

account of the Liouville equation is given by Tolman [23]. The hydrodynamical derivative is defined as the derivative evaluated at a *moving* phase point $\{\mathbf{q}(t),\mathbf{p}(t)\}$. The statement $D\rho/Dt = 0$ means that there is no tendency for phase points to "crowd" into any particular region of phase space; i.e., phase space behaves like an *incompressible* fluid whose representative point is $\{\mathbf{q}(t),\mathbf{p}(t)\}$. Put in yet another way, the density in the neighborhood of any selected moving representative point is constant along the trajectory of that point. This principle is known as the *principle of conservation of density in phase space*; in other words, phase points *stream* [41]. In mathematical terms, the principle is written as

$$\rho[\mathbf{q}(t_0),\mathbf{p}(t_0),t_0] = \rho[\mathbf{q}(t),\mathbf{p}(t),t].$$

The second important property arising from the incompressible nature of phase space is the principle of *conservation of extension* ("volume") in phase space, $d\mathbf{q}(t)d\mathbf{p}(t) = d\mathbf{q}(t_0)d\mathbf{p}(t_0)$, so that, even though the *shape* of the region $\Delta\upsilon$ in phase space may alter with the course of time, its *volume* does not [41].

Equation (1.5.6.2) is known as the *Liouville equation*, which for N particles moving in three dimensions (so that we have a $6N$-dimensional phase space or $12N$-dimensional if the rotational degrees of freedom are added) is often written as

$$\frac{D\rho}{Dt} = \frac{\partial\rho}{\partial t} + \{\rho, H\} = 0, \tag{1.5.6.4}$$

where $\{\rho, H\}$ is the Poisson bracket defined as

$$\{\rho, H\} = \sum_{i=1}^{3N}\left(\frac{\partial H}{\partial p_i}\frac{\partial\rho}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial\rho}{\partial p_i}\right). \tag{1.5.6.5}$$

We shall see later that the theorem also applies to non-additive Hamiltonians.

1.5.7. *Reduction of the Liouville equation*

The Liouville equation is an equation with a number of variables of order 10^{23} and so is not tractable. In order to discuss the average dynamical behavior of a particle or system embedded in a heat bath, it is necessary [4] to modify the Liouville equation by both reducing it and generalizing it: reducing it by limiting the degrees of freedom to a small but representative set with a well-defined potential, and generalizing it by the addition of terms on the right-hand side of Eq. (1.5.6.4) to account for the interaction between this small set and the remaining degrees of freedom (the background or heat bath). The first, and best-

known, such reduction and generalization of the Liouville equation is due to Boltzmann (this is the integro-differential equation for the single-particle distribution function [37]). Boltzmann [31], in his attempt to demonstrate that the effect of molecular collisions (whatever the initial positions and velocities of the molecules of the gas) would be to bring about a Maxwell–Boltzmann distribution of positions and velocities, formulated his famous equation [36, 37]. This equation describes the time evolution of the density of molecules in phase space provided that only encounters between two molecules (i.e., two-body interactions) are ever of any importance [31, 37].

The Boltzmann equation, which is a closed equation [31, 36, 37] for the *single*-particle distribution function, is now the fundamental equation that allows one to describe the bath itself in a microscopic way. The particular law of binary collisions (*Stosszahlansatz*) describes the interactions between the molecules of the bath. The binary collision assumption amounts to stating that encounters with other molecules occupy only a very small part of the lifetime of a molecule. Alternatively [37], it states that encounters in which *more than two* molecules take part can be neglected both in number and in their effect in comparison with binary encounters. Furthermore, in considering binary encounters between molecules having velocities within assigned ranges, it is assumed that both sets of molecules are distributed at random and without any correlation between velocity and position in the neighborhood of the point where the collision takes place. This is the "molecular chaos" assumption of Boltzmann [31, 36]. The theory of Brownian movement instigated by Einstein, Smoluchowski, and Langevin, and by Bachelier [17, 19] in 1900 for financial systems, is essentially a particular case of this reduction. Here, in an individual collision, the positions are almost unchanged and the velocities are altered by such small amounts that they can be treated as infinitesimal, so that the Boltzmann equation reduces to a linear partial differential equation in phase space. This equation for the particular case of point particles, which always have separable and additive Hamiltonians, is now known as the Klein–Kramers equation. The Klein–Kramers equation is intimately connected to the Langevin equation, which, for the sake of completeness, we will again refer to at this juncture.

1.5.8. *Langevin equation for a system with one degree of freedom*

Langevin treated the Brownian motion of a free particle embedded in a heat bath by simply writing down the Newtonian equation of motion of the particle, accounting for the interaction of the particle with the bath by adding to the Newtonian equation a systematic retarding force proportional to the velocity of

the particle (which tends to drive it towards a "dead" state [24]); superimposed on this is a rapidly fluctuating force maintaining the motion, which we now call white noise. We shall generalize Langevin's treatment by supposing that the particle moves in a potential $V(x)$, hence

$$\frac{d}{dt}x(t)=\frac{p(t)}{m},\quad \frac{d}{dt}p(t)=-\frac{d}{dx}V[x(t)]-\beta p(t)+F(t). \tag{1.5.8.1}$$

Here $\beta=\zeta/m$ is the friction coefficient per unit mass and not the fugacity. In Kramers' paper [43] of 1940, the force $-\beta p+F(t)$ ($X(t)$ in his notation) is aptly termed "irregular force due to the medium." The white noise force $F(t)$ has the following properties:

$$\overline{F(t)}=0, \tag{1.5.8.2}$$

$$\overline{F(t_1)F(t_2)}=2D\delta(t_1-t_2), \tag{1.5.8.3}$$

where $D=\zeta kT$. The overbar means the statistical average over the realizations of F, i.e., the values it actually takes on. Since $F(t)$ is a random variable, then $p(t)$ and $x(t)$ are also random variables. All averages are performed over a very small time interval τ with p and x taking *sharp* initial values at the starting time t. The statistics of $F(t)$, written down above, are, however, insufficient to describe the problem fully, as neither the Klein–Kramers equation, nor the set of statistical moments of the system generated by directly averaging the Langevin equation, can be written down without supposing that $F(t)$ is also Gaussian, i.e., $F(t)$ must obey Isserlis's theorem (see Section 1.3).

1.5.9. *Intuitive derivation of the Klein–Kramers equation*

The intuitive derivation of the Kramers equation, which we shall now give, follows that of Einstein [3] who included thermal agitation in the continuity equation for a particle subjected to a force, $K=-dV/dx$, by simply adding a diffusion term to the continuity equation for the number density or concentration of particles in configuration space. This enabled him to write down the Smoluchowski equation for the evolution of the number density in configuration space. We shall apply the same procedure to the Liouville equation. Thus, that equation is reduced to the Liouville equation for a single particle, with the behavior of all the other particles (or the bath) being represented by the drift and diffusion terms we shall add; hence the hydrodynamical derivative $D\rho/Dt$ is no longer zero and the phase points diffuse.

We shall first consider the behavior of the system governed by Eq. (1.5.8.1) without the white noise term (but including the damping term). We now have

$$\operatorname{div}(\rho\mathbf{u}) = \frac{p}{m}\frac{\partial\rho}{\partial x} - \left(\beta p + \frac{dV}{dx}\right)\frac{\partial\rho}{\partial p} + \rho\left[\frac{\partial\dot{x}}{\partial x} - \beta - \frac{\partial}{\partial p}\left(\frac{dV}{dx}\right)\right]. \tag{1.5.9.1}$$

Since $\dot{x}$ and x are independent variables they play the role of generalized coordinates, and since dV/dx is independent of p, Eq. (1.5.9.1) reduces to

$$\operatorname{div}(\rho\mathbf{u}) = \frac{p}{m}\frac{\partial\rho}{\partial x} - \left(\beta p + \frac{dV}{dx}\right)\frac{\partial\rho}{\partial p} - \beta\rho. \tag{1.5.9.2}$$

Hence, the continuity equation which would ultimately result in a "dead" state becomes

$$\frac{\partial\rho}{\partial t} + \frac{p}{m}\frac{\partial\rho}{\partial x} - \left(\beta p + \frac{dV}{dx}\right)\frac{\partial\rho}{\partial p} - \beta\rho = 0. \tag{1.5.9.3}$$

To take account of the fluctuating term causing the system to remain in a "live" state, we must now, following Einstein's method for the Smoluchowski equation, add on the diffusion term $D_p\partial^2\rho/\partial p^2$, where the diffusion coefficient D_p is independent of p, and so Eq. (1.5.9.3) becomes

$$\frac{\partial\rho}{\partial t} + \frac{p}{m}\frac{\partial\rho}{\partial x} - \frac{dV}{dx}\frac{\partial\rho}{\partial p} = \frac{\partial}{\partial p}\left(\beta\rho p + D_p\frac{\partial\rho}{\partial p}\right). \tag{1.5.9.4}$$

Now we insist, following Einstein, that the equilibrium solution (the Maxwell–Boltzmann distribution) be a solution of Eq. (1.5.9.4). Thus

$$D_p = \zeta kT, \tag{1.5.9.5}$$

and so Eq. (1.5.9.4) becomes

$$\frac{\partial\rho}{\partial t} + \frac{p}{m}\frac{\partial\rho}{\partial x} - \frac{dV}{dx}\frac{\partial\rho}{\partial p} = \beta\frac{\partial}{\partial p}\left(\rho p + mkT\frac{\partial\rho}{\partial p}\right). \tag{1.5.9.6}$$

Equation (1.5.9.6) is the Klein–Kramers equation for the evolution of the density ρ in phase space. The effect of having a nonzero right-hand side of the Liouville equation is to cause a disturbance of the streaming motion of the representative points so that they diffuse onto other energy trajectories. The energy of the Brownian particle is no longer conserved as energy is interchanged between that particle and the bath. Equation (1.5.9.6) reduces to Eq. (1.2.7) specialized to the phase space (x, v) if the replacement $\rho \to W$, $p \to m\dot{x}$, is made.

In the analysis presented in this section, and in the sections immediately preceding it, we have adhered as far as possible to the original notation used by Kramers [43, 44] in his discussion of the derivation of the Klein–Kramers equation. We shall now briefly outline how the Smoluchowski equation may be derived heuristically from the Klein–Kramers equation. Thus it is necessary to

refer to the conditions under which a Maxwellian distribution of velocities may be assumed to prevail in the Klein–Kramers equation.

1.5.10. *Conditions under which a Maxwellian distribution in the velocities may be deemed to be attained*

Having obtained the Klein–Kramers equation for the time evolution of the distribution function in the phase space (x, p), Kramers [43, 44] proceeded to examine the conditions under which equilibrium in the velocities may be assumed to have been attained, the displacement having not yet attained its equilibrium value. The importance of such an investigation is that it allows one to write, for sufficiently high values of the friction parameter, an *approximate* partial differential equation for the time evolution of the PDF in configuration space only. This *approximate* equation is known as the *Smoluchowski equation*; see Eq. (1.2.6). In order to explain Kramers' reasoning on this subject, it will be useful to recall Einstein's 1905 result for the mean square displacement of a Brownian particle, namely ($t \equiv |t|$ in all cases)

$$\langle (\Delta x)^2 \rangle = (2kT/\zeta)t. \tag{1.5.10.1}$$

This equation, as we saw in Section 1.4, was derived by constructing the partial differential equation for the time evolution in configuration space only, and was later re-derived by Langevin, as we saw in Section 1.3, by considering times well in excess of the frictional relaxation time $\tau_f = m/\zeta$, which allowed him to postulate an approximate Maxwellian distribution for the velocities. Equation (1.5.10.1) has the flaw that it is not root-mean-square differentiable at very small times. In 1930, Uhlenbeck and Ornstein [45] showed, using the Langevin equation without the assumption of Eq. (1.3.9) above (namely that equilibrium of velocities has been attained), that the exact solution for the mean-square displacement of a free Brownian particle in a time interval t is

$$\langle (\Delta x)^2 \rangle = 2kT(\beta t - 1 + e^{-\beta t})/(m\beta^2). \tag{1.5.10.2}$$

This is differentiable at short times; a derivation of Eq. (1.5.10.2) is given in Chapter 3. Moreover, if $t >> \beta^{-1}$, Einstein's result, Eq. (1.5.10.1), is regained. The mean-square displacement is thus governed by two characteristic times, viz.,

$$\tau_{\text{diff}} = m\beta\langle (\Delta x)^2 \rangle/(2kT) \tag{1.5.10.3}$$

(the diffusion time) and $\tau_f = \beta^{-1}$ (the frictional time). The ratio of these times is

$$\tau_f/\tau_{\text{diff}} = 2kT/[\langle (\Delta x)^2 \rangle m\beta^2]. \tag{1.5.10.4}$$

Now diffusion effects, where a Maxwellian distribution of velocities approximately holds, will predominate over inertial effects if $\tau_f / \tau_{diff} << 1$ which by transposition means $\langle(\Delta x)^2\rangle^{1/2} >> (kT/\beta^2 m)^{1/2}$, so that the quantity

$$(kT/\beta^2 m)^{1/2} \tag{1.5.10.5}$$

defined by Kramers is a *characteristic diffusion length*, which crucially determines whether inertial or diffusion effects will predominate.

As far as Brownian motion under the influence of a potential $V(x)$ is concerned, Kramers applied the above reasoning to this problem by supposing that the force $K = -dV/dx$ does not vary greatly over distances of the order of the diffusion length Eq. (1.5.10.5). So one would expect that, starting from an arbitrary initial distribution $\rho(x, p, 0)$, a Maxwellian distribution of the momentum p would be reached after time intervals $\Delta t >> \beta^{-1}$ allowing Kramers to postulate that

$$\rho(x,p,t) \approx f(x,t)e^{-p^2/(2mkT)}. \tag{1.5.10.6}$$

The reasoning of this section is of crucial importance in the study of dielectric relaxation, where the omission of inertial effects in the Debye theory of dielectric relaxation leads to the phenomenon of infinite integral absorption. The above considerations may now be used in the heuristic derivation of the Smoluchowski equation from the Klein–Kramers equation. The range of the friction or dissipative parameter over which the Smoluchowski equation provides an accurate description of the configuration space distribution function is termed by Kramers [43, 44] the *very-high-damping* (VHD) regime. This terminology distinguishes the region of validity of the Smoluchowski equation from the *intermediate-to-high-damping* (IHD) and *very-low-damping* (VLD) regimes where inertial effects are important, so that the complete phase space description provided by the Klein–Kramers equation must be used. The distinctions between the various damping regimes are vital in the application of the theory of Brownian movement to reaction rate theory [43, 44], as we shall describe in detail in Section 1.13.

1.5.11. *Very-high-damping (VHD) regime*

This is a limiting case of the IHD regime, in which it is supposed that the damping is so large that equilibrium of the velocity distribution has been sensibly attained. In this situation, it is possible to obtain a partial differential equation for *the evolution of the distribution function in configuration space only*. This approximate diffusion equation is called the Smoluchowski equation.

First, we recall what we mean by *large viscosity*. By large viscosity we mean that *the effect of Brownian forces on the velocity of the particle is much larger than the effect of the external force* $K(x)$. The Smoluchowski equation may be derived, according to Kramers, by assuming that K does not vary sensibly over a distance of the order of the diffusion length, Eq. (1.5.10.5). We expect that, irrespective of the initial ρ distribution, the distribution (with $m=1$ following Kramers [43, 44])

$$\rho(x,p,t) \approx f(x,t)e^{-p^2/(2kT)} \tag{1.5.11.1}$$

(i.e., a Maxwellian velocity distribution) will hold after a very short time ($\approx \beta^{-1}$). The high barrier then ensures that slow diffusion of particles over the barrier will take place, which may be expected to satisfy the Smoluchowski equation for the PDF $f(x,t)$ in configuration space:

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial x}\left(\frac{K}{\beta}f - \frac{kT}{\beta}\frac{\partial f}{\partial x}\right). \tag{1.5.11.2}$$

Kramers then examines the approximate validity of Eq. (1.5.11.1). He remarks that, as long as no perfect temperature equilibrium is attained, Eq. (1.5.11.1) will hold only approximately, even when the external force is equal to 0; see the approximate Eq. (1.5.10.1). He then claims that, while the Maxwellian velocity distribution will now hold *exactly* for each *particle*, it will *not* hold *exactly at each value of* x, since otherwise there would be no diffusion current. Thus, the *behavior is unlike that described by a single space variable* Fokker–Planck equation such as that governing the magnetization relaxation in uniaxial superparamagnets (to be treated in Section 1.18.1), which is an *exact* equation.

In order to derive Eq. (1.5.11.2) from the Klein–Kramers equation, Eq. (1.5.9.6), in heuristic fashion, we first rewrite that equation as

$$\frac{\partial \rho}{\partial t} = \left(\beta\frac{\partial}{\partial p} - \frac{\partial}{\partial x}\right)\left(\rho p + kT\frac{\partial \rho}{\partial p} - \frac{K}{\beta}\rho + \frac{kT}{\beta}\frac{\partial \rho}{\partial x}\right) - \frac{\partial}{\partial x}\left(\frac{K}{\beta}\rho - \frac{kT}{\beta}\frac{\partial \rho}{\partial x}\right). \tag{1.5.11.3}$$

This can be checked most easily by directly rewriting Eq. (1.5.11.3) in the form of Eq. (1.5.9.6). We now integrate both sides (with respect to the momentum) along a straight line in phase space $x + p/\beta = x_0$ (constant). The integration extends over all possible momentum values from $p=-\infty$ to $p=+\infty$. Note

$$\frac{\partial}{\partial x} = \frac{\partial}{\partial x_0} \quad \text{and} \quad \frac{\partial}{\partial p} = \frac{1}{\beta}\frac{\partial}{\partial x_0},$$

whence $\partial/\partial p - \beta^{-1}\partial/\partial x$ is the zero operator along this line. If we denote the integral of ρ along this line by $f(x_0,t)$, we obtain

$$\frac{\partial f}{\partial t} = -\int_{x+p/\beta=x_0} \frac{\partial}{\partial x}\left(\frac{K}{\beta}\rho - \frac{kT}{\beta}\frac{\partial \rho}{\partial x}\right) dp. \tag{1.5.11.4}$$

In Eq. (1.5.11.4), note that the line integral is strictly speaking

$$\int_{x+p/\beta=x_0} \frac{\partial}{\partial x}\left(\frac{K}{\beta}\rho - \frac{kT}{\beta}\frac{\partial \rho}{\partial x}\right) ds, \tag{1.5.11.5}$$

where ds is the element of arc length along the line in question. However, since $ds^2 = dx^2 + dp^2$ and $dp/dx = -\beta$ or $dp = -\beta dx$, and because $\beta \to \infty$, i.e., we take the high-friction limit, we can make the approximation $ds \approx dp$. Thus, the position coordinate has the value $x \approx x_0$ along the line $x + p/\beta = x_0$. We also use the fact that

$$\int_{x+p/\beta=x_0} \frac{\partial \rho}{\partial t} ds = \frac{\partial}{\partial t} \int_{x+p/\beta=x_0} \rho ds = \frac{\partial f}{\partial t}. \tag{1.5.11.6}$$

The right-hand side of Eq. (1.5.11.4) can be simplified to yield

$$-\int_{x+p/\beta=x_0} \frac{\partial}{\partial x}\left(\frac{K}{\beta}\rho - \frac{kT}{\beta}\frac{\partial \rho}{\partial x}\right) dp \approx -\frac{kT}{\beta}\frac{\partial}{\partial x_0}\left[\frac{K(x_0)}{kT} f - \frac{\partial f}{\partial x_0}\right].$$

Thus, we have the result (apparently due to Klein [4])

$$\frac{\partial}{\partial t} f = \frac{kT}{\beta}\frac{\partial}{\partial x_0}\left(\frac{\partial f}{\partial x_0} - \frac{K(x_0)}{kT} f\right), \tag{1.5.11.7}$$

which is a diffusion equation in configuration space, and is the Smoluchowski equation.

The *approximate validity* of Eq. (1.5.11.7) is a consequence of the *approximate validity* of Eq. (1.5.11.1) if it is also assumed that, in the range of values of p that dominate the integral (that is, $|p| \le \sqrt{kT}$), the variation of x (which is of the order of $\sqrt{kT}/\beta$) is small compared to distances over which the force K and the density in configuration space f undergo marked variations. These are, however, the conditions which *a priori* must be imposed in order to ensure the applicability of Eq. (1.5.11.2). However, since we integrate along the line $p/\beta = x_0 - x$, and since both x and x_0 are of the order of the diffusion length $\sqrt{kT}/\beta$, we expect p to be of the order of $\sqrt{kT}$, i.e., the thermal value.

We have given above a heuristic derivation of the approximate equation for the PDF in configuration space, known as the Smoluchowski equation, from the Klein–Kramers equation. The first rigorous treatment of the problem was given by Brinkman [46]. He showed that the solution of the Klein–Kramers equation could be found by expanding the momentum part of the phase space PDF in appropriate sets of orthogonal functions, and in the small inertial limit, the

Smoluchowski equation could be obtained. Brinkman's method may be summarized as follows. First, one expands the momentum part of the solution of the Klein–Kramers equation in an orthogonal basis of the parabolic cylinder functions $D_n(y)$ [47] as

$$\rho(x,p,t)=e^{-p^2/(4kT)}\sum_{n=0}^{\infty}D_n\left(p/\sqrt{kT}\right)\varphi_n(x,t). \qquad (1.5.11.8)$$

Now we recall that $D_n(y)$ satisfy the recurrence relations [47]

$$\frac{d}{dy}D_n(y)+\frac{y}{2}D_n(y)-nD_{n-1}(y)=0,\quad \frac{d}{dy}D_n(y)-\frac{y}{2}D_n(y)+D_{n-1}(y)=0,$$

$$D_{n+1}(y)-yD_n(y)+nD_{n-1}(y)=0, \qquad (1.5.11.9)$$

the differential equation

$$\frac{d^2}{dy^2}D_n(y)+\left(n+\frac{1}{2}-\frac{y^2}{4}\right)D_n(y)=0, \qquad (1.5.11.10)$$

and the orthogonality relation

$$\int_{-\infty}^{\infty}D_n(y)D_m(y)dy=n!\sqrt{2\pi}\delta_{mn}, \qquad (1.5.11.11)$$

where δ_{mn} denotes Kronecker's delta. By substituting Eq. (1.5.11.8) into the Klein–Kramers equation, Eq. (1.5.9.6), and using Eqs. (1.5.11.9) and (1.5.11.10), we have the following partial differential-recurrence relation for the separation functions φ_n in configuration space

$$\frac{\partial\varphi_n}{\partial t}+n\beta\varphi_n+\sqrt{kT}\left[\frac{\partial\varphi_{n-1}}{\partial x}+(n+1)\frac{\partial\varphi_{n+1}}{\partial x}\right]+\frac{1}{\sqrt{kT}}\frac{\partial V}{\partial x}\varphi_{n-1}=0. \qquad (1.5.11.12)$$

This set is now called Brinkman's hierarchy. Following Brinkman, on defining the spatial differential (or current) operators

$$J=-\frac{1}{\beta}\sqrt{kT}\left[\frac{\partial}{\partial x}+\frac{1}{kT}\frac{\partial V}{\partial x}\right],\quad J_{\mathrm{D}}=-\frac{1}{\beta}\sqrt{kT}\frac{\partial}{\partial x}, \qquad (1.5.11.13)$$

the Brinkman hierarchy becomes the three-term partial differential-recurrence relation

$$\frac{1}{\beta}\dot{\varphi}_n+n\varphi_n=J\varphi_{n-1}+(n+1)J_{\mathrm{D}}\varphi_{n+1}. \qquad (1.5.11.14)$$

If we now take the Laplace transform over the time variable and suppose that the initial velocity distribution is Maxwellian so that $\varphi_n(x,0)=0,\ n>0$, we find in the s-domain that Eq. (1.5.11.14) becomes the set

$$\begin{aligned} s\tilde{\varphi}_0 - \varphi_0(x,0) &= \beta J_{\mathrm{D}} \tilde{\varphi}_1, \\ (1+s/\beta)\tilde{\varphi}_1 &= J\tilde{\varphi}_0 + 2J_{\mathrm{D}}\tilde{\varphi}_2, \\ &\vdots \\ (n+s/\beta)\tilde{\varphi}_n &= J\tilde{\varphi}_{n-1} + (n+1)J_{\mathrm{D}}\tilde{\varphi}_{n+1}, \ \ldots \end{aligned} \tag{1.5.11.15}$$

where

$$\tilde{\varphi}_n = \tilde{\varphi}_n(x,s) = \int_0^\infty \varphi(x,t) e^{-st}\, dt.$$

This set may then be solved by successive approximations [46, 48], yielding the Laplace transform of the configuration space distribution

$$s\tilde{\varphi}_0 - \varphi_0(x,0) = \frac{\beta J_{\mathrm{D}} J}{(1+s/\beta)}\tilde{\varphi}_0 + \frac{2\beta J_{\mathrm{D}} J_{\mathrm{D}} JJ}{(2+s/\beta)(1+s/\beta)^2}\tilde{\varphi}_0 + \cdots. \tag{1.5.11.16}$$

In the *high*-dissipation and *low*-frequency (or long time) limits, where $s/\beta \to 0$, only the leading term on the right-hand side of Eq. (1.5.11.16) survives and we are left, since $J_{\mathrm{D}} J \sim O(\beta^{-1})$, with

$$s\tilde{\varphi}_0 - \varphi_0(x,0) = \beta J_{\mathrm{D}} J \tilde{\varphi}_0 \tag{1.5.11.17}$$

which, on inversion to the time domain, yields the Smoluchowski equation, i.e.,

$$\frac{\partial \varphi_0}{\partial t} = \frac{kT}{\beta}\frac{\partial}{\partial x}\left[\frac{\varphi_0}{kT}\frac{\partial V}{\partial x} + \frac{\partial \varphi_0}{\partial x}\right]. \tag{1.5.11.18}$$

We note that Eqs. (1.5.11.15) may be formally arranged in the coordinate representation as the continued fraction of operators

$$s\tilde{\varphi}_0 - \varphi_0(x,0) = \cfrac{\beta^2 J_{\mathrm{D}} J}{s+\beta - \cfrac{2\beta^2 J_{\mathrm{D}} J}{s+2\beta - \cfrac{3\beta^2 J_{\mathrm{D}} J}{s+3\beta - \cdots}}}\tilde{\varphi}_0. \tag{1.5.11.19}$$

This equation may also be written in a Heisenberg-like representation where, by postulating a suitable spatial basis and corresponding state vector, we may replace the spatial differential operators J_{D} and J by matrices, so that Eq. (1.5.11.19) may be represented as a matrix continued fraction for the observables. This representation is very useful for computational purposes and constitutes a central theme of this book.

Returning to Eq. (1.5.11.16), we remark that the strong damping limit is often defined merely by the condition $\beta^{-1} \to 0$. This definition is, however, insufficient because it is abundantly clear from Eq. (1.5.11.16) that, besides

specifying the latter condition, one must *also* impose a time- or frequency-domain condition, viz., *low* frequencies $s < \beta$ or *long* times $t > \beta^{-1}$ (cf. Einstein's discussion reproduced in Section 1.4). Thus *the Smoluchowski equation can never be used in the high-frequency region, where inertial effects are important.*

Further discussions of the problem, which are based on the Chapman–Enskog method [37] in the kinetic theory of gases, are well summarized by van Kampen [49]. The overriding advantage of considering the VHD limit discussed above is that it is possible to derive a diffusion equation in configuration space only. Moreover, this equation is in a single coordinate. Yet another example, where this may be done, is the VLD limit; this is of overwhelming importance in the application of the theory of Brownian motion to reaction rate theory (see Section 1.13 below). It is impossible, however, to derive a single-variable diffusion equation from the Klein–Kramers equation for *arbitrary* damping.

1.5.12. *Very-low-damping (VLD) regime*

We again refer to the discussion of the Klein–Kramers equation by Kramers [43], where a Brownian particle moves in the potential well generated by the force $\mathbf{K}(x)$; see Fig. (1.13.1). Here Kramers restricts the discussion to the situation in which the particle would perform an *oscillatory* motion in the well, characterized by closed phase trajectories, save for the Brownian forces. *Small viscosity means that the Brownian forces cause only a tiny perturbation in the undamped energy during one oscillation in the well,* meaning that the Brownian forces will cause *gradual changes in the distribution of the ensemble over the different energy values.* This is energy controlled diffusion.

We now write the original Klein–Kramers equation in the canonical variables (x, p) as a diffusion equation in the energy (E) and phase (w). We can do this since, for small damping, the energy is a slowly varying quantity and the phase a fast varying quantity. Thus, we will be able to average the density over the *fast phase variable* and obtain a diffusion equation in the *slow (almost-conserved) energy variable.* We define the time average along a trajectory corresponding to the saddle point (now a one-dimensional maximum) of the potential energy

$$\bar{\rho}(E,t) = \frac{1}{T'}\int_0^{T'} \rho(E,w,t)dw, \qquad (1.5.12.1)$$

where T' is the time required to execute one cycle of the almost periodic motion on the separatrix trajectory with the saddle-point energy. The average is taken along the energy trajectory, so that

$$dt = dw \tag{1.5.12.2}$$

(along a trajectory). If we define the action S at energy E by the equation

$$S(E) = \oint_{E=\text{const}} p\,dq \tag{1.5.12.3}$$

and allow the energy to vary by an amount dE over a thin ring of thickness dS, we can account for the slow diffusion of energy. (The assumption that the *damping has a negligible effect over one period* means that the energy loss per cycle of the motion at the saddle-point energy is much smaller than kT; see Section 1.13 below.) We assume that the motion of the particles in the well *would always have closed orbits* in the absence of Brownian forces, were it not for the slow diffusion of energy which interferes with the streaming librational motion. In general, the trajectories represent a leisurely spiraling towards the energy minimum, owing to the energy loss dE per cycle. Hence, the trajectories of the noisy motion at the saddle energy are almost closed (i.e., almost periodic).

Now in the Klein–Kramers Eq. (1.5.9.6), viz.,

$$\frac{\partial \rho}{\partial t} = \frac{dV}{dx}\frac{\partial \rho}{\partial p} - \frac{p}{m}\frac{\partial \rho}{\partial x} + \beta \frac{\partial}{\partial p}\left(\rho p + mkT\frac{\partial \rho}{\partial p}\right) \tag{1.5.12.4}$$

if there were no dissipation of energy, we would have by Liouville's theorem,

$$\frac{\partial \rho}{\partial t} = \frac{dV}{dx}\frac{\partial \rho}{\partial p} - \frac{p}{m}\frac{\partial \rho}{\partial x}. \tag{1.5.12.5}$$

Thus the remaining (diffusive) part of Eq. (1.5.12.4), viz.,

$$\beta \frac{\partial}{\partial p}\left(\rho p + mkT\frac{\partial \rho}{\partial p}\right) \tag{1.5.12.6}$$

describes, in the present context, the very slow dissipation of energy. We now transform Eq. (1.5.12.4) into an equation in the energy and phase variables by using the Hamiltonian

$$E = \frac{p^2}{2m} + V(x). \tag{1.5.12.7}$$

We have

$$\dot{x} = \pm\sqrt{\frac{2[E - V(x)]}{m}}, \tag{1.5.12.8}$$

which, on taking either the positive or negative sign and integrating the resulting first-order differential equation between points $x_1 = x(0)$ and x, yields

$$\int_{x_1}^{x} \left(2\left[E - V(x')\right]/m\right)^{-1/2} dx' = t + w, \tag{1.5.12.9}$$

where the constant of integration w defines the phase. Now Eq. (1.5.12.2) implies that $\dot{w} = 1$, and since the variation in energy is by hypothesis very slow, we have $\dot{E} \approx 0$; that is, almost a conservative system. Because $\dot{p} = -dV/dx$, we have, by the chain rule,

$$\frac{\partial \rho}{\partial x} = \frac{\partial \rho}{\partial E}\frac{\partial E}{\partial x} + \frac{\partial \rho}{\partial w}\frac{\partial w}{\partial x}, \quad \frac{\partial \rho}{\partial p} = \frac{\partial \rho}{\partial E}\frac{\partial E}{\partial p} + \frac{\partial \rho}{\partial w}\frac{\partial w}{\partial p}, \tag{1.5.12.10}$$

where

$$\frac{\partial E}{\partial x} = \frac{dV}{dx}, \quad \frac{\partial w}{\partial x} = \frac{1}{\dot{x}} = \frac{m}{p}, \quad \frac{\partial E}{\partial p} = \frac{p}{m}, \quad \frac{\partial w}{\partial p} = 0,$$

using Eqs. (1.5.12.7) and (1.5.12.9). Thus

$$\frac{\partial}{\partial x} = \frac{dV}{dx}\frac{\partial}{\partial E} + \frac{m}{p}\frac{\partial}{\partial w} \text{ and } \frac{\partial}{\partial p} = \frac{p}{m}\frac{\partial}{\partial E}, \tag{1.5.12.11}$$

so that the Klein–Kramers equation, Eq. (1.5.12.4), becomes

$$\frac{\partial \rho}{\partial t} = -\frac{\partial \rho}{\partial w} + \frac{\beta p}{m}\frac{\partial}{\partial E}\left(\rho p + pkT\frac{\partial \rho}{\partial E}\right). \tag{1.5.12.12}$$

Now, defining the average over one cycle of the almost-periodic motion at the energy E by Eq. (1.5.12.1), we have from Eq. (1.5.12.12)

$$\overline{\frac{\partial \rho}{\partial t}} = -\overline{\frac{\partial \rho}{\partial w}} + \overline{\frac{\beta p}{m}\frac{\partial}{\partial E}\left(\rho p + pkT\frac{\partial \rho}{\partial E}\right)}. \tag{1.5.12.13}$$

Averages of derivatives may now be expressed as derivatives of averages as follows. We have

$$\overline{\frac{\partial \rho}{\partial t}} = \frac{1}{T'}\int_0^{T'} \frac{\partial}{\partial t}\rho dw = \frac{\partial}{\partial t}\frac{1}{T'}\int_0^{T'} \rho dw = \frac{\partial \overline{\rho}}{\partial t} \text{ and } \overline{\frac{\partial \rho}{\partial w}} = \frac{1}{T'}\int_0^{T'} \frac{\partial \rho}{\partial w} dw = \frac{1}{T'}\int_0^{T'} d\rho = 0,$$

since the integral is taken over one complete cycle of the motion, $\rho(T) = \rho(0)$. Note that Eq. (1.5.12.13) holds only approximately, since

$$d\rho = \frac{\partial \rho}{\partial E}dE + \frac{\partial \rho}{\partial w}dw.$$

However, E is slowly varying, so that in one cycle $dE \approx 0$ and so

$$d\rho \approx \frac{\partial \rho}{\partial w}dw. \tag{1.5.12.14}$$

The averaged Klein–Kramers Eq. (1.5.12.13) then becomes

$$\frac{\partial \overline{\overline{\rho}}}{\partial t} = \frac{\beta}{m}\overline{\overline{\left(p^2 \frac{\partial \rho}{\partial E} + p\rho \frac{\partial p}{\partial E} + pkT \frac{\partial p}{\partial E}\frac{\partial \rho}{\partial E} + p^2 kT \frac{\partial^2 \rho}{\partial E^2} \right)}}, \tag{1.5.12.15}$$

which, using Eq. (1.5.12.10), simplifies to

$$\frac{\partial \overline{\overline{\rho}}}{\partial t} = \beta\overline{\overline{\left(\frac{p^2}{m}\frac{\partial \rho}{\partial E} + \rho + kT\frac{\partial \rho}{\partial E} + \frac{p^2 kT}{m}\frac{\partial^2 \rho}{\partial E^2} \right)}}. \tag{1.5.12.16}$$

On assuming that $\overline{\overline{p^2 \rho}} = \overline{\overline{p^2}}\,\overline{\overline{\rho}}$, and because

$$\overline{\overline{\frac{\partial \rho}{\partial E}}} = \frac{1}{T'}\int_0^{T'} \frac{\partial \rho}{\partial E} dw = \frac{1}{T'}\frac{\partial}{\partial E}\int_0^{T'} \rho dw = \frac{\partial \overline{\overline{\rho}}}{\partial E} \quad \text{and} \quad \overline{\overline{p^2}} = \frac{1}{T'}\int_0^{T'} p^2 dw,$$

we find that Eq. (1.5.12.16) finally becomes

$$\frac{\partial}{\partial t}\overline{\overline{\rho}} = \beta\left(\frac{1}{m}\overline{\overline{p^2}}\frac{\partial}{\partial E} + 1 + kT\frac{\partial}{\partial E} + \frac{kT}{m}\overline{\overline{p^2}}\frac{\partial^2}{\partial E^2} \right)\overline{\overline{\rho}}. \tag{1.5.12.17}$$

Furthermore, since we are taking the average along a closed orbit, $dw = dt$ and the periodic time in the well is $2\pi/\omega(E)$, where $\omega = \omega(E)$ is the angular frequency of oscillation in the well at energy E, so that

$$\overline{\overline{p^2}} = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} p^2 dt = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} pm\dot{x} dt = \frac{\omega m}{2\pi}\oint p dx = \frac{\omega m}{2\pi} S,$$

where S is the action over one period. Thus, Eq. (1.5.12.17) reduces to

$$\frac{\partial}{\partial t}\overline{\overline{\rho}} = \beta\left(1 + \frac{\omega S}{2\pi}\frac{\partial}{\partial E} \right)\left(\overline{\overline{\rho}} + kT\frac{\partial}{\partial E}\overline{\overline{\rho}} \right). \tag{1.5.12.18}$$

Since $\omega = 2\pi dE/dS$, Eq. (1.5.12.18) becomes (writing ρ for $\overline{\overline{\rho}}$)

$$\frac{\partial \rho}{\partial t} = \beta\frac{\partial}{\partial S}\left(S\rho + \frac{2\pi kTS}{\omega}\frac{\partial \rho}{\partial S} \right). \tag{1.5.12.19}$$

This corresponds to diffusion along the S- or E-coordinate; the proper diffusion term corresponds to a diffusion coefficient $D = 2\pi\beta kTS/\omega$. The above paragraph constitutes an extended version of Kramers' original method of arriving at the energy diffusion equation. Further discussion of this will be found in van Kampen [49], Hänggi *et al.* [50], and Coffey *et al.* [44]. The energy-controlled diffusion equation, Eq. (1.5.12.19) is essential regarding the contribution of Kramers to reaction-rate theory (cf. Chapter 1, Section 1.13).

We remark that Praestgaard and van Kampen [51], by treating the rotational Brownian motion of a fixed-axis rotator in a potential $V(\theta)$ in the energy-diffusion limit via the Fokker–Planck equation for the PDF $\rho(\theta, \dot{\theta}, t)$, viz.,

$$\frac{\partial \rho}{\partial t} = \frac{1}{I}\frac{dV}{d\theta}\frac{\partial \rho}{\partial \dot{\theta}} - \dot{\theta}\frac{\partial \rho}{\partial \theta} + \beta\frac{\partial}{\partial \dot{\theta}}\left(\rho\dot{\theta} + \frac{kT}{I}\frac{\partial \rho}{\partial \dot{\theta}}\right), \qquad (1.5.12.20)$$

have also derived a single-variable Fokker–Planck equation for the PDF $\rho(E, t)$ in energy space

$$\frac{\partial \rho}{\partial t} = \beta\left[\frac{\partial}{\partial E}\left(I\overline{\dot{\theta}^2}(E) - kT\right) + IkT\frac{\partial^2}{\partial E^2}\overline{\dot{\theta}^2}(E)\right]\rho, \qquad (1.5.12.21)$$

where I is the moment of inertia. The method of Praestgaard and van Kampen [51] is also applicable to one-dimensional translational Brownian motion. The translational analog of Eq. (1.5.12.21) is given by

$$\frac{\partial \rho}{\partial t} = \beta\left[\frac{\partial}{\partial E}\left(\frac{1}{m}\overline{p^2}(E) - kT\right) + \frac{kT}{m}\frac{\partial^2}{\partial E^2}\overline{p^2}(E)\right]\rho. \qquad (1.5.12.22)$$

We shall use Eqs. (1.5.12.21) and (1.5.12.22) in Chapter 10.

1.6. Probability theory

This section reviews the fundamental concepts of probability theory on which the theoretical treatment of Brownian motion is founded. Again, readers who are familiar with these concepts may conveniently skip this section.

By way of introduction, we cannot improve on the elegant description of the emergence of probability theory as a fundamental tool in physics, given by Born [38] in his *Natural Philosophy of Cause and Chance* (see also [31, 39]).

> "The new turn in physics was the introduction of atomistics and statistics. To follow up the history of atomistics into the remote past is not in the plan of this lecture. We can take it for granted that since the days of Democritus the hypothesis of matter being composed of ultimate and indivisible particles was familiar to every educated man. It was reviewed when the time was ripe. Lord Kelvin quotes frequently a Father Boscovich as one of the first to use atomistic considerations to solve physical problems; he lived in the eighteenth century, and there may have been others, of whom I know nothing, thinking on the same lines. The first systematic use of atomistics was made in chemistry, where it allowed the reduction of innumerable substances to a relatively small stock of elements. Physics followed considerably later because atomistics as such

> was of no great use without another fundamental idea, namely that the observable properties of matter are not intrinsic properties of its smallest parts but averages over distributions governed by the laws of chance.
>
> The theory of probability itself, which expresses these laws, is much older; it sprang not from the needs of natural science, but from gambling and other, more or less disreputable, human activities."

The most important concept of that theory that we shall need is the *random variable*. This is a quantity [25] that may take on any of the values of a specified set with a *specified relative frequency* or *probability*. The random variable could be a vector molecular property, such as center of mass velocity, angular momentum, or dipole orientation; or a tensor, such as polarizability. It is regarded as being defined not only by a set of permissible values (such as an ordinary mathematical variable has), but by an *associated probability function* expressing *the relative frequency of occurrence of* these values in the situation under discussion.

1.6.1. *Random variables and probability distributions*

We may formalize the above concepts as follows. Let Ω be a set called the *sample space* of an outcome of a random experiment or occurrence [25, 52]. Each subset $A \subseteq \Omega$ is called an *event*. We wish to formalize the idea of the *chance* of obtaining an outcome lying in a specified subset $A \subseteq \Omega$ into a definition of *probability*. We shall need a *function* that assigns a *unique number* or *measure* (called *probability*) to each such A.

Definition 1: We call $P(A)$ a *probability function* if to each event $A \subseteq \Omega$, $P(A)$ assigns a number $P(A)$ to each A such that

$$0 \le P(A) \le 1, \quad P(\Omega) = 1,$$

and if $A_1, A_2, \ldots$ are events with $A_i \cap A_j = \varnothing$ $(i \neq j)$, where $\varnothing$ denotes the empty set, then

$$P\left(\bigcup_{n=1}^{\infty} A_n\right) = \sum_{n=1}^{\infty} P(A_n).$$

For two events A and B, the *conditional probability* is given by [52]

$$P(A \mid B) = \frac{P(A \cap B)}{P(B)}, \tag{1.6.1.1}$$

where $P(A \cap B)$ is the probability function of both A and B occurring, and $P(A \mid B)$ means the probability function of event A occurring if event B occurs. If the two events A and B are *statistically independent*, then $P(A \mid B) = P(A)$ and

$$P(A \cap B) = P(A)P(B). \tag{1.6.1.2}$$

Consider the experiment of obtaining an event $\zeta \in \Omega$. The experiment can be described by a set of functions $\xi(\zeta)$. The $\xi(\zeta)$ are called *random variables* because the independent variable ξ cannot be predicted. It only takes on values (its realizations) according to the underlying *probability law*. More formally, a *random variable* may be defined as follows [52].

Definition 2: A *random variable* ξ is a real-valued function with domain Ω, i.e., for each $\zeta \in \Omega$, $\xi(\zeta) \in \Re$. For an n-dimensional random variable $\xi = (\xi_1, ..., \xi_n)$, we have $\xi(\zeta) \in \Re^n$. $\Re$ denotes the real line.

Here, we give a brief outline of some properties of a random variable, ξ, which are relevant in the present context. The notation of Gnedenko [53] for random variables and realizations is adhered to as far as possible.

Definition 3: If ξ is a random variable, its *distribution function* is defined as

$$F_\xi(x) = P[\xi \le x],$$

where x is a real number. The x's are the realizations (i.e., the values which it actually takes on) of the random variable ξ.

If it is possible to write the distribution function as [40]

$$F_\xi(x) = \int_{-\infty}^{x} f_\xi(x')dx', \tag{1.6.1.3}$$

meaning that the probability that an observed value of ξ lies in the interval $(x, x + dx)$ is $f_\xi dx$, then ξ is said to be a *continuous random variable* and $f_\xi(x)$ is its PDF. *A discrete random variable* ξ will have a *probability (mass) function* $P_\xi(A)$ such that

$$P_\xi(A) = \sum_{x \in A} p_\xi(x).$$

The *mean value* of a random variable ξ denoted by $\langle \xi \rangle$ is defined as

$$\langle \xi \rangle = \int_{-\infty}^{\infty} x f_\xi(x)dx \quad \text{for } \xi \text{ continuous} \tag{1.6.1.4}$$

and

$$\langle \xi \rangle = \sum_j x_j p_\xi(x_j) \quad \text{for } \xi \text{ discrete.} \tag{1.6.1.5}$$

Using Eqs. (1.6.1.4) and (1.6.1.5), it is obvious that

$$\langle c\xi \rangle = c\langle \xi \rangle, \quad \langle \xi_1 + \xi_2 \rangle = \langle \xi_1 \rangle + \langle \xi_2 \rangle \tag{1.6.1.6}$$

(c being a constant). When $\langle \xi \rangle$ vanishes, ξ is said to be a *centered random variable* [40]. Likewise, for any function $g(\xi)$ of a random variable ξ, we have

$$\langle g(\xi)\rangle = \int_{-\infty}^{\infty} g(x) f_\xi(x)dx \text{ for } \xi \text{ continuous,} \qquad (1.6.1.7)$$

$$\langle g(\xi)\rangle = \sum_j g(x_j) p_\xi(x_j) \text{ for } \xi \text{ discrete.} \qquad (1.6.1.8)$$

The *variance* Var $[\xi]$ of ξ, denoted by $\sigma^2(\xi)$, is defined as [40, 52] the mean of $(\xi - \langle\xi\rangle)^2$, that is,

$$\sigma^2(\xi) = \langle(\xi - \langle\xi\rangle)^2\rangle = \langle\xi^2 - 2\xi\langle\xi\rangle + \langle\xi\rangle^2\rangle = \langle\xi^2\rangle - \langle\xi\rangle^2. \qquad (1.6.1.9)$$

The positive square root of the variance, denoted by $\sigma(\xi)$ is called the *standard deviation* of ξ. This is a measure of the *spread* or *dispersion* about the mean, of the values that the random variable ξ can assume. The *covariance* $\mathrm{Cov}(\xi_1, \xi_2)$ of any two random variables ξ_1 and ξ_2 is defined as [52]

$$\mathrm{Cov}(\xi_1, \xi_2) = \langle(\xi_1 - \langle\xi_1\rangle)(\xi_2 - \langle\xi_2\rangle)\rangle = \langle\xi_1\xi_2\rangle - \langle\xi_1\rangle\langle\xi_2\rangle. \qquad (1.6.1.10)$$

$\mathrm{Cov}(\xi_1, \xi_2)$ is a measure of how ξ_1 and ξ_2 are interrelated. When ξ_1 and ξ_2 are *independent*, then

$$\mathrm{Cov}(\xi_1, \xi_2) = 0.$$

One defines the *correlation coefficient* of two random variables ξ_1 and ξ_2 as [25, 52]

$$\rho = \frac{\mathrm{Cov}(\xi_1, \xi_2)}{\sigma(\xi_1)\sigma(\xi_2)}. \qquad (1.6.1.11)$$

ρ is a measure of the *dependence* between ξ_1 and ξ_2.

1.6.2. *The Gaussian distribution*

The distribution function of a continuous random variable, ubiquitous in the theory of Brownian motion, is the *normal distribution*, also known as the *Gaussian distribution* with PDF [35]

$$f_\xi(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\langle\xi\rangle)^2}{2\sigma^2}}, \quad -\infty < x < \infty, \quad \sigma > 0, \qquad (1.6.2.1)$$

which has the following properties (i) $\langle\xi\rangle = \mu$, $\mathrm{Var}[\xi] = \sigma^2$; (ii) f_ξ has a maximum at $\xi = \mu$; and (iii) as $x \to \pm\infty$, $f_\xi \to 0$. This distribution is denoted by $N(\langle\xi\rangle, \sigma^2)$. It can be shown that the distribution of a random variable $c\,\xi$ is $N(c\langle\xi\rangle, c^2\sigma^2)$, while the distribution of $\xi - \langle\xi\rangle$ is $N(0, \sigma^2)$. Likewise the distribution of $(\xi - \langle\xi\rangle)/\sigma$ is $N(0, 1)$ called the *standard normal distribution.*

We must now introduce the concept of *multi-dimensional* random variables. Let ξ_1 and ξ_2 be two continuous random variables. Then we define their *joint PDF* $f_{\xi_1,\xi_2}(x,y)$ by the equation

$$f_{\xi_1,\xi_2}(x,y)dx\,dy = P\big(x \le \xi_1 \le x+dx,\, y \le \xi_2 \le y+dy\big).$$

We also define the corresponding *joint distribution function* by

$$F_{\xi_1,\xi_2}(x,y) = P\big(\xi_1 \le x, \xi_2 \le y\big) = \int_{-\infty}^{x}\int_{-\infty}^{y} f_{\xi_1,\xi_2}(x',y')dx'dy'.$$

Thus, if F_{ξ_1,ξ_2} is differentiable, the joint PDF is $f_{\xi_1,\xi_2}(x,y) = \partial^2_{x,y}F_{\xi_1,\xi_2}(x,y)$. We also define the *marginal distribution function* $F_{\xi_1}(x)$ of ξ_1 as

$$F_{\xi_1}(x) = P\big(\xi_1 \le x,\ \xi_2 < \infty\big) = \int_{-\infty}^{\infty}\int_{-\infty}^{x} f_{\xi_1,\xi_2}(x',y')dx'dy' = \int_{-\infty}^{x} f_{\xi_1}(x')dx',$$

where $F_{\xi_1}(x')dx'$ is called the marginal distribution function of ξ_1 with PDF

$$f_{\xi_1}(x) = \int_{-\infty}^{\infty} f_{\xi_1,\xi_2}(x,y')dy'.$$

As before we may define the average value of a function $g(\xi_1,\xi_2)$ by means of the equation

$$\big\langle g(\xi_1,\xi_2)\big\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} g(x,y)f_{\xi_1,\xi_2}(x,y)dxdy.$$

Clearly $\langle \xi_1+\xi_2\rangle = \langle\xi_1\rangle + \langle\xi_2\rangle$. We remark that

$$\langle\xi_1\xi_2\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} xyf_{\xi_1,\xi_2}(x,y)dxdy.$$

In certain cases, this may be written as

$$\langle\xi_1\xi_2\rangle = \int_{-\infty}^{\infty} xh_{\xi_1}(x)dx\int_{-\infty}^{\infty} yq_{\xi_2}(y)dy,$$

where h and q are the marginal PDFs of ξ_1 and ξ_2, respectively. Thus $\langle\xi_1\,\xi_2\rangle = \langle\xi_1\rangle\langle\xi_2\rangle$, and ξ_1 and ξ_2 are said to be *independent* random variables; by Eq. (1.6.1.10) they are uncorrelated. We remark, however, that two uncorrelated random variables are not necessarily independent – with the exception of Gaussian random variables. We have so far confined ourselves to $\Re^2$; all these results may, however, be carried over to $\Re^n$. Generally, if ξ is a vector-valued random variable, and the ξ_i are all independent, then

$$\langle\xi_1\xi_2\xi_3\cdots\xi_n\rangle = \langle\xi_1\rangle\langle\xi_2\rangle\cdots\langle\xi_n\rangle.$$

In general, if ξ is a random variable with n components $\xi_1, \xi_2, \ldots, \xi_n$, its PDF $f_{\xi_1 \ldots \xi_n}(x_1, \ldots, x_n)$ is called the *joint PDF* of the n *variables* $\xi_1, \ldots, \xi_n$. We are often interested in the distribution of a *subset* having $s < n$ variables $\xi_1, \xi_2, \ldots, \xi_s$. The probability that they have certain values between $(x_1, x_1 + dx_1)$ and $(x_2, x_2 + dx_2)$, etc., irrespective of the remaining variables $\xi_{s+1}, \ldots, \xi_n$, is

$$f_{\xi_1 \ldots \xi_s}(x_1, \ldots, x_s) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} f_{\xi_1 \ldots \xi_n}(x_1, \ldots, x_s, x_{s+1}, \ldots, x_n)\, dx_{s+1} \cdots dx_n .$$

This is the most general definition of the *marginal density function* for the subset. The most important practical example of a multi-dimensional distribution is the n dimensional Gaussian distribution defined as follows [13, 52, 54]: let $(\xi_1, \ldots, \xi_n)$ be n (not necessarily independent) random variables with means equal to zero. Let $f(x_1, \ldots, x_n)$ be their joint PDF; then we say $(\xi_1, \ldots, \xi_n)$ are normally distributed in n dimensions if (we drop the suffixes from $f_{\xi_1, \ldots, \xi_n}$ for convenience)

$$f(\mathbf{x}) = (2\pi)^{-n/2} (\det \mathbf{M})^{-1/2}\, e^{-\mathbf{x}^{\mathrm{T}} \mathbf{M}^{-1} \mathbf{x}/2}, \tag{1.6.2.2}$$

where $\mathbf{M} = |\mu_{ij}|$ is the matrix of the second moments $\mu_{ij} = \langle \xi_i \xi_j \rangle$, $i, j = 1, 2, \ldots, n$, $\mathbf{M}^{-1}$ is the inverse matrix; $\det \mathbf{M}$ is its determinant; $\mathbf{x}$ is the column vector with components $(x_1, \ldots, x_n)$, $\mathbf{x}^{\mathrm{T}}$ is its transpose, and the quadratic form is

$$\mathbf{x}^{\mathrm{T}} \mathbf{M}^{-1} \mathbf{x} = (\det \mathbf{M})^{-1} \sum_{i,j=1}^{n} M_{ij} x_i x_j \tag{1.6.2.3}$$

(M_{ij} is the cofactor of μ_{ij} in $\mathbf{M}$). The marginal density functions $f(x_{i_1}, x_{i_2}, \ldots, x_{i_r})$ for the multi-dimensional normal distribution may be determined from

$$f(x_{i_1}, \cdots, x_{i_r}) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} f(x_{i_1}, \ldots, x_{i_r}, x_{i_{r+1}}, \ldots, x_{i_N})\, dx_{i_{r+1}} \cdots dx_{i_N} .$$

These PDFs represent r-dimensional normal distributions. If the ξ_i are *independent* then $\langle \xi_i \xi_j \rangle = 0$ $(i \neq j)$ and $\mathbf{M}$ becomes a pure diagonal matrix. Here $f(x_1, \ldots, x_n) = f(x_1) f(x_2) \cdots f(x_n)$, where each $f(x_i)$ represents a one-dimensional normal distribution with mean zero and variance μ_{ii}.

We may easily evaluate the quadratic form, Eq. (1.6.2.3), explicitly, for example in the two-dimensional case [52, 54] with PDF $f(x_1, x_2)$. We have

$$\mathbf{x} = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}, \quad \mathbf{x}^{\mathrm{T}} = (x_1 \; x_2),$$

$$\mathbf{M} = \begin{pmatrix} \mu_{11} & \mu_{12} \\ \mu_{12} & \mu_{22} \end{pmatrix}, \quad \mathbf{M}^{-1} = \frac{1}{\mu_{11}\mu_{22} - \mu_{12}^2} \begin{pmatrix} \mu_{22} & -\mu_{12} \\ -\mu_{12} & \mu_{11} \end{pmatrix},$$

so that

$$\mathbf{x}^{\mathrm{T}}\mathbf{M}^{-1}\mathbf{x} = \frac{1}{\mu_{11}\mu_{22} - \mu_{12}^2}\left(\mu_{22}x_1^2 - 2\mu_{12}x_1x_2 + \mu_{11}x_2^2\right).$$

We now introduce the standard notation

$$\mu_{11} = \sigma_{x_1}^2, \quad \mu_{22} = \sigma_{x_2}^2, \quad \mu_{12} = \rho\sigma_{x_1}\sigma_{x_2},$$

where σ_{x_1} and σ_{x_2} are the *standard deviations* of the random variables ξ_1 and ξ_2 and ρ is the *correlation coefficient*. Our PDF then assumes the *standard form*

$$f_{\xi_1,\xi_2}(x_1,x_2) = \frac{1}{2\pi\sigma_{x_1}\sigma_{x_2}(1-\rho^2)^{1/2}} e^{-\frac{1}{2(1-\rho^2)}\left(\frac{x_1^2}{\sigma_{x_1}^2} - \frac{2\rho x_1x_2}{\sigma_{x_1}\sigma_{x_2}} + \frac{x_2^2}{\sigma_{x_2}^2}\right)}.$$

We have considered, for simplicity, the case of zero means. If the means are not zero, the multi-dimensional normal distribution has PDF

$$f(\mathbf{x}) = (2\pi)^{-n/2}(\det\mathbf{R})^{-1/2}\, e^{-\frac{1}{2}(\mathbf{x}-\boldsymbol{\mu})^{\mathrm{T}}\mathbf{R}^{-1}(\mathbf{x}-\boldsymbol{\mu})},$$

where $\mathbf{R}$ is now the covariance matrix with elements $\langle\xi_i\xi_j\rangle - \langle\xi_i\rangle\langle\xi_j\rangle$ and $\langle\xi_i\rangle$. For example, our two-dimensional Gaussian PDF $f_{\xi_1,\xi_2}(x_1,x_2)$ now becomes

$$f_{\xi_1,\xi_2} = \frac{1}{2\pi\sigma_{x_1}\sigma_{x_2}(1-\rho^2)^{1/2}} e^{-\frac{1}{2(1-\rho^2)}\left[\frac{(x_1-\mu_{x_1})^2}{\sigma_{x_1}^2} - \frac{2\rho(x_1-\mu_{x_1})(x_2-\mu_{x_2})}{\sigma_{x_1}\sigma_{x_2}} + \frac{(x_2-\mu_{x_2})^2}{\sigma_{x_2}^2}\right]}$$

$(-\infty < x_1, x_2 < \infty)$. In order to show that $f(\mathbf{x})$ is indeed a PDF, we have to prove that [52]

$$\int_{-\infty}^{\infty} f(\mathbf{x})d\mathbf{x} = \int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty} f(x_1,\ldots,x_n)dx_1\cdots dx_n = 1.$$

In order to accomplish this, we note that $\mathbf{R}$ must be positive definite, thus [52] there exists a non-singular real matrix $\mathbf{Q}$ such that $\mathbf{R} = \mathbf{Q}\mathbf{Q}^{\mathrm{T}}$. We now write $\mathbf{x} = \mathbf{Q}\mathbf{y} + \boldsymbol{\mu}$. The Jacobian of this transformation is $|\partial\mathbf{x}/\partial\mathbf{y}| = |\det\mathbf{Q}|$. Thus, the quadratic form is reduced to a sum of squares, and so

$$\int_{-\infty}^{\infty} f(\mathbf{x})d\mathbf{x} = (2\pi)^{-n/2}|\det\mathbf{Q}|^{-1}\int_{-\infty}^{\infty} e^{-\mathbf{y}^{\mathrm{T}}\mathbf{y}/2}|\det\mathbf{Q}|\,d\mathbf{y} = (2\pi)^{-n/2}\int_{-\infty}^{\infty} e^{-\sum_{j=1}^{n} y_j^2/2}\,d\mathbf{y} = 1.$$

1.6.3. *Moment-generating functions*

We now introduce the concept of a *moment-generating function*, which is an integral transform of a PDF. In particular, consider the function [55]

$$\phi_\xi(u) = \int_{-\infty}^{\infty} e^{iux} f_\xi(x)dx = \left\langle e^{iu\xi} \right\rangle.$$

This function is termed the *characteristic function* of the random variable ξ. Evidently, two random variables have the same characteristic functions if and only if they have the same PDF. As an example of how to compute characteristic functions, we evaluate $\phi_\xi(u)$ for ξ with the normal distribution (which, in the centered case, has the remarkable reproductive property that it is itself Gaussian)

$$f_\xi(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}.$$

We have, by completing the square in the argument of the exponential,

$$\phi_\xi(u) = e^{iu\mu - \frac{1}{2}\sigma^2u^2} \int_{-\infty}^{\infty} e^{-\frac{1}{2}(y-iu\sigma)^2} \frac{dy}{\sqrt{2\pi}} = e^{iu\mu - \frac{1}{2}\sigma^2u^2}. \qquad (1.6.3.1)$$

Furthermore, if ξ is a *centered* Gaussian random variable (i.e., $\mu = 0$), then $\phi_\xi(u) = e^{-\sigma^2u^2/2}$, so that $\left\langle e^{iu\xi} \right\rangle = e^{-\left\langle \xi^2 \right\rangle u^2/2}$. In particular, if $u = 1$, $\left\langle e^{i\xi} \right\rangle = e^{-\left\langle \xi^2 \right\rangle/2}$ which is a most useful relation. We remark that, by Fourier's integral theorem [56],

$$f_\xi(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-iux} \phi_\xi(u)du,$$

so that [25] a knowledge of the characteristic function of a random variable is equivalent to a knowledge of its PDF.

We now establish a fundamental property of characteristic functions, namely that the n^{th} *derivative* of $\phi_\xi(u)$, when evaluated at $u = 0$, gives the n^{th} *moment* about zero of the random variable ξ. We have

$$\phi_\xi(u) = \left\langle e^{iu\xi} \right\rangle, \quad \frac{d}{du}\phi_\xi(0) = i\left\langle \xi \right\rangle, \quad \frac{d^2}{du^2}\phi_\xi(0) = \left\langle (i\xi)^2 \right\rangle,$$

and so on. For example, for the normal distribution $N(\mu, \sigma^2)$, one has

$$\phi_\xi(u) = e^{iu\mu - \sigma^2u^2/2}, \quad \frac{d}{du}\phi_\xi(0) = i\mu = i\left\langle \xi \right\rangle,$$

and so on. One may continue to show that for this distribution,

$$\left\langle \xi^2 \right\rangle = \mu^2 + \sigma^2, \quad \left\langle \xi^3 \right\rangle = 3\mu\sigma^2 + \mu^3, \quad \left\langle \xi^4 \right\rangle = 3\sigma^2 + 6\mu^2\sigma^2 + \mu^4.$$

Furthermore, if $\left\langle \xi \right\rangle = \mu = 0$, we have, by successive differentiations,

$$\left\langle \xi^{2n+1} \right\rangle = 0, \quad \left\langle \xi^{2n} \right\rangle = (2n-1)!!\left\langle \xi^2 \right\rangle^n,$$

which is a most important (reproductive) property of $N(0, \sigma^2)$.

The characteristic function for the n-dimensional Gaussian PDF is

$$\phi_\xi(\mathbf{u}) = \int_{-\infty}^{\infty} e^{i\mathbf{u}^{\mathrm{T}}\mathbf{x}} f(\mathbf{x})d\mathbf{x} = \frac{1}{(2\pi)^{n/2}\sqrt{\det \mathbf{R}}} \int_{-\infty}^{\infty} e^{i\mathbf{u}^{\mathrm{T}}\mathbf{x}-(\mathbf{x}-\boldsymbol{\mu})^{\mathrm{T}}\mathbf{R}^{-1}(\mathbf{x}-\boldsymbol{\mu})/2} d\mathbf{x}.$$

By matrix multiplication, we have

$$i\mathbf{u}^{\mathrm{T}}\mathbf{x} - (\mathbf{x}-\boldsymbol{\mu})^{\mathrm{T}}\mathbf{R}^{-1}(\mathbf{x}-\boldsymbol{\mu})/2$$
$$= i\mathbf{u}^{\mathrm{T}}\boldsymbol{\mu} - \mathbf{u}^{\mathrm{T}}\mathbf{R}\mathbf{u}/2 - (\mathbf{x}-\boldsymbol{\mu}-i\mathbf{R}\mathbf{u})^{\mathrm{T}}\mathbf{R}^{-1}(\mathbf{x}-\boldsymbol{\mu}-i\mathbf{R}\mathbf{u})/2.$$

Hence

$$\phi_\xi(u) = \left\langle e^{iu^{\mathrm{T}}\xi} \right\rangle = e^{iu^{\mathrm{T}}\boldsymbol{\mu} - u^{\mathrm{T}}\mathbf{R}u/2}. \tag{1.6.3.2}$$

In particular, for the two-dimensional case with $\langle \xi_1 \rangle = \langle \xi_2 \rangle = 0$, we have

$$\phi_{\xi_1,\xi_2}(u_1, u_2) = e^{-\left(\sigma_{x_1}^2 u_1^2 + 2\rho\sigma_{x_1}\sigma_{x_2}u_1u_2 + \sigma_{x_2}^2 u_2^2\right)/2},$$

which will be widely used in what follows, because this characteristic function plays a fundamental role in the theory of Brownian movement. Several properties of Gaussian random variables may be deduced from it.

If ξ_1 and ξ_2 are *independent random* variables, and we have the linear combination $z = \alpha_1\xi_1 + \alpha_2\xi_2$, then

$$\phi_z(u) = \left\langle e^{i\alpha_1\xi_1 u} e^{i\alpha_2\xi_2 u} \right\rangle = \left\langle e^{i\alpha_1\xi_1 u} \right\rangle \left\langle e^{i\alpha_2\xi_2 u} \right\rangle = \phi_{\xi_1}(\alpha_1 u)\phi_{\xi_2}(\alpha_2 u).$$

More generally, if $(\xi_1, \ldots, \xi_n)$ are n independent random variables and we have the linear combination $z = \alpha_1\xi_1 + \alpha_2\xi_2 + \cdots + \alpha_n\xi_n$, then

$$\phi_z(u) = \prod_{i=1}^{n} \phi_{\xi_i}(\alpha_i u).$$

This may be used to establish an important property of *independent* Gaussian random variables. Let

$$\xi_1 \sim N(\mu_1, \sigma_1^2), \quad \phi_{\xi_1}(u) = e^{iu\mu_1 - \sigma_1^2 u^2/2},$$
$$\vdots \qquad\qquad \vdots$$
$$\xi_n \sim N(\mu_n, \sigma_n^2), \quad \phi_{\xi_n}(u) = e^{iu\mu_n - \sigma_n^2 u^2/2}.$$

We wish to know the PDF of the linear combination $z = \sum_{k=1}^{n} \alpha_k\xi_k$. Evidently

$$\phi_z(u) = \prod_{i=1}^{n} \phi_{\xi_k}(\alpha_k u) = e^{i\sum_{k=1}^{n}\alpha_k\mu_k u - \sum_{k=1}^{n}\alpha_k^2\sigma_k^2 u^2/2},$$

and thus

$$f_z = N\left(\sum_{k=1}^{n} \alpha_k \mu_k, \sum_{k=1}^{n} \alpha_k^2 \sigma_k^2\right).$$

So a linear combination of independent normally distributed random variables is also a normally distributed random variable with mean

$$\mu = \sum_{k=1}^{n} \alpha_k \mu_k$$

and variance

$$\sigma^2 = \sum_{k=1}^{n} \alpha_k^2 \sigma_k^2.$$

The above result applies to a sum of *independent* Gaussian random variables. We now consider the analogous result for a linear combination of n *not necessarily independent* Gaussian random variables. For simplicity, consider the sum of two Gaussian random variables $\xi_1 + \xi_2$ and calculate the characteristic function of this sum, that is, $\phi_{\xi_1+\xi_2}(u)$. This may be evaluated by simply writing $u_1 = u_2$ in our expression for the characteristic function of the two-dimensional Gaussian distribution above. We have

$$\phi_{\xi_1+\xi_2}(u) = \left\langle e^{iu(\xi_1+\xi_2)} \right\rangle = e^{i(\mu_{x_1}+\mu_{x_2})u-(\sigma_{x_1}^2+2\rho\sigma_{x_1}\sigma_{x_2}+\sigma_{x_2}^2)u^2/2}.$$

Thus, $\xi_1 + \xi_2$ is a Gaussian random variable with mean $\mu_{x_1} + \mu_{x_2}$ and variance $\sigma_{x_1}^2 + 2\rho\sigma_{x_1}\sigma_{x_2} + \sigma_{x_2}^2$.

In the general case, for any real constants c_1 and c_2, the variables $c_1\,\xi_1$ and $c_2\,\xi_2$ are Gaussian [40]. It follows that *any linear combination* of $\xi_1 + \xi_2$ is Gaussian. This may be extended to show that *any linear combination of n Gaussian random variables is itself Gaussian.* Furthermore, if $\{\xi_i\}$ are all centered, so too is the linear combination: if $\xi_1, \xi_2, \ldots, \xi_n$ are centered Gaussian random variables and $c_1, c_2, \ldots, c_n$ is a set of real numbers, then $\xi = \xi_1 c_1 + \ldots + \xi_n c_n$ is also a centered Gaussian random variable.

This result may be used to prove Isserlis's theorem [26], which is of central importance in the theory of Brownian motion. We now establish, following [40] Isserlis's theorem (also known as Wick's theorem), that (see Section 1.3)

$$\left\langle \xi_1 \cdots \xi_{2n-1} \right\rangle = 0, \quad \left\langle \xi_1 \cdots \xi_{2n} \right\rangle = \sum_{\substack{i_1<\cdots<i_n \\ i_1<j_1,\ldots,i_n<j_n}} \left\langle \xi_{i_1} \xi_{j_1} \right\rangle \cdots \left\langle \xi_{i_n} \xi_{j_n} \right\rangle. \qquad (1.6.3.3)$$

(Although this result is often quoted in literature on Brownian motion and is crucial to the theory, the proof of it is not easily available.) For ξ defined above

$$\left\langle e^{i\xi} \right\rangle = \frac{1}{\sqrt{2\pi\langle\xi^2\rangle}} \int_{-\infty}^{\infty} e^{ix} e^{-\frac{x^2}{2\langle\xi^2\rangle}} dx = e^{-\frac{1}{2}\langle\xi^2\rangle} \qquad (1.6.3.4)$$

and, therefore,

$$\sum_{r=0}^{\infty}\frac{i^r}{r!}\left\langle \xi^r\right\rangle=\sum_{s=0}^{\infty}\frac{(-1)^s}{2^s s!}\left\langle \xi^2\right\rangle^s. \tag{1.6.3.5}$$

The multiplier of $c_1c_2\cdots c_n$ in $\langle \xi^r\rangle=\langle(\xi_1c_1+\cdots+\xi_nc_n)^r\rangle$ is $\delta_{n,r}n!\langle\xi_1\xi_2\cdots\xi_n\rangle$, while the multiplier of $c_1c_2\cdots c_{2s}$ in $\langle\xi^2\rangle^s$ is

$$2^s s!\sum_{\substack{i_1<i_2<\cdots<i_{2s}\\ i_1<j_1,\ldots,i_{2s}<j_{2s}}}\left\langle\xi_{i_1}\xi_{j_1}\right\rangle\cdots\left\langle\xi_{i_{2s}}\xi_{j_{2s}}\right\rangle.$$

Thus, on comparing the coefficients of $c_1c_2\cdots c_n$ on both sides of Eq. (1.6.3.5), we have Isserlis's theorem. The second Eq. (1.6.3.3) may also be written in the form

$$\left\langle\xi_1\xi_2\cdots\xi_n\right\rangle=\sum\prod_{i_r>i_s}\left\langle\xi_{i_r}\xi_{i_s}\right\rangle,$$

the summation being over all products of mean values of different pairs with decreasing suffixes.

1.6.4. *Central limit theorem*

The properties of characteristic functions are of considerable use in developing a fundamental statistical theorem known [18, 35, 54] as the *Central Limit Theorem*, which may be stated as follows.

Let $\{\xi_i\}$ be a sequence of *independent* random variables each having *arbitrary* distributions. Then the *sums*

$$\xi=\left(\xi_1+\xi_2+\xi_3+\cdots+\xi_n\right)/\sqrt{n}$$

approach a *normally* distributed random variable as n approaches infinity. Further, if ξ_i has mean zero and variance $\langle\xi_i^2\rangle=\sigma_i^2<\infty$, then ξ has mean zero and variance

$$\sigma^2=(1/n)\sum_{i=1}^{n}\sigma_i^2.$$

The theorem may be proved heuristically as follows. Let

$$\langle\xi_i^3\rangle=\tau_i^3,\ \langle\xi_i^4\rangle=v_i^4,\ i=1,2,\ldots,n$$

(the exact values of these higher order moments will be of no concern to us in the present investigation as long as they are uniformly bounded). The characteristic function $\phi_\xi(u)$ may be written as

$$\phi_\xi(u)=\left\langle e^{iu\xi}\right\rangle=\prod_{k=1}^{n}\left\langle e^{iu\xi_k/\sqrt{n}}\right\rangle.$$

Taking the logarithm of this gives the logarithmic characteristic function

$$\ln\phi_\xi(u)=\sum_{k=1}^{n}\ln\left(1-\frac{u^2\sigma_k^2}{2n}-\frac{i\tau_k^3u^3}{6n\sqrt{n}}+\frac{u^4v_k^4}{24n^2}\cdots\right).$$

For $n \to \infty$, the term on the right-hand side under the summation sign may be approximated by $-u^2\sigma_k^2/(2n)$. Hence,

$$\lim_{n\to\infty}\left[\ln\phi_\xi(u)\right]=-u^2\sigma^2/2$$

and thus

$$\phi_\xi(u)=e^{-u^2\sigma^2/2},$$

where $\sigma^2=\lim_{n\to\infty}n^{-1}\sum_{k=1}^{n}\sigma_k^2$. The PDF $f_\xi(x)$ of ξ is then

$$f_\xi(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\phi_\xi(u)e^{-iux}du=\frac{1}{\sigma\sqrt{2\pi}}e^{-x^2/(2\sigma^2)}, \qquad (1.6.4.1)$$

which proves the theorem. It should be noted that a rigorous proof of the theorem requires justification of the various limiting processes involved in getting to Eq. (1.6.4.1). This can be done by appealing to Lebesgue's dominated convergence theorem [57].

The most important concept of probability theory in relation to Brownian motion is the notion of a *random process* [25], which we now outline.

1.6.5. *Random processes*

Consider a random variable ξ which depends on the time t, i.e., $\xi=\xi(t)$ (Fig. 1.6.5.1). A *random process* (also known as a *stochastic process*) is [12, 25, 58] a family of random variables $\{\xi(t), t\in T\}$, where t is some parameter, generally

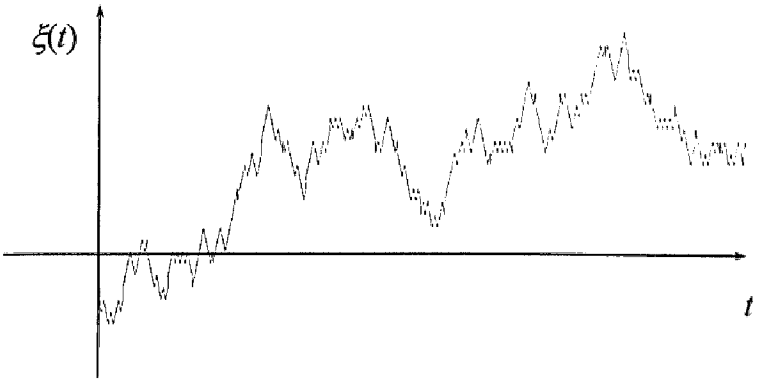


Figure 1.6.5.1. A realization of the random variable $\xi(t)$.

the time, defined on a set T. $\xi(t)$ does not depend in a completely definite way on the independent variable t [13]. Instead, one obtains different functions $y(t)$ in different observations. To describe the random process completely [58], we partition the set T into instants $t_1 < t_2 \cdots < t_n < T$ and then approximate the family of random variables $\xi(t)$ by $\xi(t_1),...,\xi(t_n)$. We may then use the following set of PDFs: $P_1(y_1,t_1)dy_1$ is the probability of finding $\xi(t_1)$ in the interval (y_1, y_1+dy_1); $P_2(y_1,t_1;y_2,t_2)dy_1dy_2$ is the joint probability of finding $\xi(t_1)$ in the interval (y_1, y_1+dy_1) and $\xi(t_2)$ in the interval (y_2, y_2+dy_2); $P_3(y_1,t_1;y_2,t_2;y_3,t_3)dy_1dy_2dy_3$ is the joint probability of finding $\xi(t_1)$ in the interval (y_1, y_1+dy_1), $\xi(t_2)$ in the interval (y_2, y_2+dy_2) and $\xi(t_3)$ in the interval (y_3, y_3+dy_3). This may be continued up to $P_n(y_1,t_1;...;y_n,t_n)dy_1 \cdots dy_n$.

The process is *wide-sense stationary* when the underlying probability distribution during a given interval of time depends only on the *length* of that interval and not on *when* the interval began. Another way of saying this is that the fundamental mechanism that causes the set of random variables $\{\xi(t)\}$ to fluctuate does not change over the course of time (temporal invariance) [24]. Hence a *shift of the time axis does not influence the functions* P_n, so that our set becomes $P_1(y,t)dy$ which is the probability of finding ξ in $(y, y+dy)$, $P_2(y_1,y_2,t)dy_1dy_2$, which is the joint probability of finding a pair of values of ξ in ranges (y_1, y_1+dy_1) and (y_2, y_2+dy_2) which are a time interval $t = |t_2 - t_1|$ apart from each other, and so on (for examples of non-stationary processes see Ref. [25]).

The functions P_n may now be determined [13, 25] by experiment from a single record $\xi(t)$ taken over a sufficiently long time. One may then cut the record into segments of length T, where T *is long in comparison to all periods contained in the process*. The different segments may then be regarded as the different records of an *ensemble* or *collection* of observations. One must, *in general*, distinguish between an ensemble average and a time average. The two methods of averaging for a *stationary process* will nevertheless always give the same result [13, 25].

A random process is said to be *purely random* if the successive values of ξ are *statistically independent*. This kind of process is described by [13, 58]

$$\begin{aligned} P_1(y_1,t_1), \\ P_2(y_1,t_1;y_2,t_2) &= P_1(y_1,t_1)P_1(y_2,t_2), \\ P_3(y_1,t_1;y_2,t_2;y_3,t_3) &= P_1(y_1,t_1)P_1(y_2,t_2)P_1(y_3,t_3),.... \end{aligned} \qquad (1.6.5.1)$$

A random process is called a *Markov process* if all the information about the process is contained in P_2 [13, 58]. Recalling the definition of conditional

probability, we write [13] $P_2(y_2,t_2 \mid y_1,t_1)dy_2$ for the probability of y being in the interval (y_2, y_2+dy_2) at time t_2 given that y_1 had occurred at time t_1. Analogously, this can be extended to higher order probabilities. Thus, a *Markov process* is a process such that [13] the conditional probability that y lies in the interval (y_n, y_n+dy_n) at time t_n, given that $y_1, y_2, ..., y_{n-1}$ had already occurred at times $t_1, t_2, ..., t_{n-1}$, depends only on the value of y at time t_{n-1}, i.e., on the immediate past value, so that

$$P_2(y_n,t_n \mid y_1,t_1; y_2,t_2; ...; y_{n-1},t_{n-1}) = P_2(y_n,t_n \mid y_{n-1},t_{n-1}). \qquad (1.6.5.2)$$

A property of a stochastic process of particular interest in connection with the Brownian motion is the *correlation function* [59]. The *time correlation function* of two-time dependent random variables $\xi_i(t)$ and $\xi_j(t)$ with zero average values is defined by supposing that the physical system has obtained a steady state (thermal equilibrium), as [40] the ensemble average $\langle \xi_i^*(t_1)\xi_j(t_2)\rangle$ (the symbol * denotes the complex conjugate). ξ_i and ξ_j at time t will, in general, depend on position and velocity variables or position and conjugate momentum variables of the system, which we can denote by $u(t)$. Thus

$$\langle \xi_i^*(t_1)\xi_j(t_2)\rangle = \int \xi_i^*[u(t_1)]\xi_j[u(t_2)]P_2[u(t_2),t_2|u(t_1),t_1]P_0[u(t_1)]du(t_2)du(t_1),$$

where $P_0[u(t_1)]$ is the PDF of the system at time t_1 in the steady state. If $i \neq j$, then $\langle \xi_i^*(t_1)\xi_j(t_2)\rangle$ is called the *cross-correlation function* of ξ_i and ξ_j. If $i=j$, $\langle \xi_i^*(t_1)\xi_i(t_2)\rangle$ is called the *autocorrelation function (ACF)* of ξ. It is a measure of the dependence of the *same* random variables at different times. The definition using the complex conjugate ensures that $\langle \xi^2(t)\rangle$ must be real. The ACF of a *stationary* stochastic process is not affected by a shift in time, i.e.,

$$\langle \xi_i^*(t_1)\xi_j(t_2)\rangle = \langle \xi_i^*(t_1-t_2)\xi_j(0)\rangle.$$

1.6.6. *Wiener–Khinchin theorem*

We now consider a stationary random process $\xi(t)$ with zero average value, where $\xi(t)$ is now a real causal function of time. We consider the Fourier transform of $\xi(t)$ [13, 21, 35, 49], namely

$$\tilde{\xi}(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t}\xi(t)dt. \qquad (1.6.6.1)$$

Then we have the Wiener–Khinchin theorem [21] (proved in Chapter 3)

$$C_\xi(t) = \langle \xi(t')\xi(t'+t)\rangle = \frac{1}{\pi}\int_0^{\infty} \Phi_\xi(\omega)\cos\omega t d\omega, \qquad (1.6.6.2)$$

$$\Phi_\xi(\omega) = 2\int_0^\infty \langle \xi(t')\xi(t'+t)\rangle \cos\omega t dt, \tag{1.6.6.3}$$

where [25, 35]

$$\Phi_\xi(\omega) = \lim_{T'\to\infty} \frac{1}{T'}\left|\tilde{\xi}(\omega, T')\right|^2 = \lim_{T'\to\infty} \frac{1}{T'}\left[\tilde{\xi}(\omega, T)\tilde{\xi}^*(\omega, T')\right]$$

is called the *spectral density* of the random function $\xi(t)$. Equation (1.6.6.3) can be rewritten (recalling that the ACF $C_\xi(t)$ is an even function of t) as

$$\Phi_\xi(\omega) = \int_{-\infty}^{\infty} \langle \xi(t')\xi(t'+t)\rangle e^{i\omega t} dt; \tag{1.6.6.4}$$

that is, for a wide-sense stationary process, the spectral density is the Fourier transform of the ACF. In addition, by the ergodic theorem, we will have [25]

$$C_\xi(t) = \langle \xi(t')\xi(t'+t)\rangle = \overline{\xi(t')\xi(t'+t)}.$$

1.7. Application to the Langevin equation

To illustrate the use of the concepts developed in Section 1.6, we consider how they may be used to evaluate the mean square value of the velocity from the Langevin equation (1.3.1). This also will serve as an introduction to the Ornstein–Uhlenbeck theory of Brownian movement [45] which is discussed in detail in Chapter 3. We write the Langevin Eq. (1.3.1) as

$$\dot{x}(t) = v(t), \quad \dot{v}(t) = -\beta v(t) + \frac{1}{m}F(t), \tag{1.7.1}$$

where β is the friction coefficient per unit mass. We seek solutions of Eqs. (1.7.1) with initial conditions that describe sharp values at $t = 0$ (corresponding to delta function initial conditions in the associated Fokker–Planck equation). These solutions are given by

$$v(t) = v_0 e^{-\beta t} + \frac{1}{m}\int_0^t e^{-\beta(t-t')}F(t')dt', \tag{1.7.2}$$

$$x(t) = x_0 + \frac{v_0}{\beta}\left(1 - e^{-\beta t}\right) + \frac{1}{m\beta}\int_0^t \left(1 - e^{-\beta(t-t')}\right)F(t')dt', \tag{1.7.3}$$

where we have assumed that the particle started off at the sharp phase point (x_0, v_0). Taking averages, and noting that $\overline{F(t)} = 0$, we use Eq. (1.7.2) to obtain the mean and mean square velocities, viz.,

$$\overline{v(t)} = v_0 e^{-\beta t}, \tag{1.7.4}$$

$$\overline{v^2(t)} = v_0^2 e^{-2\beta t} + \frac{1}{m^2}\overline{\int_0^t \int_0^t e^{-\beta(2t-t'-t'')} F(t'')F(t')dt''dt'}. \tag{1.7.5}$$

Using Eq. (1.5.8.3), we have

$$\overline{v^2(t)} = v_0^2 e^{-2\beta t} + e^{-2\beta t}\frac{2\zeta kT}{m^2}\int_0^t \int_0^t e^{\beta(t'+t'')}\delta(t'-t'')dt'dt''$$

$$= v_0^2 e^{-2\beta t} + e^{-2\beta t}\frac{2\zeta kT}{m^2}\int_0^t e^{2\beta t'}dt' = v_0^2 e^{-2\beta t} + \frac{kT}{m}\left(1-e^{-2\beta t}\right). \tag{1.7.6}$$

Here we have used the properties of the Dirac delta function [21]

$$\int_p^q f(t)\delta(t-a)dt = f(a), \quad p < a < q. \tag{1.7.7}$$

The variance is given by

$$\sigma^2 = \overline{v^2(t)} - \left(\overline{v(t)}\right)^2 = kT\left(1-e^{-2\beta t}\right)/m. \tag{1.7.8}$$

In the long-time limit, we have from Eq. (1.7.8)

$$\lim_{t\to\infty} \overline{v^2(t)} = kT/m. \tag{1.7.9}$$

Equation (1.7.9) is in complete agreement with the assumption that, for long times, the Maxwellian distribution sets in [1, 5, 45].

Now the spectral density $\Phi_F(\omega)$ of the fluctuating force $F(t)$ in the Langevin equation, Eq. (1.7.1), is, according to the Wiener–Khinchin theorem, given by

$$\Phi_F(\omega) = \int_{-\infty}^{\infty} e^{i\omega\tau}\overline{F(0)F(\tau)}d\tau = 2\zeta kT\int_{-\infty}^{\infty} e^{i\omega\tau}\delta(\tau) = 2D. \tag{1.7.10}$$

(From now on, we shall follow the notation of Wang and Uhlenbeck [13] and regard $2D$ as the spectral density; D is also used as a symbol for the diffusion coefficient; however, the difference will be apparent from the context wherever we speak of white noise.) Hence $\Phi_F(\omega)$ is independent of the angular frequency ω; $F(t)$ is called a *white noise force* by analogy with white light, where the spectral density is constant over the visible range of frequencies. If $\Phi_F(\omega)$ depends on ω, then $F(t)$ is called a *colored noise force.*

Nyquist's theorem, Eq. (1.4.23), [34] may be proved using the above results by considering the Langevin equation for the series LR circuit:

$$L\frac{d}{dt}i(t) + Ri(t) = e(t), \tag{1.7.11}$$

where L is the inductance, R is the resistance, $i(t)$ is the current, and $e(t)$ is the random e.m.f. with

$$\overline{e(t)} = 0, \quad \overline{e(t_1)e(t_2)} = 2D\delta(t_1 - t_2), \tag{1.7.12}$$

where $D = RkT$. By replacing ζ by R in Eq. (1.7.10), we have

$$\Phi_e(\omega) = 2D = 2RkT \tag{1.7.13}$$

as the spectral density of the noise voltage. We emphasize [25] that pure white noise cannot actually exist, since the power dissipated in R in a frequency range (ω_1, ω_2) is

$$R^{-1}\int_{\omega_1}^{\omega_2} \Phi_e(\omega)\, d\omega = 2kT(\omega_2 - \omega_1),$$

which is *infinite* if we extend the integral to all frequencies. In practice, both quantum and memory effects will come into play, limiting the "flatness" property of the spectrum. Although pure white noise does not occur [25] as a physically realizable process, it is of fundamental importance as an idealization of many real physical processes leading, *inter alia,* to the Stratonovich and Itô calculi (see Chapter 2, Section 2.3), which play such an important role in the interpretation of the Langevin equation. We shall consider neither quantum nor memory effects in the present work.

The process described by the Langevin equation (1.7.1) with a δ-correlated fluctuating force $F(t)$ is a *Markov process* [21], because the solution of the first-order equation (1.7.1) is *uniquely* determined by its initial conditions. Hence the conditional probability of the process at time t_n depends only on the value $x(t_{n-1})$. The δ-correlated force $F(t)$ at time $t < t_{n-1}$ cannot change the conditional probability at time $t > t_{n-1}$. The Markov property ceases to be valid if $F(t)$ is no longer δ-correlated.

1.8. Wiener process

We now consider the special type of stochastic process known as the *Wiener process* [1], which was introduced by Wiener in 1923 [55] to provide a rigorous mathematical description of the statistical properties of the trajectory of a Brownian particle. The fundamental properties of the Wiener process are set out in this section.

Let $\xi(t) = X(t)$ which, for the purpose of illustration, denotes the displacement after a time t of a particle undergoing Brownian motion, so that $X(0) = 0$ by definition. Consider a time interval (s, t) which is long compared

with the time between impacts on the Brownian particle by the particles in the surrounding medium. In other words, the Brownian particle has been "drummed" during (s, t). We make the following assumptions:

(1) The displacement $[X(t)-X(s)]$ of the Brownian particle over the time interval (s, t) is the sum

$$\sum_{k=1}^{n}[X(t_k)-X(t_{k-1})]$$

of the infinitesimal displacements $X(t_k)-X(t_{k-1})$ of the Brownian particle caused by the impacts of the particles of the surrounding medium.

(2) The PDF of $X(t_k)$ depends only on $X(t_{k-1})$ and not on $X(t_{k-2})$, $X(t_{k-3})$, etc., so that we have a Markov process, whence

$$[X(t_1)-X(s)],\ [X(t_2)-X(t_1)],\ ...,\ [X(t)-X(t_{n-1})],$$

are independent random variables. Formally, we say that the process has *independent increments*.

(3) $\langle X(t_1)-X(s)\rangle=\langle X(t_k)-X(t_{k-1})\rangle=0$.

(4) Since $[X(t)-X(s)]$ is the sum of a large number of independent random variables $[X(t_k)-X(t_{k-1})]$, each having *arbitrary distributions*, it follows from the central limit theorem that $[X(t)-X(s)]/\mathrm{Var}\,[X(t)-X(s)]$ approaches a Gaussian distribution as $n\to\infty$. In other words, the characteristic function of $[X(t)-X(s)]$ is $\exp\{-u^2\mathrm{Var}[X(t)-X(s)]/2\}$.

Formally, we say that a stochastic process consisting of a family of random variables $\{X(t), t=0\}$ is a Wiener process if (i) $\{X(t), t=0\}$ has stationary independent increments; (ii) $X(t)$ is normally distributed for $t=0$; (iii) $\langle X(t)\rangle=0$ for $t=0$; and (iv) $X(0)=0$.

1.8.1. *Variance of the Wiener process*

Assuming that $\mathrm{Var}\,[X(t)]=f(t)$, we have

$$f(t_1+t_2)=\langle X^2(t_1+t_2)\rangle=\langle[X(t_1+t_2)-X(t_1)+X(t_1)-X(0)]^2\rangle,$$

since $X(0)=0$. On multiplying out, we have

$$f(t_1+t_2)=\langle[X(t_1+t_2)-X(t_1)]^2\rangle+\langle[X(t_1)-X(0)]^2\rangle, \qquad (1.8.1.1)$$

since

$$\langle[X(t_1+t_2)-X(t_1)][X(t_1)-X(0)]\rangle=\langle X(t_1+t_2)-X(t_1)\rangle\langle X(t_1)-X(0)\rangle=0,$$

because $X(t_1+t_2)-X(t_1)$ and $X(t_1)-X(0)$ are independent random variables and $\langle X(t)\rangle = 0$. By stationarity, we may express Eq. (1.8.1.1) as

$$f(t_1+t_2)=\left\langle\left[X(t_2)-X(0)\right]^2\right\rangle+\left\langle\left[X(t_1)-X(0)\right]^2\right\rangle=f(t_2)+f(t_1).$$

Let $t_2=t$, $t_1=-s$; then $f(t-s)=f(t)+f(-s)$ and the only function which satisfies this functional equation is

$$f(t-s)=c^2(t-s), \tag{1.8.1.2}$$

where c is a constant to be determined. By stationarity,

$$\mathrm{Var}\left[X(t)-X(s)\right]=\mathrm{Var}\left[X(t-s)-X(0)\right]=\mathrm{Var}\left[X(t-s)\right]$$

since $X(0)=0$; so that from Eq. (1.8.1.2)

$$\mathrm{Var}\left[X(t)-X(s)\right]=c^2\,|t-s| \tag{1.8.1.3}$$

in order to ensure a positive variance. Therefore, $X(t)-X(s)$ is a Gaussian random variable with PDF

$$\left[c\left(2\pi|t-s|\right)^{1/2}\right]^{-1} e^{-[X(t)-X(s)]^2/(2c^2|t-s|)}.$$

Now, we wish to evaluate the covariance $K(s,t)$ given by

$$K(s,t)=\mathrm{Cov}\left\langle X(s),X(t)\right\rangle=\left\langle\left[X(s)-\langle X(s)\rangle\right]\left[X(t)-\langle X(t)\rangle\right]\right\rangle.$$

Since $\left\langle X(s)-X(t)\right\rangle=0$, we have

$$K(s,t)=\left\langle X(s)X(t)\right\rangle=\left\langle X(s)\left[X(t)-X(s)\right]\right\rangle+\left\langle X^2(s)\right\rangle=\left\langle X^2(s)\right\rangle$$

as $X(s)$ and $X(t)-X(s)$ are independent. Therefore

$$K(s,t)=\langle X^2(s)\rangle=\mathrm{Var}\left[X(s)\right]=c^2\,\min(s,t), \tag{1.8.1.4}$$

where "min" denotes the minimum of s and t. On comparison with Eq. (1.3.14), and since we have chosen $X(t)$ as the displacement, it is obvious that $c^2=2kT/\zeta$ here.

We now consider the differences $\xi(\Delta)$ of the Wiener process; these will allow us to evaluate integrals involving that process. Thus, the random variable $X(t)$ above is replaced by the symbol $B(t)$, and we shall no longer necessarily suppose that $B(t)$ represents the displacement of a Brownian particle, so that the constant c^2 will alter. For example, the white noise force $F(t)$ in the Langevin equation is usually written as $F(t)=m\dot{B}(t)$ (strictly speaking, this is a meaningless equation, as $B(t)$ is not differentiable), so that

$$\left\langle F(t_1)F(t_2)\right\rangle=m^2\left\langle\dot{B}(t_1)\dot{B}(t_2)\right\rangle=2kT\zeta\delta(t_1-t_2).$$

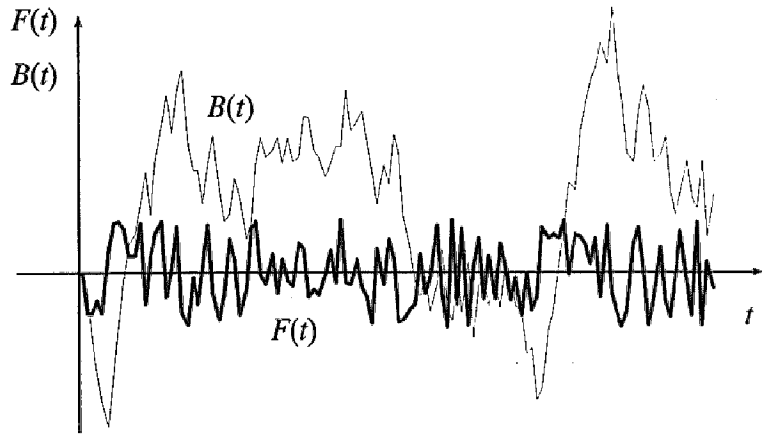


Figure 1.8.1. A crude picture of realizations of $F(t)$ and of $B(t)=\int_0^t F(t')dt'$.

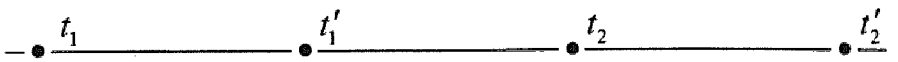
Hence c^2 becomes $c^2 = 2kT\zeta / m^2$. We also remark that the Wiener process $B(t)$ is itself *not stationary*, since $B(0)=0$; however, the *increment* $B(t+\Delta t)-B(t)$ is *stationary*, therefore, $dB(t)$ and so $\dot{B}(t)$ are stationary processes [40]. Furthermore, the white noise force $F(t)$ used by Langevin is related to $B(t)$ by the integral [21]

$$B(t)=\int_0^t F(t')dt', \tag{1.8.1.5}$$

so that the Wiener process *smoothes* the white noise process (see Fig. 1.8.1).

1.8.2. *Wiener integrals*

We consider two overlapping time intervals $\Delta=[t_1,t_2]$ and $\Delta'=[t_1',t_2']$ with $t_1<t_1'<t_2<t_2'$



and

$$\xi(\Delta)=[B(t_2)-B(t_1)], \qquad \xi(\Delta')=[B(t_2')-B(t_1')].$$

Multiplying these two equations together, and averaging using Eq. (1.8.1.4), we have

$$\langle \xi(\Delta)\xi(\Delta')\rangle = c^2\,|t_1'-t_2| = c^2\,|\Delta\cap\Delta'| \tag{1.8.2.1}$$

and the special case $|\Delta=\Delta'|$

$$\langle \xi^2(\Delta)\rangle = c^2\,|\Delta|. \tag{1.8.2.2}$$

We may interpret differentials such as $dB(t)$ in terms of ξ because

$$dB(t) = [\xi(t+dt) - \xi(t)] = \xi(dt), \tag{1.8.2.3}$$

so that

$$\int_{-\infty}^{\infty} f(t)dB(t) = \int_{-\infty}^{\infty} f(t)\xi(dt), \tag{1.8.2.4}$$

written as a Stieltjes integral [55] and termed a Wiener integral. Hence [1] even though the sample paths (realizations) of the Wiener process are *continuous* with probability 1, but *not differentiable*, integrals of the form of Eq. (1.8.2.4) can still be defined for any square integrable f since integration by parts is permitted.

We now wish to discuss in detail the Wiener integral

$$\xi[f] = \int_{-\infty}^{\infty} f(t)\xi(dt). \tag{1.8.2.5}$$

We take for $f(t)$ the step functions

$$f_n(t) = c_1\chi_{\Delta_1}(t) + c_2\chi_{\Delta_2}(t) + \cdots + c_n\chi_{\Delta_n}(t), \tag{1.8.2.6}$$

where $\Delta_i = t_i - t_i'$ and $\chi_{\Delta_i}(t)$ is the *indicator function* of the interval Δ_i defined as

$$\chi_{\Delta_i}(t) = \begin{cases} 1, & \text{if } t \in \Delta_i \\ 0, & \text{if } t \notin \Delta_i. \end{cases}$$

Thus

$$\xi[f_n] = \sum_{i=1}^{n} c_i \left[B(t_i) - B(t_i')\right] = \sum_{i=1}^{n} c_i \xi(\Delta_i).$$

We now define the Wiener integral $\xi[f]$ by

$$\xi[f] = \lim_{n\to\infty} \xi[f_n]. \tag{1.8.2.7}$$

(It is sufficient to define the integral for the step functions, since we may approximate any continuous function $f(t)$ in the interval $(-\infty, \infty)$ by a series of step functions [57]). Taking mean values, we have

$$\langle \xi[f] \rangle = \lim_{n\to\infty} \langle \xi[f_n] \rangle = \lim_{n\to\infty} \sum_{i=1}^{n} c_i \langle \xi(\Delta_i) \rangle = 0.$$

Consider now

$$\langle \xi^2[f_n] \rangle = \left\langle \left(\int_{-\infty}^{\infty} f_n(t)\xi(dt) \right)^2 \right\rangle = \left\langle \sum_{i,j=1}^{n} c_i c_j \xi(\Delta_i)\xi(\Delta_j) \right\rangle$$

$$= c^2 \sum_{i,j=1}^{n} |\Delta_i \cap \Delta_j| c_i c_j = c^2 \sum_{i=1}^{n} c_i^2 |\Delta_i|.$$

Thus

$$\left\langle \xi^2[f] \right\rangle = \lim_{n\to\infty} \left\langle \xi^2[f_n] \right\rangle = c^2 \int_{-\infty}^{\infty} f^2(t)dt. \qquad (1.8.2.8)$$

In like manner

$$\left\langle \xi[f]\xi[g] \right\rangle = c^2 \int_{-\infty}^{\infty} f(t)g(t)dt. \qquad (1.8.2.9)$$

Equations (1.8.2.8) and (1.8.2.9) are very useful formulas. For further detailed treatment, the reader is referred to the fundamental paper of Doob reprinted in the anthology edited by Wax [4]. More mathematical details are given by Nelson [1] and Doob [55]. The merit of the formulation of the theory in terms of the Wiener integral is that it allows all the mathematical operations used in the theory to be precisely defined.

We are now equipped with the mathematical tools necessary for our treatment of the theory of Brownian movement.

1.9. The Fokker–Planck equation

The Fokker–Planck equation is an equation for the evolution of the PDF (which is defined on the phase space for the problem) of fluctuating macroscopic variables [21]. It is essentially a specialized form of the Boltzmann integral equation [13, 21] with the *Stosszahlansatz* of Brownian motion. The diffusion equation, Eq. (1.4.8), for the PDF of an assembly of free Brownian particles is a simple example of such an equation. The main use of the Fokker–Planck equation is as an approximate description for any Markov process $\xi(t)$ in which the individual jumps are small [49].

Consider a stochastic process $\xi(t)$ in which we take a set of instants $t_1 < t_2 < t_3$ where, for the present, we assume that y_1 and t_1 are fixed. We define the conditional probability $P_2(y_2, t_2| y_1, t_1)\, dy_2$ as the probability that $\xi(t_2)$ lies in the interval $(y_2, y_2 + dy_2)$, given that $\xi(t_1)$ had a value y_1 at time t_1, and $P_3(y_3, t_3|y_2, t_2; y_1, t_1)dy_3$ as the probability that $\xi(t_3)$ lies in the interval $(y_3, y_3 + dy_3)$, given that $\xi(t_2)$ had a value y_2 at time t_2 and $\xi(t_1)$ had a value y_1 at time t_1. If we multiply P_2 by P_3 and integrate with respect to y_2, the resulting PDF will only depend on y_1 and t_1, i.e.,

$$P_3(y_3,t_3 \mid y_1,t_1) = \int_{-\infty}^{\infty} P_2(y_2,t_2 \mid y_1,t_1) P_3(y_3,t_3 \mid y_2,t_2;y_1,t_1)\, dy_2, \qquad (1.9.1)$$

which is called the *Chapman–Kolmogorov equation*. If we restrict ourselves to a *Markov process*, we will then have

$$P_3(y_3,t_3 \mid y_2,t_2;y_1,t_1) = P_2(y_3,t_3 \mid y_2,t_2) \tag{1.9.2}$$

and

$$P_2(y_3,t_3 \mid y_1,t_1) = \int_{-\infty}^{\infty} P_2(y_2,t_2 \mid y_1,t_1) P_2(y_3,t_3 \mid y_2,t_2)\, dy_2, \tag{1.9.3}$$

which is the Chapman–Kolmogorov equation for a Markov process also known as the *Smoluchowski integral equation*, essentially due to Einstein [3]. In Eq. (1.9.3) we write $P_2 = W$, $y_3 = y$, $y_2 = z$, $y_1 = x$, $t_2 = t$, $t_3 = t + \Delta t$ and suppress the t_1 dependence so that, by comparison with Eq. (1.4.1),

$$W(y,t+\Delta t \mid x) = \int_{-\infty}^{\infty} W(z,t \mid x) W(y,t+\Delta t \mid z,t)\, dz. \tag{1.9.4}$$

In Eq. (1.9.4), for economy of notation, we write $W(y,t+\Delta t \mid z,t) = W(y,\Delta t \mid z)$ so that

$$W(y,\Delta t \mid x) = \int_{-\infty}^{\infty} W(z,t \mid x) W(y,\Delta t \mid z)\, dz. \tag{1.9.5}$$

We wish to derive a partial differential equation for the *transition probability* $W(y,t \mid x)$ from this integral equation under certain limiting conditions. We have to consider

$$\int_{-\infty}^{\infty} R(y) \frac{\partial}{\partial t} W(y,t \mid x)\, dy, \tag{1.9.6}$$

where $R(y)$ is an arbitrary function satisfying

$$\lim_{y \to \pm\infty} R(y) = 0, \text{ and } R^{(n)}(y) \text{ exists at } y = \pm\infty. \tag{1.9.7}$$

In Eq. (1.9.7), $R^{(n)}(y)$ is the n^{th} derivative of $R(y)$ with respect to y. Using the definition of the partial derivative, we have

$$\int_{-\infty}^{\infty} R(y) \frac{\partial W}{\partial t}\, dy = \int_{-\infty}^{\infty} R(y) \lim_{\Delta t \to 0} \left[\frac{W(y,t+\Delta t \mid x) - W(y,t \mid x)}{\Delta t} \right] dy. \tag{1.9.8}$$

By substituting the conditional probability $W(y,t+\Delta t \mid x)$ from Eq. (1.9.5) into Eq. (1.9.8) and by interchanging the order of the limit and integration, we obtain

$$\int_{-\infty}^{\infty} R(y) \frac{\partial W}{\partial t}\, dy = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \left[\int_{-\infty}^{\infty} W(z,t \mid x) \int_{-\infty}^{\infty} R(y) W(y,\Delta t \mid z)\, dy dz - \int_{-\infty}^{\infty} R(z) W(z,t \mid x) dz \right].$$

By expanding $R(y)$ in a Taylor series about the point $y = z$ so that

$$R(y) = R(z) + (y-z)R'(z) + (y-z)^2 R''(z)/2! + \cdots$$

($R' = dR/dz$ and $(R'' = d^2R/dz^2)$, we have

$$\int_{-\infty}^{\infty} R(y)\frac{\partial W}{\partial t}dy = \lim_{\Delta t\to 0}\frac{1}{\Delta t}\left[\int_{-\infty}^{\infty} W(z,t\mid x)\int_{-\infty}^{\infty}\{R(z)+(y-z)R'(z) + \frac{(y-z)^2}{2!}R''(z)+\cdots\}W(y,\Delta t\mid z)dydz - \int_{-\infty}^{\infty} R(z)W(z,t\mid x)dz\right]. \tag{1.9.9}$$

Since $W(y,\Delta t\mid z)$ is a PDF, $\int_{-\infty}^{\infty} W(y,\Delta t\mid z)dy = 1$ and therefore

$$\int_{-\infty}^{\infty} R(y)\frac{\partial W(y,t\mid x)}{\partial t}dy = \int_{-\infty}^{\infty} W(z,t\mid x)\int_{-\infty}^{\infty}\lim_{\Delta t\to 0}\frac{1}{\Delta t}\{(y-z)R'(z) + (y-z)^2\,R''(z)/2+\cdots\}W(y,\Delta t\mid z)dydz \tag{1.9.10}$$

or

$$\int_{-\infty}^{\infty} R(y)\frac{\partial W}{\partial t}dy = \int_{-\infty}^{\infty} W\lim_{\Delta t\to 0}\left[\frac{a_1(z,\Delta t)}{\Delta t}R'(z)+\frac{a_2(z,\Delta t)}{2!\Delta t}R''(z)+\cdots\right]dz, \tag{1.9.11}$$

where

$$a_n(z,\Delta t) = \int_{-\infty}^{\infty}(y-z)^n W(y,\Delta t\mid z)dy. \tag{1.9.12}$$

We now suppose that

$$\lim_{\Delta t\to 0}\frac{a_n(z,\Delta t)}{\Delta t} = 0 \text{ for } n>2;$$

see Eq. (1.9.20) below. Thus

$$\int_{-\infty}^{\infty} R(y)\frac{\partial W}{\partial t}dy = \int_{-\infty}^{\infty} W(z,t\mid x)\left[D^{(1)}(z,t)R'(z)+D^{(2)}(z,t)R''(z)\right]dz, \tag{1.9.13}$$

where

$$D^{(1)}(z,t) = \lim_{\Delta t\to 0}\frac{a_1(z,\Delta t)}{\Delta t},\quad D^{(2)}(z,t) = \lim_{\Delta t\to 0}\frac{a_2(z,\Delta t)}{(2\Delta t)}. \tag{1.9.14}$$

To form a PDE for W, we need to factor $R(z)$ out of the right-hand side of Eq. (1.9.13). To do this we use integration by parts. Thus, we have for the first term

$$\int_{-\infty}^{\infty} W(z,t\mid x)D^{(1)}(z,t)R'(z)dz = -\int_{-\infty}^{\infty} R(z)\frac{\partial}{\partial z}\left[D^{(1)}(z,t)W(z,t\mid x)\right]dz \tag{1.9.15}$$

by Eq. (1.9.7). Similarly, applying integration by parts twice to the last term of Eq. (1.9.13), we have

$$\int_{-\infty}^{\infty} W(z,t\,|\,x)D^{(2)}(z,t)R''(z)dz = \int_{-\infty}^{\infty} R(z)\frac{\partial^2}{\partial z^2}\left[D^{(2)}(z,t)W(z,t\,|\,x)\right]dz. \tag{1.9.16}$$

Substituting Eqs. (1.9.15) and (1.9.16) into Eq. (1.9.13), we have

$$\int_{-\infty}^{\infty} R(y)\left(\frac{\partial W}{\partial t}+\frac{\partial}{\partial y}\left[D^{(1)}W\right]-\frac{\partial^2}{\partial y^2}\left[D^{(2)}W\right]\right)dy = 0 \tag{1.9.17}$$

(since z is a dummy variable). Thus we have the PDE

$$\frac{\partial W}{\partial t} = -\frac{\partial}{\partial y}\left[D^{(1)}W\right]+\frac{\partial^2}{\partial y^2}\left[D^{(2)}W\right]. \tag{1.9.18}$$

Equation (1.9.18) is the *Fokker–Planck equation* for a one-dimensional Markov process governed by the random variable $\xi(t)$. $D^{(1)}$ is called the *drift coefficient* and $D^{(2)}$ the *diffusion coefficient*, which are to be calculated from the Langevin equation. The condition that the Taylor series may be truncated at $n=2$ can be justified if the driving stimulus is Gaussian white noise in the accompanying Langevin equation. This is apparent from the white noise properties of Eq. (1.5.8.3) and Isserlis's theorem, Eq. (1.3.5). For $n=2$, for example, Isserlis's theorem yields

$$\begin{aligned}\overline{F(t_1)F(t_2)F(t_3)F(t_4)} = 4D^2\{&\delta(t_1-t_2)\delta(t_3-t_4)\\ &+\delta(t_1-t_3)\delta(t_2-t_4)+\delta(t_1-t_4)\delta(t_2-t_3)\},\end{aligned} \tag{1.9.19}$$

which gives rise to a_4 of order $(\Delta t)^2$ in Eq. (1.9.12). From Eqs. (1.5.8.3) and (1.3.5), we see that $a_3, a_5, \ldots, a_{2n+1}$, etc. are all zero and $a_{2n} \sim (\Delta t)^n$. Hence

$$\lim_{\Delta t\to 0}\frac{a_{2n}}{\Delta t} = 0, \quad n>1. \tag{1.9.20}$$

However, if the driving stimulus is not Gaussian white noise, higher order terms must be included in the *Kramers–Moyal* expansion, Eq. (1.9.11), and one no longer has the Fokker–Planck equation. With Wang and Uhlenbeck [13], we emphasize in relation to Eq. (1.9.18) that Eqs. (1.9.14) are *necessarily only approximations*. The basic equation is *always* Boltzmann's equation [5, 36].

Since in general we will be dealing with the multivariable form of the Fokker–Planck equation, it is necessary to quote the form of that equation for many dimensions characterized by a set of vector valued random variables $\{\xi\}=\{\xi_1,\ldots,\xi_n\}$. The multivariable form of the Fokker–Planck equation is with $W=W(\{\mathbf{y}\},t\,|\,\{\mathbf{x}\})$, $\{\mathbf{y}\}$ and $\{\mathbf{x}\}$ denoting a set of realizations of $\{\xi\}$ [21]:

$$\frac{\partial W}{\partial t} = -\sum_i \frac{\partial}{\partial y_i}\left[D_i^{(1)}(\mathbf{y},t)W\right] + \sum_{k,l}\frac{\partial^2}{\partial y_k \partial y_l}\left[D_{k,l}^{(2)}(\mathbf{y},t)W\right], \qquad (1.9.21)$$

where the drift and diffusion coefficients are

$$D_i^{(1)} = \lim_{\Delta t\to 0}\frac{\overline{\Delta y_i}}{\Delta t}, \qquad D_{i,j}^{(2)} = \lim_{\Delta t\to 0}\frac{\overline{\Delta y_i \Delta y_j}}{2\Delta t} \quad (i,j = 1, 2, \ldots, N). \qquad (1.9.22)$$

We reiterate that we have assumed in writing down our Fokker–Planck equation, referring to Eq. (1.9.18) for convenience, that $D^{(1)} \neq 0$, $D^{(2)} \neq 0$, and $D^{(n)} = 0$ for $n > 2$. This allows us to truncate the Kramers–Moyal expansion, Eq. (1.9.11). In the Fokker–Planck equation, these quantities (expressing the fact that, for small times Δt in the process, the only alteration in the random variable ξ is due to the rapidly fluctuating Brownian force $F(t)$, which is the central idea underlying the theory of Brownian motion) are to be calculated from the Langevin equation. The procedure emphasizes again that the Langevin equation is the basic equation of the theory of Brownian movement. We remark that the time Δt is of such short duration that (taking as example $\mathbf{y}$ the position and momentum of a particle) *the momentum does not significantly alter during the time Δt, and neither does any external conservative force.* Nevertheless, Δt is supposed to be *sufficiently long for the chance that the rapidly fluctuating stochastic force $F(t)$ takes on a given value at time $t+\Delta t$ to be independent of the value which that force possessed at time t.* In other words, the Brownian force has *no memory.*

We shall now explicitly calculate the drift and diffusion coefficients in the Fokker–Planck equation for the simplest one-dimensional model, which is as follows. The Langevin equation for the process characterized by the one-dimensional random variable $\xi(t)$, which describes, for example, the velocity of a particle of mass m undergoing one-dimensional Brownian motion, is

$$\dot{\xi}(t) + \beta\xi(t) = F(t)/m. \qquad (1.9.23)$$

If we integrate this equation over a short time Δt, we have the integral equation with $\xi(t+\Delta t)$ being the solution of Eq. (1.9.23) which at time t has the *sharp* value y, so that

$$\xi(t+\Delta t) - y = -\int_t^{t+\Delta t}\beta\xi(t')dt' + \frac{1}{m}\int_t^{t+\Delta t}F(t')dt'. \qquad (1.9.24)$$

Thus (for a detailed exposition, see Section 1.10), taking the statistical average of the realizations of ξ in a small time Δt, we have the drift coefficient $D^{(1)}$:

$$D^{(1)}(y,t) = \lim_{\Delta t\to 0}\overline{[\xi(t+\Delta t) - y(t)]/\Delta t} = -\beta y. \qquad (1.9.25)$$

In order to calculate the diffusion coefficient $D^{(2)}$, we square $\xi(t+\Delta t)-y$ to obtain

$$[\xi(t+\Delta t)-y]^2=\beta^2y^2(\Delta t)^2-\frac{2\Delta t\beta y}{m}\int_t^{t+\Delta t}F(t')dt'+\frac{1}{m^2}\int_t^{t+\Delta t}\int_t^{t+\Delta t}F(t')F(t'')dt'dt''.$$

The first term on the right-hand side is of the order $(\Delta t)^2$. The middle term vanishes because F and the sharp initial value y are, by hypothesis, statistically independent. The last term becomes, on averaging,

$$\frac{2\beta kT}{m}\int_t^{t+\Delta t}\int_t^{t+\Delta t}\delta(t'-t'')\,dt'dt''=\frac{2\beta kT}{m}\Delta t, \tag{1.9.26}$$

where we have noted the property of the Dirac delta function Eq. (1.7.7). Hence

$$D^{(2)}(y,t)=\lim_{\Delta t\to 0}\frac{\overline{[\xi(t+\Delta t)-y]^2}}{2\Delta t}=\frac{\beta kT}{m}. \tag{1.9.27}$$

The third coefficient $D^{(3)}(y,t)$ is calculated as follows. We form

$$[\xi(t+\Delta t)-y]^3=-\beta^2y^3(\Delta t)^3+3y^2\beta^2(\Delta t)^2\frac{1}{m}\int_t^{t+\Delta t}F(t')dt'$$

$$-3y\beta\Delta t\left(\frac{1}{m}\int_t^{t+\Delta t}F(t')dt'\right)^2+\left(\frac{1}{m}\int_t^{t+\Delta t}F(t')dt'\right)^3.$$

The only term $\sim\Delta t$ to contribute on averaging this equation, is the one involving the triple integral. However, this will vanish for a white noise driving force because, by Isserlis's theorem, all odd values are zero. Thus

$$D^{(3)}(y,t)=0.$$

Likewise, we can prove that all the $D^{(n)}(y,t)=0$ for all $n\geq 3$. Hence, the transition probability $W(y,t\mid y_0,0)$ satisfies the Fokker–Planck equation

$$\frac{\partial W}{\partial t}=\beta\frac{\partial}{\partial y}(yW)+\frac{\beta kT}{m}\frac{\partial^2W}{\partial y^2} \tag{1.9.28}$$

corresponding to the Langevin equation (1.9.23). Since it is a transition probability, W must also satisfy

$$\lim_{t\to 0}W(y,t\mid y_0,0)=\delta(y-y_0),$$

$$\lim_{t\to\infty}W(y,t\mid y_0,0)=W_0(y), \tag{1.9.29}$$

where $W_0(y)$ denotes the stationary solution.

We shall now discuss how drift and diffusion coefficients may be evaluated in the most general case.

1.10. Drift and diffusion coefficients

The drift and diffusion coefficients may be calculated from nonlinear Langevin equations in the following way [21]. The most general Langevin equation in one stochastic variable ξ has the form [21]

$$\dot{\xi}(t) = h[\xi(t), t] + g[\xi(t), t]F(t). \tag{1.10.1}$$

If g is constant, Eq. (1.10.1) is called a Langevin equation with an *additive noise term*, while if g depends on ξ, Eq. (1.10.1) is called a Langevin equation with a *multiplicative noise term.* We shall consider only the multiplicative noise case since it is more general. We wish to evaluate [21]

$$D^{(1)} = \lim_{\Delta t \to 0} \frac{\overline{[\xi(t+\Delta t) - y]}}{\Delta t} \text{ and } D^{(2)} = \lim_{\Delta t \to 0} \frac{\overline{[\xi(t+\Delta t) - y]^2}}{2\Delta t}, \tag{1.10.2}$$

where $\xi(t+\Delta t)$ is the solution of Eq. (1.10.1) which at time t has a *sharp* value y such that $\overline{\xi(t)} = y$ (Fig. 1.10.1).

Following [21], we write the Langevin equation (1.10.1) in the integral form (see also Chapter 2)

$$\xi(t+\Delta t) - y = \int_t^{t+\Delta t} \{h[\xi(t'), t'] + g[\xi(t'), t']F(t')\}\, dt'. \tag{1.10.3}$$

Now expanding h and g as Taylor series about the sharp point $\xi = y$ and noting that the increment during the interval (t, t') is $\xi(t') - y$, we obtain

$$h[\xi(t'), t'] = h(y, t') + [\xi(t') - y]\frac{\partial}{\partial y} h(y, t') + \cdots, \tag{1.10.4}$$

$$g[\xi(t'), t'] = g(y, t') + [\xi(t') - y]\frac{\partial}{\partial y} g(y, t') + \cdots. \tag{1.10.5}$$

Using these expansions in the integral equation, Eq. (1.10.3), we have

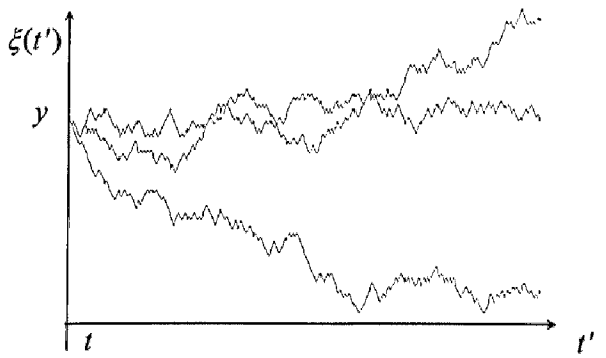


Figure 1.10.1. Three realizations of $\xi(t')$ starting from a sharp initial point $\xi(t) = y$.

$$\xi(t+\Delta t)-y=\int_t^{t+\Delta t}h(y,t')dt'+\int_t^{t+\Delta t}[\xi(t')-y]\frac{\partial}{\partial y}h(y,t')dt'$$
$$+\int_t^{t+\Delta t}g(y,t')F(t')dt'+\int_t^{t+\Delta t}[\xi(t')-y]\frac{\partial}{\partial y}g(y,t')F(t')dt'+\cdots. \qquad (1.10.6)$$

We now iterate for $\xi(t')-y$ in the integrand using Eq. (1.10.3) to obtain

$$\xi(t+\Delta t)-y=\int_t^{t+\Delta t}h(y,t')\,dt'+\int_t^{t+\Delta t}\frac{\partial h(y,t')}{\partial y}\int_t^{t'}h(y,t'')\,dt'dt''$$
$$+\int_t^{t+\Delta t}\frac{\partial h(y,t')}{\partial y}\int_t^{t'}g(y,t'')F(t'')\,dt'dt''$$
$$+\int_t^{t+\Delta t}g(y,t')F(t')\,dt'+\int_t^{t+\Delta t}\frac{\partial g(y,t')}{\partial y}\int_t^{t'}h(y,t'')F(t')\,dt''dt'$$
$$+\int_t^{t+\Delta t}\frac{\partial g(y,t')}{\partial y}\int_t^{t'}g(y,t'')F(t'')F(t')dt''dt'+\cdots \qquad (1.10.7)$$

so that the last term involves a *product* of noises which will not then vanish on averaging. Now, recalling the properties of the random force $F(t)$, Eq. (1.5.8.3), and the property of the Dirac delta function [21]

$$\int_a^b\delta(b-x)y(x)dx=\frac{1}{2}y(b), \qquad (1.10.8)$$

we have from Eq. (1.10.7) the averaged equation

$$\overline{\xi(t+\Delta t)-y}=\int_t^{t+\Delta t}h(y,t')\,dt'+2D\int_t^{t+\Delta t}\frac{\partial}{\partial y}g(y,t')\int_t^{t'}g(y,t'')\delta(t'-t'')\,dt''dt'+\cdots$$
$$=h(y,t+\Theta_1\Delta t)\Delta t+Dg(y,t+\Theta_2\Delta t)\frac{\partial}{\partial y}g(y,t+\Theta_2\Delta t)\Delta t+\cdots, \qquad (1.10.9)$$

where $0\le\Theta_i\le 1$ and $D=\zeta kT$. Here we have also used Eq. (1.10.8) as well as the mean value theorem. The other integrals in Eq. (1.10.7) have been ignored, because they will either give a contribution of the form $(\Delta t)^n$ for $n=2$ if there are $2n$ F's and by Eq. (1.9.20) they will vanish, or if there are $(2n+1)$ F's they will vanish by Isserlis's theorem. Thus, we obtain the drift coefficient

$$D^{(1)}(y,t)=\lim_{\Delta t\to 0}\frac{\overline{\xi(t+\Delta t)-y}}{\Delta t}=h+Dg\frac{\partial g}{\partial y}. \qquad (1.10.10)$$

Equation (1.10.10) may also be considered as an *evolution equation* for the sharp value y. This is always the basis for the Langevin equation approach: the sharp initial condition corresponding to the delta function initial distribution in

the Fokker–Planck equation. We emphasize that $\xi(t)$ in Eq. (1.10.1) and y in Eq. (1.10.10) have different meanings: $\xi(t)$ is a stochastic variable while $y = \xi(t)$ is a sharp (definite) value at time t. We have distinguished the sharp values from the stochastic variables by deleting the time argument. The last term in Eq. (1.10.10) is known as the *noise-induced drift.*

Similarly for the diffusion coefficient $D^{(2)}(y, t)$, we have from Eq. (1.10.3)

$$[\xi(t+\Delta t)-y]^2 = \int_t^{t+\Delta t}\int_t^{t+\Delta t} h(\xi,t')h(\xi,t'')dt'dt'' + 2\int_t^{t+\Delta t} h(\xi,t')dt' \int_t^{t+\Delta t} g(\xi,t')F(t')dt' + \int_t^{t+\Delta t}\int_t^{t+\Delta t} g(\xi,t')g(\xi,t'')F(t')F(t'')dt'dt''. \tag{1.10.11}$$

The first two terms of Eq. (1.10.11) will give contributions of the order $(\Delta t)^2$ and will vanish according to Eq. (1.9.20). Thus

$$\overline{[\xi(t+\Delta t)-y]^2} = 2D\int_t^{t+\Delta t}\int_t^{t+\Delta t} g(\xi,t')g(\xi,t'')\delta(t'-t'')dt'dt''. \tag{1.10.12}$$

Therefore, we have for the diffusion coefficient

$$D^{(2)}(y,t) = \lim_{\Delta t\to 0}\overline{[\xi(t+\Delta t)-y]^2/(2\Delta t)} = Dg^2(y,t). \tag{1.10.13}$$

Having illustrated the one-dimensional problem, we shall now obtain the drift and diffusion coefficients for the two-dimensional Fokker–Planck equation in phase space for a free Brownian particle. This equation is, as we have seen, often called the *Kramers* equation or *Klein–Kramers* equation [21]. In general, the Fokker–Planck equation for a dynamical system, the motion of which in the absence of a heat bath is governed by Hamilton's equations with a *separable* and *additive* Hamiltonian comprising the sum of the kinetic and potential energies, is known as the Klein–Kramers equation.

We have seen in Section 1.7 that the Langevin equation for a free Brownian particle may be represented by Eq. (1.7.1). The corresponding Fokker–Planck equation for the PDF W in phase space with $x = y_1$, $v = y_2$ in Eq. (1.9.21) is

$$\frac{\partial W}{\partial t} = -\frac{\partial}{\partial x}\left[D_1^{(1)}W\right] - \frac{\partial}{\partial v}\left[D_2^{(1)}W\right] + \frac{\partial^2}{\partial x^2}\left[D_{1,1}^{(2)}W\right] + \frac{\partial^2}{\partial v^2}\left[D_{2,2}^{(2)}W\right] + 2\frac{\partial^2}{\partial x\partial v}\left[D_{1,2}^{(2)}W\right]. \tag{1.10.14}$$

Since $x = y_1$, $\Delta x = \Delta y_1$ and proceeding as in Eq. (1.9.14), we have

$$D_1^{(1)} = \lim_{\Delta t\to 0}\overline{\Delta y_1/\Delta t} = \lim_{\Delta t\to 0}\overline{\Delta x/\Delta t} = v. \tag{1.10.15}$$

Now, the change in velocity in a small time Δt is

$$\Delta v \approx -\beta v \Delta t + \frac{1}{m}\int_t^{t+\Delta t} F(t')dt'.$$

Thus, the drift coefficient $D_2^{(1)}$ is

$$D_2^{(1)} = \lim_{\Delta t \to 0} \frac{\overline{\Delta v}}{\Delta t} = -\beta v. \tag{1.10.16}$$

Likewise, the diffusion coefficients $D_{1,1}^{(2)}$ and $D_{1,2}^{(2)}$ are

$$D_{1,1}^{(2)} = \lim_{\Delta t \to 0} \frac{\overline{(\Delta x)^2}}{2\Delta t} = \lim_{\Delta t \to 0} \frac{\overline{v^2 (\Delta t)^2}}{2\Delta t} = 0, \tag{1.10.17}$$

$$D_{1,2}^{(2)} = \lim_{\Delta t \to 0} \frac{\overline{\Delta x \Delta v}}{2\Delta t} = \frac{1}{2}\lim_{\Delta t \to 0} \overline{-\beta v^2 \Delta t + v\int_t^{t+\Delta t} \frac{F(t')}{m} dt'} = 0 \tag{1.10.18}$$

because $\overline{F(t)} = 0$. In order to evaluate $D_{2,2}^{(2)} = \lim_{\Delta t \to 0} \overline{(\Delta v)^2}/(2\Delta t)$, consider

$$(\Delta v)^2 = \beta^2 v^2 (\Delta t)^2 - \frac{2\beta v \Delta t}{m}\int_t^{t+\Delta t} F(t')\,dt' + \frac{1}{m^2}\int_t^{t+\Delta t}\int_t^{t+\Delta t} F(t')F(t'')dt'dt''. \tag{1.10.19}$$

The first term on the right-hand side of Eq. (1.10.19) is of order $(\Delta t)^2$, the second term vanishes on averaging, and

$$\int_t^{t+\Delta t}\int_t^{t+\Delta t} \overline{F(t')F(t'')}\,dt'dt'' = 2\beta kTm\int_t^{t+\Delta t}\int_t^{t+\Delta t} \delta(t'-t'')dt'dt'' = 2\beta kTm\Delta t,$$

whence the diffusion coefficient is $D_{2,2}^{(2)}(x,v) = kT\beta/m$. Thus, we obtain

$$\frac{\partial W}{\partial t} + v\frac{\partial W}{\partial x} = \beta\left[\frac{\partial (vW)}{\partial v} + \frac{kT}{m}\frac{\partial^2 W}{\partial v^2}\right], \tag{1.10.20}$$

which is the desired Fokker–Planck equation in phase space.

1.11. Solution of the one-dimensional Fokker–Planck equation

As an example of the solution of the Fokker–Planck equation, we consider the Brownian motion of a free particle in velocity space only. The Langevin equation for this problem is Eq. (1.7.1). The corresponding Fokker–Planck equation for the transition probability $W(v,t\,|\,v_0,0)$ in velocity space is Eq. (1.9.28), which is a special case of Eq. (1.10.20), namely

$$\frac{\partial W}{\partial t} = \beta \frac{\partial}{\partial v}(vW) + \frac{\beta kT}{m} \frac{\partial^2 W}{\partial v^2}. \tag{1.11.1}$$

The easiest way to solve this equation is to construct the characteristic function. On taking Fourier transforms, we have

$$\tilde{W}(u,t) = \int_{-\infty}^{\infty} W(v,t \mid v_0, 0) e^{-iuv} dv, \tag{1.11.2}$$

so that, on integrating by parts,

$$\int_{-\infty}^{\infty} \frac{\partial}{\partial v}(\beta v W) e^{-iuv} dv = -\beta u \frac{\partial \tilde{W}}{\partial u},$$

$$\int_{-\infty}^{\infty} \frac{\partial^2 W}{\partial v^2} e^{-iuv} dv = -u^2 \tilde{W}.$$

Hence, our original Fokker–Planck equation is transformed into the *first-order* linear partial differential equation

$$\frac{\partial \tilde{W}}{\partial t} + \beta u \frac{\partial \tilde{W}}{\partial u} = -\frac{\beta kT}{m} u^2 \tilde{W}. \tag{1.11.3}$$

We make a small digression here, and consider the general solution of the first-order linear partial differential equation of the form

$$P(x,y,z)\frac{\partial z}{\partial x} + Q(x,y,z)\frac{\partial z}{\partial y} = R(x,y,z).$$

This equation is satisfied by the function ϕ defined by the equation $\phi(x, y, z) = 0$ if [13]

$$P\frac{\partial \phi}{\partial x} + Q\frac{\partial \phi}{\partial y} + R\frac{\partial \phi}{\partial z} = 0. \tag{1.11.4}$$

To solve the equation, we form the subsidiary system

$$\frac{dx}{P(x,y,z)} = \frac{dy}{Q(x,y,z)} = \frac{dz}{R(x,y,z)}.$$

Here $P = 1$, $Q = \beta u$, and $R = -(\beta kTu^2 / m)\tilde{W}$. Hence, our subsidiary system is

$$\frac{dt}{1} = \frac{du}{\beta u} = -\frac{d\tilde{W}}{(\beta kTu^2 / m)\tilde{W}}$$

with general solution

$$\tilde{W}(u,t) = \Psi\left(ue^{-\beta t}\right) e^{-kTu^2 / (2m)}, \tag{1.11.5}$$

where Ψ is an arbitrary function which is determined as follows. The initial distribution of velocities has the form $W(v,0\,|\,v_0,0)=\delta(v-v_0)$ so that $\tilde{W}(u,0)=\exp(-iuv_0)$. On setting $t=0$ in Eq. (1.11.5), we have

$$\Psi(u)=e^{-iuv_0+kTu^2/(2m)}.$$

Hence

$$\Psi\left(ue^{-\beta t}\right)=e^{-iv_0ue^{-\beta t}+\frac{kTu^2}{2m}e^{-2\beta t}}$$

and

$$\tilde{W}(u,t)=e^{-iv_0ue^{-\beta t}-\frac{kTu^2}{2m}\left(1-e^{-2\beta t}\right)}.$$

The above equation represents the *characteristic function* of a one-dimensional Gaussian random variable having mean

$$\langle v(t)\rangle=v_0e^{-\beta t} \tag{1.11.6}$$

[see Eqs. (1.7.4) and (1.7.8)] and variance

$$\sigma^2=\left\langle\left[v(t)-\langle v(t)\rangle\right]^2\right\rangle=\frac{kT}{m}\left(1-e^{-2\beta t}\right). \tag{1.11.7}$$

(We showed in Section 1.7 how these results can be obtained directly from the Langevin equation). Thus the conditional PDF (transition probability) of the velocities in the (Ornstein–Uhlenbeck) process is

$$W(v,t\,|\,v_0,0)=\frac{1}{\sigma\sqrt{2\pi}}e^{-\frac{(v-\langle v(t)\rangle)^2}{2\sigma^2}}, \tag{1.11.8}$$

with σ^2 and $\langle v(t)\rangle$ given by the two preceding equations. The stationary solution is found by taking $\lim_{t\to\infty}W$, which by inspection is

$$\lim_{t\to\infty}W(v,t\,|\,v_0,0)=\sqrt{\frac{m}{2\pi kT}}e^{-\frac{mv^2}{2kT}},$$

which is independent of v_0. Suppose that v_0 also has this distribution, then

$$W(v_0)=\sqrt{\frac{m}{2\pi kT}}e^{-\frac{mv_0^2}{2kT}}.$$

Thus by using $P(A\,|\,B)P(B)=P(A\cap B)$, we have the *joint* PDF

$$W(v_0,v,t)=\frac{m}{2\pi kT\sqrt{1-e^{-2\beta t}}}e^{-\frac{m(v^2+v_0^2-2v_0ve^{-\beta t})}{2kT(1-e^{-2\beta t})}}. \tag{1.11.9}$$

Since the process is *stationary* (i.e., the underlying mechanism does not depend on when the process began), by shifting the time axis we can write

$$v_0 = v(t_1),\ \ v = v(t_2),\ \text{and}\ \ \tau = |t_2 - t_1|.$$

Thus, W is the *two*-dimensional Gaussian PDF

$$W(v(t_1), v(t_2),\ \tau) = \frac{m}{2\pi kT\sqrt{1-\rho^2(\tau)}} e^{-\frac{m}{2kT}\frac{[v^2(t_1)-2v(t_1)v(t_2)\rho(\tau)+v^2(t_2)]}{1-\rho^2(\tau)}},$$

which depends on the time only through the time difference $\tau = |t_1 - t_2|$, $\rho(\tau) = e^{-\beta|\tau|}$ is the correlation coefficient [25], which we shall obtain in Chapter 3 using the Wiener–Khinchin theorem and the Langevin equation. This procedure may be also applied for many dimensions as in [13]. Note that the same symbol W is used for the various probabilities for notational convenience, the particular context being indicated by the arguments.

1.12. The Smoluchowski equation

We have remarked that the *Smoluchowski equation* is a special form of the Fokker–Planck equation, first given by M. von Smoluchowski in 1906 [4, 5, 10], which approximately describes the time evolution of the concentration of Brownian particles if inertial effects are small. In particular, Smoluchowski considered the Brownian movement of a particle under the influence of an *external force* [5, 21]. He showed that, if an external force $K(x, t)$ acts on the particle, then the PDF $W(x, t)$ in configuration space satisfies the approximate equation [5, 21] (see also Sections 1.2 and 1.9)

$$\frac{\partial W}{\partial t} = D\left(\frac{\partial^2 W}{\partial x^2} - \frac{1}{kT}\frac{\partial}{\partial x}KW\right). \tag{1.12.1}$$

Equation (1.12.1) is a one-dimensional Smoluchowski equation. It is a differential equation in configuration space, because W does not explicitly depend on the velocity. The general form of the Smoluchowski equation for Brownian motion under an external force $\mathbf{K} = -\text{grad}V$ is given by Eq. (1.2.6).

The Fokker–Planck equation (1.4.8) derived by Einstein (see Section 1.4) is an example of the simplest form of the Smoluchowski equation for the PDF $W(x, t\,|\,0)$, viz.,

$$\frac{\partial W}{\partial t} = D\frac{\partial^2 W}{\partial x^2} \quad (-\infty < x < \infty), \tag{1.12.2}$$

where for convenience we place the assembly of particles at the origin so that $x_0 = 0$. In mathematical terms, our problem is to solve this equation subject to the delta function initial condition $W(x, 0\,|\,0) = \delta(x)$. This is a way of stating

that all the particles of the ensemble were definitely at $x=0$ at $t=0$ (sharp initial condition). The solution of Eq. (1.12.2) subject to the delta function initial condition is called the *fundamental* solution of the equation; mathematically speaking this solution is the *Green function* of Eq. (1.12.2). The solution can be obtained using Fourier transforms. On taking the Fourier transform of Eq. (1.12.2) over the variable x, we have

$$\frac{\partial \tilde{W}}{\partial t} = -Du^2 \tilde{W}, \tag{1.12.3}$$

where $\tilde{W}(u,t)$ is the characteristic function defined as

$$\tilde{W}(u,t) = \int_{-\infty}^{\infty} W(x,t \mid 0) e^{iux} dx, \quad \tilde{W}(u,0) = \int_{-\infty}^{\infty} \delta(x) e^{iux} dx = 1.$$

Hence

$$\tilde{W}(u,t) = e^{-Du^2 t}$$

and

$$W(x,t \mid 0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-Du^2 t} e^{-iux} du = \frac{1}{(4\pi Dt)^{1/2}} e^{-\frac{x^2}{4Dt}}. \tag{1.12.4}$$

The above equation is a one-dimensional Gaussian distribution with zero mean and variance (note that W tends to zero as x tends to infinity, and to the delta function as t tends to zero), such that $\sigma^2 = 2D|t|$. Thus

$$\langle x^2 \rangle = 2D|t| = \frac{kT}{3\pi\eta a}, \tag{1.12.5}$$

where η is the viscosity of the suspension and a is the radius of the Brownian grain. This result is the same as that obtained in 1908 by Langevin by simply writing down the equation of motion of the Brownian particle and averaging it directly as in Section 1.3.

Equation (1.12.2) also serves to define the Wiener process $X(t)$ with PDF given by

$$W(X(t),t \mid X(s),s) = \frac{1}{c(2\pi|t-s|)^{1/2}} e^{-[X(t)-X(s)]^2/(2c^2|t-s|)}, \tag{1.12.6}$$

which is the fundamental solution of the diffusion equation (1.12.2) with $c^2 = 2kT/\zeta$ and $X = x$ in this case.

We shall now summarize the last fundamental result of the early investigations of the theory of Brownian movement, namely the escape-rate theory of Kramers [4, 21, 43], originally developed to explain the breaking of a chemical bond under the influence of thermal agitation.

1.13. Escape of particles over potential barriers: Kramers' theory

The origin of modern reaction-rate theory which we must very briefly outline before describing the Kramers theory, stems from the 1880s when Arrhenius [44, 49, 50, 60, 61] proposed, from an analysis of experimental data, that the rate coefficient in a chemical reaction should obey the law

$$\Gamma = \nu_0 e^{-\frac{\Delta V}{kT}}, \tag{1.13.1}$$

where ΔV denotes the threshold energy for activation and ν_0 is a prefactor [44]. After very many developments, summarized in [50], this equation led to the concept of chemical reactions as an assembly of particles situated at the bottom of a potential well. Rare members of this assembly will have enough energy to escape over the potential hill, owing to the shuttling action of thermal agitation, and will never return [50] (see Fig. 1.13.1), thus constituting a model of a chemical reaction.

The escape over the potential barrier represents the breaking of a chemical bond [50]. The Arrhenius law for the escape rate Γ (reaction velocity in the case of chemical reactions) of particles that are initially trapped in a potential well at A, and that may subsequently, under the influence of thermal agitation, escape over a high ($>> kT$) barrier of height ΔV at C and never return to A, may be written using transition state theory (TST) [49, 50] as

$$\Gamma^{\mathrm{TST}} = \frac{\omega_A}{2\pi} e^{-\frac{\Delta V}{kT}}. \tag{1.13.2}$$

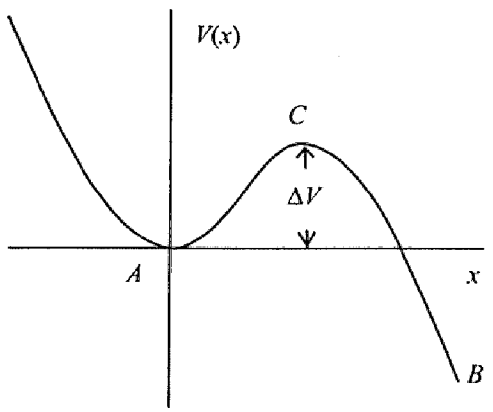


Figure 1.13.1. Single-well potential function as the simplest example of escape over a barrier. Particles are initially trapped in the well near the point A by a high potential barrier at the point C. They are thermalized very rapidly in the well. Due to thermal agitation, however, very few may attain enough energy to escape over the barrier into region B, from which they never return (a sink of probability). The barrier C is assumed to be sufficiently large so that the rate of escape of particles is very small.

Here the subscript TST stands for transition state while the attempt frequency, ω_A, is the angular frequency of a particle executing oscillatory motion (i.e., libration) at the bottom of a well. The barrier arises from the potential function of some external force, which may be electrical, magnetic, gravitational, and so on. The formula represents an attempt frequency times a Boltzmann factor, which weights the escape from the well.

A very unsatisfactory feature of the Arrhenius formula is that it appears to predict *escape in the absence of coupling to a heat bath*, in contradiction of the fluctuation–dissipation theorem. This defect was remedied, and reaction rate theory was firmly set in the framework of nonequilibrium statistical mechanics by the pioneering work of Kramers [43]. In order to take into account *nonequilibrium effects* in the barrier-crossing process which manifest themselves as a frictional dependence (i.e., a coupling to the heat bath of the prefactor in the TST formula) he chose, as a microscopic model of a chemical reaction, a classical particle moving in a potential (see Fig. 1.13.1). The fact that a typical particle is embedded in a heat bath is modeled by Brownian motion. In the single-particle distribution function, this represents (essentially through a dissipation parameter) all the remaining degrees of freedom of the system, consisting of the selected particle and the heat bath, which is in *perpetual thermal equilibrium* at temperature T. In Kramers' model [43, 49], the particle coordinate x represents the *reaction coordinate* (i.e., the distance between two fragments of a dissociated molecule – a concept first introduced in 1936 by Christiansen [44, 49]). The value of this coordinate, x_A, at the first minimum of the potential represents the *reaction state*; the value x_B, significantly over the summit of the well at B (i.e., when the particle has crossed over the summit) represents the *product state*, and the value x_C, at the saddle point, represents the *transition state*. We remark that, in his calculations of 1940, Kramers [43, 44] assumed that the particles are initially trapped in a well near the minimum of the potential at the point A. They then receive energy from the surroundings, and the Maxwell–Boltzmann distribution is rapidly attained in the well. Over a long period of time, however, rare particles gain energy in excess of the barrier height ΔV. Kramers then assumed that these particles escape over the barrier C (so that there is a perturbation of the Maxwell–Boltzmann distribution in the well) and reach a minimum at B, which is of lower energy than A, and once there, never return. We list the assumptions of Kramers:

(1) The particles are initially trapped in A (which is a *source* of probability).
(2) The barrier heights are very large compared with kT.

(3) In the well, the number of particles with energy between E and $E + dE$ is proportional to

$$e^{-E/(kT)}dE;$$

that is, a Maxwell–Boltzmann distribution is attained extremely rapidly in the well.

(4) Quantum effects are negligible.

(5) The escape of particles over the barrier is very slow (i.e., is a quasi-stationary process) so that the disturbance to the Maxwell–Boltzmann distribution (assumption 3) is almost negligible at all times.

(6) Once a particle escapes over the barrier it practically never returns (i.e., B is a *sink* of probability).

(7) A typical particle of the reacting system may be modeled by the theory of Brownian motion, including the inertia of the particles.

It is worth mentioning here that assumption 5 above relies heavily on assumption 2. If the barrier is too low, the particles escape too quickly to allow a Boltzmann distribution to be set up in the well. If the barrier is high, on the other hand, before many particles can escape, the Boltzmann distribution is set up. As required by assumption 3, we therefore assume that the ratio $\Delta V/(kT)$, is at least of the order, say, 5.

This model, which yields explicit formulas for the escape rate for very low and intermediate-to-high dissipative coupling to the bath (thereby including nonequilibrium effects in the TST formula), is ubiquitous in any physical system in which there is noise-activated escape from a potential well. It has attained importance in connection with fields as diverse as the dielectric relaxation of nematic liquid crystals [62], the magnetic relaxation of fine ferromagnetic particles [63], laser physics [64, 65], and Josephson junctions [21].

Kramers' objective was to calculate the prefactor Λ in the escape rate, viz.

$$\Gamma = \Lambda\Gamma^{\mathrm{TST}} = \Lambda\frac{\omega_A}{2\pi}e^{-\Delta V/(kT)} \tag{1.13.3}$$

from a *microscopic model* of the chemical reaction. Now a microscopic model of the reacting system incorporating dissipation (viz., an assembly of Brownian particles in a potential well) is used to determine Λ. Thus Λ indicates that the prefactor is closely associated both with the *stochastic differential equation* underlying Brownian motion, i.e., the Langevin equation for the evolution of the random variables (position and momentum), and the *associated probability density diffusion equation* describing the evolution of the density of the realizations (phase points) of these random variables in phase space. This is the

Fokker–Planck equation which, like the Boltzmann equation, is a *closed* equation for the *single*-particle PDF.

By supposing that $\dot{p} \approx 0$ (quasi-stationarity) in the Klein–Kramers equation, Eq. (1.5.9.6), Kramers discovered two asymptotic formulas for the rate of escape from a well for a system governed by the Langevin equation. The first is the intermediate-to-high damping (IHD) formula

$$\Gamma^{\mathrm{IHD}} = \left(\sqrt{1 + \frac{\beta^2}{4\omega_C^2}} - \frac{\beta}{2\omega_C} \right) \Gamma^{\mathrm{TST}}, \tag{1.13.4}$$

where ω_C is the characteristic frequency of the inverted oscillator approximation to the potential $V(x)$ in the vicinity of the barrier. In the IHD formula, the correction Λ to the TST result in the prefactor of Eq. (1.13.3) is essentially the positive eigenvalue (characterizing the unstable barrier-crossing mode) of the Langevin equation, Eq. (1.5.8.1), omitting the noise, linearized about the saddle point of the potential $V(x)$. In the case considered by Kramers, this is a one-dimensional maximum. A further discussion of this is given later.

Equation (1.13.4) formally holds [44], when the energy loss per cycle of the motion of a particle librating in the well with energy equal to the barrier energy $E_C = \Delta V$, is much greater than kT. The energy loss per cycle of the motion of a barrier-crossing particle is $\beta S(E_C)$, where E_C is the energy contour through the saddle point of the potential, and S is the action evaluated at $E = E_C$. This criterion effectively follows from the Kramers very-low-damping result (see below). The IHD asymptotic formula is derived by supposing that

(i) the barrier is so high and the dissipative coupling to the bath so strong that a Maxwell–Boltzmann distribution always holds at the bottom of the well; and

(ii) the Langevin equation may be linearized in the region very close to the potential barrier, meaning that all the coefficients in the corresponding Klein–Kramers equation are linear in the positions and velocities.

If these simplifications can be made, then the Klein–Kramers equation, although it remains an equation in the two phase variables (x, p), may be integrated by introducing an independent variable which is a linear combination of x and p so that it becomes an ordinary differential equation in a single variable.

A particular case of the IHD formula, Eq. (1.13.4), is the very high damping (VHD) limit, $\beta / (2\omega_C) >> 1$, where the escape rate from Eq. (1.13.4) becomes

$$\Gamma^{\mathrm{VHD}} = \frac{\omega_C}{\beta} \Gamma^{\mathrm{TST}} = \frac{\omega_A \omega_C}{2\pi\beta} e^{-\frac{\Delta V}{kT}}. \tag{1.13.5}$$

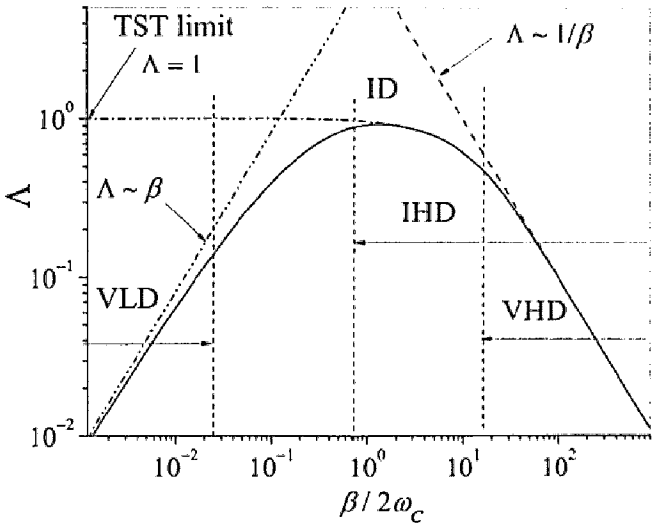


Figure 1.13.2. Diagram of damping regions for the prefactor Λ in Eq. (1.13.3). Three regions exist, namely VLD, intermediate damping (ID) (TST), and VHD, and two crossovers between them. Kramers' turnover refers to the under-damped region between ID and VLD.

Here the quasi-stationary solution, $\dot{\rho} \approx 0$, may be obtained in integral form by quadratures, and the high-barrier limit of the solution (which is appropriate to the escape rate) may be found by the method of steepest descents (see Fig. 1.13.2). It is now unnecessary to linearize the Langevin equation about the saddle point (here a one-dimensional maximum), as the solution may be obtained by means of the Smoluchowski equation.

For small friction β (such that $\beta S(E_C) << kT$, however, the IHD formula fails, predicting, just as with the TST formula, escape in the *absence of coupling to the bath*, because [44] the tacit assumption that the particles approaching the barrier from the depths of the well are in thermal equilibrium (so that the stationary solution applies) is violated (owing to the smallness of the dissipation of energy to the bath). Thus, the spatial region of significant departure from the Maxwell–Boltzmann distribution in the well extends far beyond the region over which the potential may sensibly be approximated by an inverted parabola.

Kramers showed how his second formula, valid in the very-low-damping (VLD) case, where the energy loss per cycle $\beta S(E_C)$ of a librating particle is very much less than kT, may be obtained by again reducing the Klein–Kramers equation to a partial differential equation in a single spatial variable (see Section 1.5.12). This variable is the *energy* or, equivalently, the *action*. Here the energy trajectories diffuse very slowly so that they do not differ significantly from those of the undamped librational motion in a well with energy corresponding to the

saddle energy ΔV or E_C. Thus, the only effect of escape is to produce a very slow spiraling of the closed energy trajectories towards the origin in the phase space (x, p). He solved the VLD problem (see Section 1.5.12) by writing the Klein–Kramers equation in angle–action (or angle–energy) variables (the angle is the *phase* or *instantaneous state* of the system along an energy trajectory) and taking a time average of the motion along a closed energy trajectory infinitesimally close to the saddle energy trajectory. Thus, by dint of thermal fluctuations, the (noisy) trajectory may become the separatrix or the open trajectory on which the particle exits the well (see Fig. 1.13.2.1 below). Now the average, being along a trajectory, is, of course, equivalent to an average over the fast phase variable; hence a diffusion equation, Eq. (1.5.12.19), in the slow energy (or action) variable emerges. Thus, once again, the time derivative of ρ (when ρ is written as a function of the energy using the averaging procedure above) is *exponentially small* at the saddle point. Hence, the stationary solution in the energy variable may be used. This procedure, which will shortly be described in detail following the original approach of Kramers, yields the Kramers' VLD formula:

$$\Gamma^{\mathrm{VLD}} = \frac{\beta S(E_C)}{kT}\Gamma^{\mathrm{TST}} = \frac{\omega_A}{2\pi}\frac{\beta S(E_C)}{kT}e^{-\frac{\Delta V}{kT}}. \tag{1.13.6}$$

This formula holds when in Eq. (1.13.3) $\Lambda << 1$, i.e., $\beta S(E_C) << kT$; unlike the TST result it vanishes when $\beta \to 0$, so that escape is impossible without coupling to the bath. Thus, in all cases, analytical formulas for the escape rate rest on the fact that, in the relevant damping regimes, the Klein–Kramers equation may be reduced to an equation in a single coordinate.

In summary, the VLD formula demonstrates that escape is impossible in the absence of coupling to the bath. Likewise, if the coupling to the bath is very large, the escape rate vanishes. Kramers made several estimates of the range of validity of both IHD and VLD formulas and the intermediate (or moderate) damping (ID) region where the TST, Eq. (1.13.2), holds with a high degree of accuracy. He was, however, unable to give a formula in the under-damped region between IHD and VLD, as there $\beta S(E_C) \approx kT$ so that no small perturbation parameter now exists. In essence, this problem, known as the Kramers turnover, was solved nearly 50 years later by Mel'nikov [66] and Mel'nikov and Meshkov [67], and elaborated upon by Grabert [68] and Pollak *et al.* [69]. They constructed an integral equation for the evolution of the energy distribution function which they solved using the Wiener–Hopf method [44, 56, 70], and so obtained an escape-rate formula which is valid for all values of the friction β (see Section 1.13.7), viz.,

$$\Gamma = A\left[\frac{\beta S(E_C)}{kT}\right]\Gamma^{\mathrm{IHD}}, \tag{1.13.7}$$

where

$$A(\Delta) = \exp\left(\frac{1}{2\pi}\int_{-\infty}^{\infty} \ln\left[1 - e^{-\Delta\left(\lambda^2+1/4\right)}\right]\frac{d\lambda}{\lambda^2+1/4}\right) \tag{1.13.8}$$

is called the depopulation factor (see further discussion in Section 1.13.7).

1.13.1. *Escape rate in the IHD limit*

To calculate the reaction rate in the IHD limit, where the damping forces are strong enough to ensure equilibrium in the system (except for a small region near the barrier top C, where the potential may be approximated by an inverted harmonic oscillator potential), we note that the Langevin equation may, in this limit, be linearized in the vicinity of the maximum of the potential at C. This corresponds in the Klein–Kramers equation to coefficients linear in the momentum and displacement and such an equation is a "linearized" Klein–Kramers equation.

Just as for small viscosity, the process is governed by diffusion in a single coordinate which is now a linear combination of the displacement and the momentum rather than the energy. The appropriate diffusion equation is the Klein–Kramers equation, Eq. (1.5.9.6), which we derived in Section 1.5.9.

We now assume that the function V is sufficiently well-behaved for it to be expanded as a Taylor series about x_C (the value of x where the top of the barrier is located). Taking $m = 1$, we write

$$V \approx \Delta V - \omega_C^2 (x - x_C)^2 / 2, \tag{1.13.1.1}$$

where the barrier height

$$\Delta V = V(x_C) - V(x_A). \tag{1.13.1.2}$$

Considering the situation as quasi-stationary, i.e., very slow diffusion over the barrier, made possible by the condition $\Delta V >> kT$, the Klein–Kramers equation, Eq. (1.5.9.6), becomes the stationary equation

$$\omega_C^2 x' \frac{\partial \rho}{\partial p} + p\frac{\partial \rho}{\partial x'} - \beta\frac{\partial}{\partial p}\left(\rho p + kT\frac{\partial \rho}{\partial p}\right) = 0, \tag{1.13.1.3}$$

where $x' = x - x_C$. Substituting

$$\rho = g(x', p)\, e^{-\Delta V/(kT)} e^{-(p^2 - \omega_C^2 x'^2)/(2kT)} \tag{1.13.1.4}$$

into Eq. (1.13.1.3), we have

$$\omega_C^2 x' \frac{\partial g}{\partial p} + p \frac{\partial g}{\partial x'} + \beta p \frac{\partial g}{\partial p} - \beta kT \frac{\partial^2 g}{\partial p^2} = 0. \tag{1.13.1.5}$$

Here $g(x', p)$ is a crossover function, which varies rapidly near the barrier.

We see immediately that $g =$ constant is a solution of Eq. (1.13.1.5). However, this solution corresponds to thermal equilibrium, and hence to a situation of no diffusion, i.e., the current of particles is zero over the top of the barrier. This would yield, of course, the Maxwell–Boltzmann distribution. We can obtain, however, the quasi-stationary solution if we assume that the crossover function satisfies the condition

$$g = g(u), \tag{1.13.1.6}$$

where $u = p - ax'$ and a is a constant. The solution must satisfy the following conditions: (i) to the right of the barrier, the density must go to zero, because at the beginning of the process, practically no particles have reached the sink B; and (ii) near the source point A, the Maxwell–Boltzmann distribution holds to a high degree of accuracy. We include both of these conditions by imposing the boundary conditions:

$$g \to 0 \text{ as } x \to \infty \text{ (i.e., for } x >> x_C) \text{ and } g = \text{const at } x = x_A = 0. \tag{1.13.1.7}$$

Equation (1.13.1.5) with Eq. (1.13.1.6) now leads to

$$\left[(a-\beta)p - \omega_C^2 x'\right] \frac{dg}{du} + \beta kT \frac{d^2 g}{du^2} = 0. \tag{1.13.1.8}$$

To solve this equation, we write the coefficient $(a-\beta)p - \omega_C^2 x'$ in terms of the single variable $u = p - ax'$ rather than x' and p. This can be achieved in a very neat way if we write

$$(a-\beta)p - \omega_C^2 x' = (a-\beta)(p - ax') = (a-\beta)u,$$

which imposes on the constant a the condition:

$$\omega_C^2 = a(a-\beta) \text{ or } a = (\beta/2) \pm \sqrt{\omega_C^2 + \beta^2/4}. \tag{1.13.1.9}$$

If we ignore the minus sign in Eq. (1.13.1.9), then

$$a - \beta = -\beta/2 + \sqrt{\omega_C^2 + \beta^2/4} = \lambda_+ \tag{1.13.1.10}$$

will be positive, and Eq. (1.13.1.8) will therefore represent a diffusion of particles over the barrier at C. The quantity λ_+ then corresponds to the unique positive eigenvalue of the Langevin equation (1.5.8.1) linearized about C *with the noise term omitted*, and characterizes the (unstable) barrier-crossing mode.

Equation (1.13.1.8) now becomes a conventional ordinary differential equation in u:

$$\beta kT\frac{d^2g}{du^2}+(a-\beta)u\frac{dg}{du}=0, \tag{1.13.1.11}$$

with solution

$$g(u)=C'\int_{-\infty}^{u}e^{-(a-\beta)u'^2/(2\beta kT)}du', \tag{1.13.1.12}$$

where C' is a constant of integration and we have taken $-\infty$ for the lower limit of the integral in Eq. (1.13.1.12) corresponding to the boundary condition $g\to 0$ as $u\to-\infty$, i.e., $g\to 0$ for $x>>x_C$ or far to the right of the barrier top, i.e., outside the well. Now, in the region $x\approx x_A$, that is, in the depths of the well far to the left of the barrier top $(x<<x_C)$, we may extend the upper limit of integration in Eq. (1.13.1.12) to $+\infty$ to obtain

$$g(\text{near } x_A)\approx g(\infty)=C'\sqrt{\frac{2\pi\beta kT}{a-\beta}}, \tag{1.13.1.13}$$

since

$$\int_{-\infty}^{\infty}e^{-\alpha x^2}dx=\sqrt{\frac{\pi}{\alpha}}. \tag{1.13.1.14}$$

Thus, the PDF $\rho(x,p)$ *near* A (the minimum of the potential) will be:

$$\rho(x,p)\approx C'\sqrt{\frac{2\pi\beta kT}{a-\beta}}\,e^{-(p^2+\omega_A^2x^2)/(2kT)}, \tag{1.13.1.15}$$

where the potential is approximated by $V(x)\approx\omega_A^2x^2/2$ near the bottom of the well $(x\approx x_A=0)$.

The number of particles passing the barrier top in unit time, i.e., the probability current J, may be obtained [44] by integrating ρp over p from $-\infty$ to $+\infty$ (in this one-dimensional case, J strictly means the number of particles crossing unit area in unit time; the calculation of the current from the current density in more than one dimension is a complicated mathematical task [44]). By putting $x'=0$ so that $x=x_C$ (i.e., the line of flow is through the saddle line), since ρp is the current density, we obtain from Eqs. (1.13.1.4) and (1.13.1.12) using integration by parts

$$J=\int_{-\infty}^{\infty}\rho p\,dp=C'e^{-\frac{\Delta V}{kT}}\int_{-\infty}^{\infty}pe^{-\frac{p^2}{2kT}}\int_{-\infty}^{p}e^{-\frac{(a-\beta)p'^2}{2\beta kT}}dp'dp=C'kT\,e^{-\frac{\Delta V}{kT}}\sqrt{\frac{2\pi\beta kT}{a}},$$

while the number of particles n_A trapped near the minimum A is, from Eq. (1.13.1.15),

$$n_A = C'\sqrt{\frac{2\pi\beta kT}{a-\beta}}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\frac{p^2+\omega_A^2 x^2}{2kT}}\,dpdx$$

$$= C'\frac{2\pi kT}{\omega_A}\sqrt{\frac{2\pi\beta kT}{a-\beta}}. \qquad (1.13.1.16)$$

The escape rate is therefore the number of particles crossing the saddle line in unit time divided by the number in the well (total population), viz.,

$$\Gamma^{\mathrm{IHD}} = J/n_A, \qquad (1.13.1.17)$$

which, together with the eigenvalue Eq. (1.13.1.9), yields

$$\Gamma^{\mathrm{IHD}} = \frac{\omega_A}{2\pi\omega_C}\left(\sqrt{\omega_C^2+\beta^2/4}-\beta/2\right)e^{-\Delta V/(kT)}. \qquad (1.13.1.18)$$

If we now take the limit of the right-hand side of this equation, in the two cases of large and small β, we find in the first instance ($\beta >> 2\omega_C$) the VHD equation, Eq. (1.13.5). The result embodied in Eq. (1.13.5) is, in effect, the non-inertial limit, where the dissipation in the system is so large that the inertia of the escaping particles has practically no effect (compare this to the original Einstein theory of Brownian movement with the later inertia corrected version of Uhlenbeck and Ornstein; see Chapter 3). In the second instance, i.e., the weak damping limit ($\beta << 2\omega_C$), we obtain, from Eq. (1.13.1.18),

$$\Gamma = \lim_{\beta\to 0}\Gamma^{\mathrm{IHD}} \approx \frac{\omega_A}{2\pi}e^{-\Delta V/(kT)}, \qquad (1.13.1.19)$$

which is the TST result, Eq. (1.13.2), predicting escape in the absence of coupling to the bath, i.e., $\beta\to 0$. *However, regarding this limit as the solution for very low damping is erroneous, as we shall now explain.* This limit is, in fact, the moderate or intermediate damping case.

We first remark that the IHD solution, Eq. (1.13.1.18), which we have described relies [44] on the assumption that the friction is large enough to ensure that the particles approaching the barrier from the depths of the well are in thermal equilibrium. If the friction coefficient becomes too small, this condition is violated, and the IHD solution is no longer valid *because the space interval in which the nonequilibrium behavior prevails exceeds that where an inverted parabola approximation to the potential is valid.* This is the origin of the need for a different treatment for VLD such that $\beta S(E_C) << kT$, and for crossover values of the friction, where $\beta S(E_C) \approx kT$. Put in a simpler way, in the VLD

case, the coupling to the bath is so weak that the assumption of a Maxwell–Boltzmann distribution in x and p in a relatively large region extending almost to the top of the barrier is not valid, *because the damping is so small that the motion of an escaping particle is almost that of a librating particle with energy equal to the barrier energy and without dissipation.*

1.13.2. *Kramers' calculation of the escape rate in the VLD limit*

We now consider very low damping, i.e., energy controlled diffusion. We follow, as closely as possible, the original reasoning and phraseology of Kramers, using the energy-controlled diffusion equation of Section 1.5.12. As usual, a stationary state of diffusion, i.e., $\dot{\rho} = 0$, with current density J corresponds to

$$J = -\beta\left(S\rho + kTS\frac{\partial \rho}{\partial E}\right) = -\beta kTSe^{-E/(kT)}\frac{\partial}{\partial E}\left(\rho e^{E/(kT)}\right), \qquad (1.13.2.1)$$

because the continuity equation is in S (action) space $\dot{\rho} = -\partial J / \partial S$. Integrating with respect to E between two points A and B along the E (or S) coordinate yields

$$J = \beta kT\left[\rho e^{E/(kT)}\right]_B^A \Big/ \int_A^B S^{-1}e^{E/(kT)}dE. \qquad (1.13.2.2)$$

The density ρ is practically constant along lines of constant energy (since a Boltzmann distribution is set up with $\rho = \rho_0 e^{-E/(kT)}$), so $E = \text{const}$ implies $\rho = \text{const}$ over a range of curves starting at A and extending to energy curves that cut the x-axis, not at C itself but at some point D very close to C. This restriction is necessary if the potential function has a smooth saddle point as the frequency tends to zero as E tends to ΔV, so that the viscosity is no longer small in the sense used in Section 1.5.12. (This restriction is unnecessary if the saddle point is not a smooth function of the space variables.) Equation (1.13.2.2) may be written as

$$J = \beta kT\frac{\left(\rho e^{E/(kT)}\right)_{\text{near } A} - \left(\rho e^{E/(kT)}\right)_C}{\int_{\text{near } A}^{C} S^{-1}e^{E/(kT)}dE}. \qquad (1.13.2.3)$$

We avoid integrating from the point A itself, because at this point $E = S = 0$ and so the integral would diverge. We may take it that "near A" means an energy value of the order of the thermal energy kT, and so corresponds to points in phase space, where ρ is still of the same order as at A itself, and where practically all the particles are trapped. The condition that particles leaving at C

practically never return to the well means, according to Kramers, that the concentration $[\rho e^{E/(kT)}]_C$ may be taken to be 0, and that the upper limit of the integral may be taken to be the barrier energy at C. We write

$$\rho_A = [\rho e^{E/(kT)}]_{\text{near } A}. \tag{1.13.2.4}$$

Thus, Eq. (1.13.2.3) becomes:

$$J = \beta k T \rho_A \left[\int_{kT}^{\Delta V} S^{-1} e^{E/(kT)} dE \right]^{-1}. \tag{1.13.2.5}$$

Now the main contribution to this integral comes from energies which differ from the barrier energy ΔV by an amount of order of magnitude kT, so that we may take S to have the value S_C corresponding to the noise-induced energy trajectory through the saddle point C on which a particle may escape. Hence, the integral in Eq. (1.13.2.5) governing the overbarrier current J now becomes

$$\int_{kT}^{\Delta V} S^{-1} e^{E/(kT)} dE \approx S(E_C)^{-1} \int_{-\infty}^{\Delta V} e^{E/(kT)} dE = kTS(E_C)^{-1} e^{\Delta V/(kT)}. \tag{1.13.2.6}$$

Here by integrating over E from $-\infty$ (i.e., deep in the well) to ΔV, we have assumed the high-barrier limit. Thus the current J is

$$J \approx \beta \rho_A S(E_C) e^{-\Delta V/(kT)}. \tag{1.13.2.7}$$

Hence, since the number of particles trapped in the well near the bottom A is

$$n_A \approx \rho_A \frac{2\pi kT}{\omega_A}, \tag{1.13.2.8}$$

the escape rate Γ^{VLD} is given by

$$\Gamma^{\text{VLD}} = \frac{J}{n_A} = \beta \frac{S(E_C)}{kT} \frac{\omega_A}{2\pi} e^{-\Delta V/(kT)}. \tag{1.13.2.9}$$

Kramers now roughly approximates the action of the almost periodic motion at the saddle point by $S_C = 2\pi E_C / \omega_A$, which is the action of a harmonic oscillator of energy equal to the barrier energy and natural frequency $\omega_A / (2\pi)$ [44, 71], so that Eq. (1.13.2.9) becomes

$$\Gamma \sim \frac{\beta \Delta V}{kT} e^{-\Delta V/(kT)}, \tag{1.13.2.10}$$

which is Eq. (28) of Kramers [43]. Note the discrepancy between this equation and the *low-damping limit of the IHD equation*, Eq. (1.13.1.18), i.e., Eq. (1.13.1.19), which predicts escape in the absence of dissipative coupling. We remark that Eq. (1.13.2.9) may also be written as

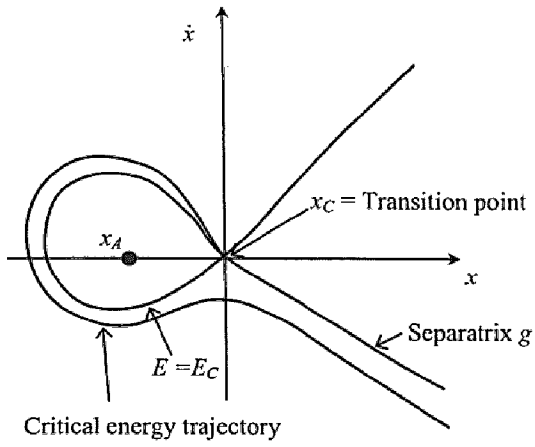


Figure 1.13.2.1. Diagram of the critical energy curve and separatrix given by Matkowsky *et al.* [72]. Here we show the critical energy curve ($E = E_C$) and the separatrix (g) in phase space [44]. The critical energy, E_C, is the energy required by a particle to just escape the well. When a particle reaches this energy, it may either escape from or remain in the well with equal probability. The separatrix separates the bounded and unbounded motions. In other words, when a particle reaches the separatrix it exits the well. The separation of these curves (greatly exaggerated in the diagram) is *infinitesimally small.*

$$\Gamma^{\mathrm{VLD}} = \frac{\Delta E}{kT}\frac{\omega_A}{2\pi}e^{-\Delta V/(kT)}, \tag{1.13.2.11}$$

where $\Delta E = \beta S(E_C) << kT$ is the energy loss per cycle of the noisy motion at the saddle point, and

$$S(E_C) = \oint_{E_C} p dx \tag{1.13.2.12}$$

is the action of a particle librating in the well with energy equal to the saddle point energy or critical energy.

We shall also need the escape rate Γ^{TST} as rendered by the TST theory. That result is easily obtained because, in TST, Boltzmann statistics hold everywhere, unlike in the treatment of Kramers. Thus the probability of a jump (that is, of an event occurring) is simply $P = C'e^{-E/(kT)}$, where C' is a constant. In using this equation for reaction rates, the constant C' is written as $\omega_A/(2\pi)$ so that, according to TST, $P = \Gamma^{\mathrm{TST}} = \omega_A \exp[-\Delta V/(kT)]/(2\pi)$. $\omega_A/(2\pi)$ is called the *attempt frequency.* We now write Eq. (1.13.2.9) in the form given by Kramers. Thus as before in the low-damping limit (yielding μ explicitly),

$$\Gamma^{\mathrm{VLD}} = \frac{\beta S(E_C)}{kT}\Gamma^{\mathrm{TST}}. \tag{1.13.2.13}$$

We note that Hänggi *et al.* [50] re-derived the VLD equation, Eq. (1.13.2.9), by calculating, in their Eq. (4.49), the mean first-passage time (Hänggi *et al.* [50]

use ω_0 instead of ω_A). Essentially they used the mean first-passage time method of Matkowsky *et al.* [72], which is explained in detail in the context of magnetic spins in [44]. In their notation, $\Gamma^{-1} = \tau(A) + 2\tau_{A\to\text{sep}}$. Here $\tau(A)$ is the time to go from the well to the critical energy curve. The critical energy is the energy required by a particle in order to escape the well; thus without any extra energy a particle, on reaching the critical energy curve, may either remain in or escape from the well with equal probability. Now $\tau_{A\to\text{sep}}$ is the time required to go from the critical energy curve to the separatrix. The separatrix is a curve whose distance from the critical energy curve is infinitesimal; however, all particles reaching the separatrix are assumed to be on their way out of the region A (Fig. 1.13.2.1). Note that $\tau_{A\to\text{sep}}$ is regarded as negligible with respect to $\tau(A)$.

1.13.3. *Range of validity of the IHD and VLD formulas*

The IHD escape rate Γ^{IHD} given by Eq. (1.13.1.18) in the limit of vanishing friction becomes the TST result, Eq. (1.13.2). This limiting behavior is, however, inconsistent with the derivation of the IHD result in Eq. (1.13.1.18) because, in the limit of vanishing friction, the variation of x is not the same as the variation of u. So the correct formula to use is Eq. (1.13.2.9), that is,

$$\Gamma^{\text{VLD}} = \frac{\beta S(E_C)\omega_A}{2\pi kT} e^{-\Delta V/(kT)}. \tag{1.13.3.1}$$

In order for Eq. (1.13.3.1) to hold, β must be small compared with ω_A (underdamping). If $\beta = 2\omega_A$, we have aperiodic damping, and we might expect that there would be a plentiful supply of particles near point C, so that the escape rate would be described by the IHD formula. Kramers [43], however, confesses (see Fig. 1.13.2) that he was unable to extend Eq. (1.13.3.1) (the VLD result) to values of β which were not small compared with $2\omega_A$, i.e., in the *crossover (turnover) region* between VLD and IHD and *a fortiori* to the entire underdamped region.

The approximate formula for the escape rate in the VLD limit, Eq. (1.13.3.1), is useful for obtaining a criterion in terms of the barrier height for the ranges of friction in which the VLD and IHD Kramers formulas are valid. With the harmonic oscillator action $S_C = 2\pi\Delta V/\omega_A$, Eq. (1.13.3.1) is

$$\Gamma = \Gamma^{\text{VLD}} = \frac{\beta\Delta V}{kT} e^{-\Delta V/(kT)}. \tag{1.13.3.2}$$

If now we define a dimensionless friction parameter $\alpha = 2\pi\beta/\omega_A$, Eq. (1.13.3.2) becomes $\Gamma = \alpha\Delta V\Gamma^{\text{TST}}/(kT)$ so that $\alpha\Delta V$ is approximately the

energy loss per cycle. Hence, the condition for the validity of the VLD equation, Eq. (1.13.3.2), becomes $\alpha\Delta V << kT$, while one would expect the IHD formula, Eq. (1.13.1.18), to be valid if $\alpha\Delta V >> kT$. The damping region given by $\alpha\Delta V \approx kT$ defines the *crossover region*, where neither the VLD nor the IHD formula is valid. This is called the *Kramers turnover region* and is the reason behind the calculation of Mel'nikov and Meshkov mentioned above. We shall now give a physical interpretation of the three regions identified above.

We may summarize the results of our calculation. In the *mechanical* Kramers problem pertaining to point particles and, by extension, to rigid bodies, which all have separable and additive Hamiltonians, three regimes of damping appear:

(i) Intermediate-to-high damping: the general picture here [44] being that inside the well the distribution function is almost the Maxwell–Boltzmann distribution prevailing in the depths of the well. However, near the barrier it deviates from that equilibrium distribution, owing to the slow draining of particles across the barrier. The barrier region is so small that one may approximate the potential in this region by an inverted parabola.

(ii) Very low damping: here the damping is so small that the assumption in (i), namely that the particles approaching the barrier region have the Maxwell–Boltzmann distribution, completely breaks down. Thus, the region where deviations occur extends far beyond the region where the potential may be approximated by an inverted parabola. Thus we may now, by transforming the Klein–Kramers equation into energy and phase variables obtain the escape rate (this is done by averaging over the phase and by supposing that the motion of a particle attempting to cross the barrier is almost conserved, and is the librational motion in the well of a particle with energy equal to the barrier energy). We remark that the assumption of almost-conservative behavior (meaning that the energy loss per cycle is almost negligible and is equal to the friction times the action of the undamped motion at the barrier energy) ensures that the Liouville term in the Klein–Kramers equation vanishes (unlike in IHD, where strong coupling between the diffusion and the Liouville term exists). Thus, only the diffusion term in the energy variable remains, the dependence on the phase having been eliminated by averaging the distribution in energy–phase variables along a closed trajectory of the energy, since we assume a librational motion in the well.

(iii) An intermediate (crossover) friction region and, by extension, almost the entire under-damped region, where neither the IHD nor the VLD formula applies. Thus, none of the above approaches can be used. In contrast to the VLD case, the Liouville term in the Klein–Kramers equation does not vanish,

meaning that one cannot average out the phase dependence of the distribution function. This is ultimately taken account of by constructing, from the Klein–Kramers equation, a diffusion equation for the PDF with the energy and action as independent variables. This diffusion equation allows one to express the calculation of the energy distribution function at a given action, as a Fredholm integral equation which can be converted into one, or several, Wiener–Hopf equations [44]. This procedure yields an integral equation, Eq. (1.13.8), for the depopulation factor, the product of which, with the IHD escape rate from Eq. (1.13.7), provides an expression for the escape rate which is valid for all values of the damping, so allowing the complete solution of Kramers' problem. The depopulation factor effectively allows for coupling between the Liouville term and the dissipative term in the Klein–Kramers equation written in terms of energy–action variables, which is ignored in the VLD limit.

The Kramers theory may be verified numerically for large potential barrier heights by calculating the smallest non-vanishing eigenvalue of the Klein–Kramers equation [44]. This procedure is possible because of the exponential nature of the escape rate, so that, in effect, that eigenvalue is very much smaller than all the higher-order eigenvalues, which pertain to the fast motion inside the well. Thus the Kramers escape rate is approximately given by the smallest non-vanishing eigenvalue if the barrier height is sufficiently large ($>5kT$). This method has been extensively used to verify the Kramers theory, in particular the application of that theory to magnetic relaxation of single-domain ferromagnetic particles (see Section 1.18 below). We shall now briefly summarize the extension of the Kramers theory to many dimensions, due to Langer [73].

1.13.4. *Extension of Kramers' theory to many dimensions in the IHD limit*

We have seen that the original IHD treatment of Kramers pertained to a mechanical system of one degree of freedom specified by the coordinate x with additive Hamiltonian $H = p^2/2m + V(x)$. Thus, the motion is separable and described by a 2D phase space with state variables (x, p). However, this is not always so. For example, the motion of the magnetic moment in a single-domain ferromagnetic particle is governed by a non-additive Hamiltonian, which is simply the magnetocrystalline anisotropy energy of the particle, so that the system is non-separable (see Section 1.17).

The phase-space trajectories in the Kramers problem of the under-damped motion are approximately ellipses. The corresponding trajectories in the magnetic problem are much more complicated because of the non-separable form of the energy. Similar considerations hold in the extension of the Debye

theory of dielectric relaxation (see Section 1.15) to include inertia, as in this case one would usually (albeit with a separable Hamiltonian) have a six-dimensional phase space corresponding to the orientations and angular momenta of the rotator. These, and other considerations, suggest that the Kramers theory should be extended to a multi-dimensional phase space.

Such generalizations, having been instigated by Brinkman [74], were further developed by Landauer and Swanson [75]. However, the most complete treatment is due to Langer in 1969 [73], who considered the IHD limit. As specific examples of the application of the theory, we shall apply it to the Kramers IHD limit, and to calculation of the magnetic relaxation time for a single-domain ferromagnetic particle for an arbitrary non-axially symmetric potential of the magnetocrystalline anisotropy in that limit (see Section 1.18.2).

Before proceeding, we remark that a number of other interesting applications of the theory, which, as the reader will appreciate, is generally concerned with the nature of metastable states and the rates at which these states decay, have been mentioned by Langer [73] and we briefly summarize these. Examples are:

(1) A supersaturated vapor [76] which can be maintained in a metastable state for a very long time but which will eventually undergo condensation into the more stable liquid phase.
(2) A ferromagnet, which can persist with its magnetization pointing in a direction opposite to that of an applied magnetic field.
(3) In metallurgy, an almost identical problem occurs in the study of alloys whose components tend to separate on ageing or annealing.
(4) The final examples quoted by Langer are the theories of superfluidity and superconductivity, where states of nonzero superflow are metastable and so may undergo spontaneous transitions to states of lower current and greater stability.

According to Langer [73], all the phase transitions above take place via the nucleation and growth of some characteristic disturbance within the metastable system. Condensation of the supersaturated vapor is initiated by the formation of a sufficiently large droplet of the liquid. If this droplet is big enough, it will be more likely to grow than to dissipate, and will bring about condensation of the entire sample. If the nucleating disturbance appears spontaneously as a thermodynamic fluctuation it is said to be *homogeneous*. This is an intrinsic thermodynamic property of the system and is the type of disturbance described by Langer [73], which we shall summarize here. The other type of nucleation is *inhomogeneous nucleation*, which occurs when the disturbance leading to the

phase transition is caused by a foreign object, e.g., an irregularity in the walls of the container or some agent that is not part of the system of direct interest.

The above examples have been chosen in order to illustrate the breadth of applicability of the theory. In the present context, we remark that Langer's method, since it can in effect be applied to a system of multiple degrees of freedom, is likely to be of much use in calculating relaxation times for fine particle magnetic systems in which other types of interaction, such as exchange and dipole–dipole coupling, also appear. We also emphasize that Langer's treatment of the homogeneous nucleation problem contains within it the magnetic case of the Kramers' IHD calculation which we shall treat in Section 1.18. The multi-dimensional Kramers problem was first solved in the VHD limit by Brinkman [74] and Landauer and Swanson [75]; see also [44]. We should also mention that Langer's treatment is also, in effect, a generalization of a calculation of Becker and Döring [76] of the rate of condensation of a supersaturated vapor. A general discussion of this problem is given in Chapter 7 of Frenkel [77] on the kinetics of phase transitions.

1.13.5. *Langer's treatment of the IHD limit*

For easy comparison with previous work, we shall adopt the notation of Ref. [44]. Thus, we shall consider the Fokker–Planck equation for a multi-dimensional random process governed by a state vector $\{\boldsymbol{\eta}\} = \{\eta_1, \eta_2, \ldots, \eta_{2N}\}$ which is [50, 73]

$$\frac{\partial}{\partial t}\rho(\{\boldsymbol{\eta}\},t) = \sum_{i=1}^{2N}\sum_{n=1}^{2N}\frac{\partial}{\partial \eta_i}\left[M_{in}\left(\frac{\partial E}{\partial \eta_n} + kT\frac{\partial}{\partial \eta_n}\right)\right]\rho(\{\boldsymbol{\eta}\},t). \qquad (1.13.5.1)$$

In Eq. (1.13.5.1), $E(\{\boldsymbol{\eta}\})$ is a Hamiltonian (energy) function having two minima at points A and B, separated by a saddle point C surrounded by two wells. One well, say the one at B, is at a much lower energy than the other. The particles have to traverse the saddle point, which acts as a barrier at C. We again assume that the barrier height $\Delta V = E_C - E_A$ is very high (at least of the order of $5kT$), so that the diffusion over the barrier is slow enough to ensure that a Maxwell–Boltzmann distribution is established and maintained near A at all times. The high barrier also assures that the contribution to the flux over the saddle point will come mainly from a small region around C. The $2N$ state variables $\{\boldsymbol{\eta}\} = \{\eta_1, \eta_2, \ldots, \eta_{2N}\}$ are parameters, which could equally well be the coordinates and momenta of a point in phase space, or angular coordinates describing the orientation of the magnetization vector of a single-domain

ferromagnetic particle (see Section 1.18.2 below). Generally, however, the first N of the η_i's will be functions of the N coordinates of position [50]

$$\eta_i = \eta(x_i), \quad i = 1, 2, \ldots, N. \tag{1.13.5.2}$$

The second N of the η_i's will be the conjugate momenta π_i, namely

$$\eta_{i+N} = \pi_i \quad i = 1, 2, \ldots, N. \tag{1.13.5.3}$$

In fact, the η_i's will often (although not necessarily) be the coordinates themselves, in which case (obviously) $\eta_i = x_i, i = 1, 2, \ldots, N$. Here, when the noise term in the Langevin equation is ignored, the system evolves in accordance with the deterministic equation

$$\dot{\eta}_i = -\sum_n M_{in} \frac{\partial E}{\partial \eta_n}, \tag{1.13.5.4}$$

where M_{ij} are the matrix elements of the transport matrix $\mathbf{M}$, which, for simplicity, we shall assume to be constant. An example of such a system is the translational Brownian motion of a particle in a potential in the IHD limit considered in Section 1.13.6, Eq. (1.13.6.2). Another example is the magnetization relaxation of a superparamagnetic particle (see Section 1.18.2).

We may define the matrices $\mathbf{D}$ and $\mathbf{A}$ by the equations

$$\mathbf{D} = \frac{1}{2}(\mathbf{M} + \mathbf{M}^{\mathrm{T}}) \text{ and } \mathbf{A} = \frac{1}{2}(\mathbf{M} - \mathbf{M}^{\mathrm{T}}), \tag{1.13.5.5}$$

where $\mathbf{M} = (M_{ij})$ is the *transport* matrix resulting from Eq. (1.13.5.4), and the symbol "T" means matrix transposition. Matrix $\mathbf{D}$ is called the *diffusion* matrix, which characterizes the thermal fluctuations due to the heat bath, while matrix $\mathbf{A}$ describes the motion in *the absence of the bath*, i.e., the inertial term in the case of mechanical particles, and if $\mathbf{D}$ is not identically zero, then the dissipation of energy satisfies [50]

$$\dot{E} = -\sum_{i,n} \frac{\partial E}{\partial \eta_i} D_{in} \frac{\partial E}{\partial \eta_n} \leq 0. \tag{1.13.5.6}$$

We consider, as before, a single well and suppose that, at finite temperatures, a Maxwell–Boltzmann distribution is set up and the density at equilibrium is

$$\rho_{\mathrm{eq}}(\{\boldsymbol{\eta}\}) = \frac{1}{Z} e^{-\frac{E(\{\boldsymbol{\eta}\})}{kT}}, \tag{1.13.5.7}$$

where

$$Z \equiv \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-\frac{E}{kT}} d\eta_1 \cdots d\eta_{2N} \tag{1.13.5.8}$$

is the partition function. The IHD escape rate for this multivariable problem may again be calculated by the flux-over-population method.

We make the following assumptions about $\rho(\{\boldsymbol{\eta}\})$:

(1) It obeys the stationary Fokker–Planck equation (i.e., $\dot{\rho} = 0$), which is (on linearization about the saddle point):

$$\sum_{i,n} \frac{\partial}{\partial \eta_i} M_{in} \left[\sum_k e_{nk} \left(\eta_k - \eta_k^S \right) + kT \frac{\partial}{\partial \eta_n} \right] \rho(\{\boldsymbol{\eta}\}) = 0, \qquad (1.13.5.9)$$

where the e_{jk} are the coefficients in the Taylor expansion of the energy about the saddle point truncated at the second term, namely the quadratic (form) approximation

$$E(\{\boldsymbol{\eta}\}) = E_C - \frac{1}{2} \sum_{i,n} e_{in} (\eta_i - \eta_i^C)(\eta_n - \eta_n^C), \qquad (1.13.5.10)$$

$\{\boldsymbol{\eta}\} \approx \{\boldsymbol{\eta}^C\}$, and E_C is the value of the energy function at the saddle point (compare Kramers' method above: there the saddle point is a one-dimensional maximum). Equation (1.13.5.10) constitutes the paraboloidal approximation to the potential in the vicinity of the saddle point. For example, in magnetic relaxation in a uniform field with uniaxial anisotropy, the energy surface in the vicinity of the saddle point will be a hyperbolic paraboloid [78]. Equation (1.13.5.9) is the multi-dimensional Fokker–Planck equation linearized in the region of the saddle point.

(2) Owing to the high barrier, just as in the Kramers high-damping problem, a Maxwell–Boltzmann distribution is set up in the vicinity of the bottom of the well, i.e., at A, so:

$$\rho(\{\boldsymbol{\eta}\}) \approx \rho_{\text{eq}}(\{\boldsymbol{\eta}\}), \quad \{\boldsymbol{\eta}\} \approx \{\boldsymbol{\eta}^A\}. \qquad (1.13.5.11)$$

(3) Practically speaking, no particles have arrived at the far side of the saddle point, so we have the sink boundary condition

$$\rho(\{\boldsymbol{\eta}\}) = 0, \quad \{\boldsymbol{\eta}\} \text{ beyond } \{\boldsymbol{\eta}^C\}. \qquad (1.13.5.12)$$

This is Kramers' condition that only rare particles of the assembly ever cross the barrier. Just as in the Klein–Kramers problem for one degree of freedom, we make the substitution

$$\rho(\{\boldsymbol{\eta}\}) = g(\{\boldsymbol{\eta}\}) \rho_{\text{eq}}(\{\boldsymbol{\eta}\}). \qquad (1.13.5.13)$$

(Again, the function g is known as the crossover function). Thus, we obtain from Eqs. (1.13.5.7) and (1.13.5.9), as before, an equation for g, namely

$$\sum_{i,n} M_{ni}\left[-\sum_{k} e_{nk}\left(\eta_k-\eta_k^C\right)-kT\frac{\partial}{\partial\eta_n}\right]\frac{\partial}{\partial\eta_i}g(\{\boldsymbol{\eta}\})=0, \qquad (1.13.5.14)$$

where $\{\boldsymbol{\eta}\}\approx\{\boldsymbol{\eta}^C\}$. We postulate (see Section 1.13.1) that g may be written in terms of a single variable u, viz.,

$$g(u)=\frac{1}{2\pi kT}\int_u^\infty e^{-\frac{z^2}{2kT}}dz, \qquad (1.13.5.15)$$

and we assume that u has the form of the linear combination

$$u=\sum_i U_i(\eta_i-\eta_i^C). \qquad (1.13.5.16)$$

This is Kramers' method of forcing the multi-dimensional Fokker–Planck equation into an equation in a single variable u (in his original case, a linear combination of the two variables, position and velocity, so that $u=p-ax'$). We must now determine the coefficients U_i of the linear combination u of the η_i. This is accomplished as follows. We define the matrix $\tilde{\mathbf{M}}=-\mathbf{M}^{\mathrm{T}}$. Then we shall have the coefficients U_i of the linear combination as a solution of the *eigenvalue problem*

$$-\sum_{i,n} U_i\tilde{M}_{in}e_{nk}=\lambda_+U_k. \qquad (1.13.5.17)$$

The eigenvalue λ_+ is the *deterministic growth rate of a small deviation from the saddle point*, and is the positive eigenvalue of the system matrix of the noiseless Langevin equations, linearized about the saddle point. It characterizes the unstable barrier-crossing mode. Thus, in order to calculate λ_+, all that is required is a knowledge of the energy landscape; Eq. (1.13.5.17) need not, in practice, be involved. Equation (1.13.5.17) is obtained essentially by substituting the linear combination u, i.e., Eq. (1.13.5.16), into Eq. (1.13.5.14) for the crossover function, and requiring the resulting equation to be a proper ordinary differential equation in the single variable u with solution given by Eq. (1.13.5.15) (the details of this are given in [44]). Equation (1.13.5.17) may also be written in the matrix form

$$-\mathbf{U}^{\mathrm{T}}\tilde{\mathbf{M}}\mathbf{E}^C=\lambda_+\mathbf{U}^{\mathrm{T}}. \qquad (1.13.5.18)$$

(Hänggi *et al.* [50] describe this equation by stating that $\mathbf{U}^{\mathrm{T}}$ is a "left eigenvector" of the matrix $-\tilde{\mathbf{M}}\mathbf{E}^C$. The usual eigenvalue equation of an arbitrary matrix $\mathbf{A}$ is $\mathbf{AX}=\lambda\mathbf{X}$. In the above terminology, $\mathbf{X}$ would be a "right eigenvector" of $\mathbf{A}$). In Eq. (1.13.5.18), $\mathbf{E}^C\equiv(e_{ij})$ is the matrix of the second derivatives of the potential evaluated at the saddle point, which is used in

the Taylor expansion of the energy near the saddle point. The determinant of this (Hessian) matrix is the Hessian itself. The normalization of U_i is fixed, so that

$$\lambda_+ = \sum_{i,n} U_i M_{in} U_n, \tag{1.13.5.19}$$

which is equivalent to

$$\sum_{i,n} U_i e_{in}^{-1} U_n = -1. \tag{1.13.5.20}$$

This condition ensures that the crossover function, Eq. (1.13.5.15), retains the form of an error function and so may describe diffusion over a barrier. Alternatively, one may say that the foregoing conditions require that the entry in the diffusion matrix in the direction of flow (that is, the unstable direction) is nonzero; that is, *we have current over the barrier and so particles escape the well.*

Now the Fokker–Planck equation, Eq. (1.13.5.1), is a continuity equation for the representative points, just as described earlier, so that

$$\dot{\rho} + \nabla \cdot \mathbf{J} = 0. \tag{1.13.5.21}$$

Thus by inspection, we find that the current density becomes

$$j_i = -\sum_n M_{in} \left(\frac{\partial E}{\partial \eta_n} + kT \frac{\partial}{\partial \eta_n} \right) \rho \tag{1.13.5.22}$$

and we obtain, using Eqs. (1.13.5.7), (1.13.5.14), and (1.13.5.15) for the *stationary* current density, i.e., $\dot{\rho} = 0$,

$$j_i(\{\eta\}) = \frac{1}{\sqrt{2\pi}} \sum_n M_{in} U_n \rho_{\text{eq}}(\{\boldsymbol{\eta}\}) e^{-\frac{u^2}{2kT}}. \tag{1.13.5.23}$$

We now take advantage of the condition stated above, namely that the flux over the barrier emanates from a small region around the saddle point C. We integrate the current density over a plane containing the saddle point but not parallel to the flow of particles. The plane $u = 0$ will suffice here. Thus the total current is

$$J = \sum_i \int_{u=0} j_i(\{\boldsymbol{\eta}\}) dS_i. \tag{1.13.5.24}$$

Using Eq. (1.13.5.24) with the quadratic approximation of Eq. (1.13.5.10) for the energy near the saddle point, the integration for the total flux (current) now yields, after a long calculation [44],

$$J \approx \frac{1}{2\pi Z} \sum_{i,j} U_i M_{ij} U_j \left| \sum_{i,j} U_i e_{ij}^{-1} U_j \det\left(\frac{1}{2\pi kT} \mathbf{E}^C \right) \right|^{-1/2} e^{-\frac{E_C}{kT}}. \tag{1.13.5.25}$$

From Eqs. (1.13.5.19) and (1.13.5.20), we immediately obtain

$$J = \frac{\lambda_+}{2\pi Z}\left|\det\left((2\pi kT)^{-1}\mathbf{E}^C\right)\right|^{-1/2} e^{-\frac{E_C}{kT}}. \tag{1.13.5.26}$$

Now, we assume that the energy function near the bottom of the well A may again be written in the quadratic approximation

$$E = E_A + \frac{1}{2}\sum_{i,j} a_{ij}\left(\eta_i - \eta_i^A\right)\left(\eta_j - \eta_j^A\right), \tag{1.13.5.27}$$

and we write $\mathbf{E}^A = \left(a_{ij}\right)$ so that the number of particles in the well is [44]

$$n_A = \left\{\det[(2\pi kT)^{-1}\mathbf{E}^A]\right\}^{-1/2} Z^{-1}. \tag{1.13.5.28}$$

Now the escape rate Γ, by the usual flux-over-population method, is defined to be $\Gamma = J/n_A$, and so from Eqs. (1.13.5.26) and (1.13.5.28), in terms of the unique positive eigenvalue λ_+ of the set of *noiseless* Langevin equations linearized about the saddle point, we have

$$\Gamma = \frac{\lambda_+}{2\pi}\sqrt{\frac{\det\{\mathbf{E}^A\}}{\left|\det\{\mathbf{E}^C\}\right|}}\, e^{-\frac{E_C - E_A}{kT}}, \tag{1.13.5.29}$$

which is Langer's [73] expression in terms of the Hessians of the saddle and well energies for the escape rate for a multi-dimensional process in the IHD limit. The result again pertains to this limit because of our postulate that the potential in the vicinity of the saddle point may be approximated by the first two terms of its Taylor series. Thus, Eq. (1.13.5.29) fails for very small damping corresponding to *energy controlled diffusion*, because the region of deviation from the Maxwell–Boltzmann distribution prevailing in the depths of the well extends far beyond the narrow region at the top of the barrier in which the potential may be replaced by its quadratic approximation. In passing, we remark that rate theory at weak friction is generally known as "unimolecular rate theory" [50], the Kramers VLD limit treated earlier being an example of this. For a general discussion see Ref. [50].

1.13.6. *Kramers' formula as a special case of Langer's formula*

As an example of Langer's method, we shall use it to derive the IHD result of Kramers. To recover the Kramers formula, Eq. (1.13.4), by Langer's method, we take $N = 1$; thus the state variables are the position and momentum, so that

$$\eta_1 = x, \quad \eta_2 = p. \tag{1.13.6.1}$$

The noiseless Langevin equations are

$$\dot{x} = \frac{p}{m}, \quad \dot{p} = -\beta p - \frac{dV}{dx}. \tag{1.13.6.2}$$

Here V denotes the potential energy and β is the friction coefficient. Because

$$\frac{\partial E}{\partial p} = \frac{p}{m}, \qquad \frac{\partial E}{\partial x} = \frac{dV}{dx},$$

where $E = p^2/(2m) + V(x)$, Eqs. (1.13.6.2) can be rewritten as

$$\dot{\eta}_1 = \frac{\partial E}{\partial \eta_2}, \quad \dot{\eta}_2 = -m\beta \frac{\partial E}{\partial \eta_2} - \frac{\partial E}{\partial \eta_1}. \tag{1.13.6.3}$$

Hence, we have the equation of motion in terms of the state variables (η_1, η_2) of the general case of Langer's method above, as

$$\begin{pmatrix} \dot{\eta}_1 \\ \dot{\eta}_2 \end{pmatrix} = -\begin{pmatrix} 0 & -1 \\ 1 & m\beta \end{pmatrix} \begin{pmatrix} \partial E/\partial \eta_1 \\ \partial E/\partial \eta_2 \end{pmatrix}, \tag{1.13.6.4}$$

where the transport matrix $\mathbf{M}$ is

$$\mathbf{M} = \left(M_{ij}\right) = \begin{pmatrix} 0 & -1 \\ 1 & m\beta \end{pmatrix}. \tag{1.13.6.5}$$

Here we can take the saddle point C as the origin, so $\eta_1^C = 0$ and $E_C = 0$. The momentum of a particle just escaping is zero also, so $\eta_2^C = 0$. Equation (1.13.5.10) then yields the energy in the vicinity of the saddle point

$$E = -\frac{m}{2}\omega_C^2 \eta_1^2 + \frac{1}{2m}\eta_2^2. \tag{1.13.6.6}$$

We now determine λ_+. From Eqs. (1.13.6.4) and (1.13.6.6), we have the linearized noiseless Langevin equation:

$$\begin{pmatrix} \dot{\eta}_1 \\ \dot{\eta}_2 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & -m\beta \end{pmatrix} \begin{pmatrix} \partial E/\partial \eta_1 \\ \partial E/\partial \eta_2 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & -m\beta \end{pmatrix} \begin{pmatrix} -m\omega_C^2 \eta_1 \\ \eta_2/m \end{pmatrix}$$
$$= \begin{pmatrix} 0 & 1/m \\ m\omega_C^2 & -\beta \end{pmatrix} \begin{pmatrix} \eta_1 \\ \eta_2 \end{pmatrix}$$

or

$$\dot{\boldsymbol{\eta}} = \mathbf{A}\boldsymbol{\eta}, \quad \mathbf{A} = \begin{pmatrix} 0 & 1/m \\ m\omega_C^2 & -\beta \end{pmatrix} \tag{1.13.6.7}$$

with secular equation

$$\det(\mathbf{A} - \lambda \mathbf{I}) = 0. \tag{1.13.6.8}$$

We thus solve the secular equation, namely

$$\lambda(\lambda+\beta)-\omega_C^2=0,$$

to find

$$\lambda_{\pm}=\pm\sqrt{\omega_C^2+\frac{\beta^2}{4}}-\frac{\beta}{2}. \tag{1.13.6.9}$$

We pick the upper sign so that the solution (which is now always positive) corresponds to the *unstable barrier-crossing mode*, hence

$$\lambda_{+}=\sqrt{\omega_C^2+\frac{\beta^2}{4}}-\frac{\beta}{2}. \tag{1.13.6.10}$$

Now the Hessian matrices of the saddle and well energies are given by

$$\mathbf{E}^C=\begin{pmatrix} m\omega_C^2 & 0 \\ 0 & -1/m \end{pmatrix} \text{ and } \mathbf{E}^A=\begin{pmatrix} m\omega_A^2 & 0 \\ 0 & 1/m \end{pmatrix}.$$

Thus, the Hessians are given by

$$\det\{\mathbf{E}^C\}=-\omega_C^2 \text{ and } \det\{\mathbf{E}^A\}=\omega_A^2,$$

and so

$$\sqrt{\frac{\det\{\mathbf{E}^A\}}{\left|\det\{\mathbf{E}^C\}\right|}}=\frac{\omega_A}{\omega_C}.$$

The escape rate is given by Eq. (1.13.5.29), which now becomes

$$\Gamma=\frac{\lambda_{+}\omega_A}{2\pi\omega_C}e^{-\frac{\Delta V}{kT}}=\frac{\omega_A}{2\pi}\left(\sqrt{1+\frac{\beta^2}{4\omega_C^2}}-\frac{\beta}{2\omega_C}\right)e^{-\frac{\Delta V}{kT}}. \tag{1.13.6.11}$$

Equation (1.13.6.11) is Kramers' IHD equation, Eq. (1.13.4). We will return to Langer's method when we discuss magnetic relaxation in Section 1.18.2. The various applications of the theory of Brownian motion in a potential, and of the Kramers theory, are summarized in Section 1.14.

1.13.7. *Kramers' turnover problem*

We have briefly mentioned that the VLD equation, Eq. (1.13.6), is of particular significance in that it clearly demonstrates that escape is impossible in the absence of coupling to the bath. Similarly, if the coupling to the bath is very large, the escape rate becomes zero. In his original paper, Kramers made several estimates of the range of validity of both IHD and VLD formulas and the region in which the TST theory, embodied in Eq. (1.13.2), holds with a high degree of

accuracy. He was, however, unable to give a formula in the Kramers turnover region between IHD and VLD, as there $\beta S(E_C) \approx kT$ so that no small perturbation parameter now exists. Here the coupling between the Liouville and dissipative terms in the Klein–Kramers equation enters, so that one may no longer ignore the Liouville term as was done in the very-low-damping regime. This problem, named the Kramers turnover, was solved nearly 50 years later by Mel'nikov and Meshkov [66, 67]. They constructed an integral equation for the evolution of the energy distribution function in the vicinity of the separatrix, which they solved using the Wiener–Hopf method [66, 70] and so obtained a simple integral formula for the escape rate Γ bridging the VLD and IHD solutions. Now both the IHD and VLD rates, already derived using two completely different approaches, are invalid in the Kramers turnover region, and in almost the entire under-damped regime $\Delta E = \delta = \beta S(E_C) \leq kT$ between ID (TST) and VLD. The nomenclature *turnover* or *crossover* follows because, in IHD, the prefactor of the escape rate is inversely proportional to the damping β, while in VLD, where the coupling between the dissipative and conservative terms in the Fokker–Planck equation is ignored, it is directly proportional to it (see Fig. 1.13.2). Thus it is intuitively clear that the under-damped case requires its own mathematical technique accounting for the coupling between these terms [66, 67]. This was initiated by Iche and Nozières [79] who showed that the Klein–Kramers equation can then be reduced to an integral equation. However, independently of them, Mel'nikov [66] (whose notation we shall follow as far as possible) also proposed the reduction of that equation to an integral equation in the energy variable, with a Gaussian kernel with sole parameter $\Delta = \delta / kT$. Thus [67], just as in VLD, the under-damped Brownian particle moves in a potential well in an almost deterministic way, being only slightly perturbed by the stochastic forces. The total energy of the particle is again the most slowly varying quantity, and we require only the unperturbed trajectory corresponding to the absolute minimum energy needed to escape the well. We then consider *small perturbations of this undamped trajectory* due to thermal fluctuations and friction.

The solution of the Kramers problem was then described in detail [66, 67] both for single- and double-well potentials (see Hänggi *et al.* [50] and Coffey *et al.* [44] for reviews). For a single isolated well, the escape rate Γ is given by

$$\Gamma \sim \Lambda \Gamma^{\mathrm{TST}}, \tag{1.13.7.1}$$

where the prefactor Λ is now given by

$$\Lambda = [\sqrt{1 + \beta^2 / (4\omega_C^2)} - \beta / (2\omega_C)] A(\Delta), \tag{1.13.7.2}$$

$\Delta = \beta S(E_C)/kT$ is the ratio of the energy loss per cycle to the thermal energy of a librating particle with energy equal to the barrier energy, and $A(\Delta)$ is a depopulation factor interpolating between the VLD and ID damping regimes defined by Eq. (1.13.8). Thus the coupling to the heat bath is absorbed into the two factors in Λ, while Γ^{TST} pertains to equilibrium properties of the system and does not require knowledge of the dynamics. Here the depopulation factor $A(\Delta)$ effectively allows for the coupling between the Liouville and dissipative terms, which is ignored in the VLD limit. In the VLD limit, $\Delta << 1$, $A(\Delta) \to \Delta$ and so we regain the VLD escape rate while in the IHD limit $A(\Delta) \to 1$; thus we ultimately regain the VHD escape rate using Eq. (1.13.7.1). For a double-well potential with two non-equivalent wells, the escape rate Γ is given by [67]

$$\Gamma = \left(\sqrt{1 + \frac{\beta^2}{4\omega_C^2}} - \frac{\beta}{2\omega_C} \right) \frac{A(\Delta_1)A(\Delta_2)}{A(\Delta_1 + \Delta_2)} \left(\Gamma_1^{TST} + \Gamma_2^{TST} \right), \qquad (1.13.7.3)$$

where Δ_i is the ratio of the energy loss per cycle to the thermal energy of a librating particle having the barrier energy of well i, and Γ_i^{TST} are the respective TST escape rates.

Equations (1.13.7.1) and (1.13.7.3) represent a complete solution of the Kramers turnover problem for a single and a double well, respectively. Everywhere they rely on the facts: (i) that one may rewrite the under-damped Klein–Kramers equation as a diffusion equation with the energy and action as independent variables, and (ii) that the Green function is Gaussian. The energy distribution function for particles at various positions in a potential well can then be found in integral form by superposition. When complemented by boundary conditions, these integral relations can be converted into an integral equation for the energy distribution function for (potentially) escaping particles librating in a well at the barrier energy. The resulting one-sided convolution equation with a Gaussian kernel is solved by the Wiener–Hopf method [56, 70], which leads to an explicit expression for the escape rate in the under-damped case. Moreover, the precise shape of the potential well only enters the result via Δ, which also governs the average energy of the escaping particles. It is then postulated that Eq. (1.13.7.1), which is valid for all damping regimes, can be written down by simply taking the product of the depopulation factor and the Kramers IHD result. We remark that, subsequently, Grabert [68] and Pollak *et al.* [69] have presented a more rigorous solution of the Kramers turnover problem, showing that Eq. (1.13.7.1) can be obtained without the *ad hoc* interpolation between the VLD and ID regimes postulated by Mel'nikov and Meshkov [67].

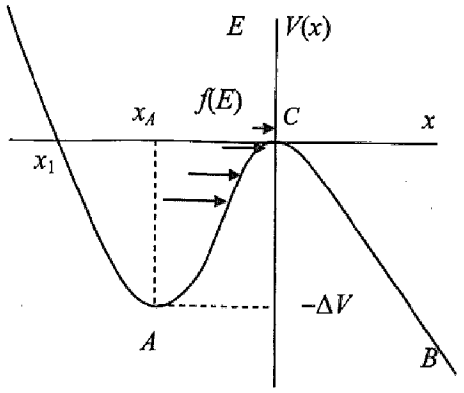


Figure 1.13.7.1 Escape from a single well.

Here we shall indicate briefly how Eq. (1.13.7.1) may be derived and we shall demonstrate how the VLD result follows naturally from it. Thus we shall first describe how the quasi-stationary Klein–Kramers equation, Eq. (1.5.9.6), i.e., with $\dot{\rho} = 0$, may for weak damping be transformed into an energy/action diffusion equation.

We again consider the simplest example of the metastable state, i.e., when Brownian particles, having escaped over the barrier, never return. The corresponding single-well potential $V(x)$ is shown in Fig. 1.13.7.1. We choose the zero of the potential to be the barrier top (so that E_C corresponds to $E = 0$), and as before the depth of the well is $\Delta V >> kT$, while the boundary condition $\lim_{x\to\infty} \rho(p, x, t) = 0$ states that, initially, no particles exist at the far side of the barrier (cf. Fig. 1.13.7.1). Furthermore, the current of particles

$$J = m^{-1} \int_0^\infty p\rho(x, p, t)dp \tag{1.13.7.4}$$

calculated *near* the barrier top does not depend on x, provided that $|V(x)| << \Delta V$. As before, the conservation of the total number of particles of the ensemble (continuity equation) $\dot{N} = -J$ yields the connection between the lifetime $\tau = \Gamma^{-1}$ of a particle in the well and the current. Normalizing the distribution ρ to one particle in the well, we have

$$\Gamma = J, \tag{1.13.7.5}$$

which we shall use to calculate Γ. In accordance with Kramers, we shall assume that the flux over the barrier is due only to those particles having energy E in the *neighborhood* of the barrier top (the separatrix region) with $|E| \leq kT$. Moreover $\Delta V >> kT$, and the friction-induced energy loss per cycle $\delta \leq kT$. Hence, just as in VLD, the total energy $E = p^2/(2m) + V(x)$ of a particle moving in the well is the most slowly varying quantity, so we use that as a new variable in the Klein–Kramers equation, instead of the momentum, while retaining the

(relatively fast) position x which will later be subsumed in an action variable. Here the relevant quantity is the quasi-stationary energy distribution function $f(E)$ of particles with a possibility of escaping, because the decay rate $\Gamma = \tau^{-1}$ by the flux-over-population method is

$$\Gamma = J = \int_0^\infty f(E)dE. \tag{1.13.7.6}$$

Equation (1.13.7.6) follows from Eqs. (1.13.7.5) and (1.13.7.4) for the number of particles crossing the barrier in unit time, the fact that $dE = pdp/m$, and that in order for a particle to escape its momentum must be positive. Mel'nikov's method [66] of calculation of $f(E)$ and $\Gamma = \tau^{-1}$ is as follows.

Green function of the energy/action diffusion equation

Mel'nikov's procedure [66] for the evaluation of $f(E)$, unlike that used by Kramers in the VLD limit, requires one to treat right- and left-going particles with respect to the barrier, denoted by the suffixes R, L separately. First, we note that the quasi-stationary equation

$$\frac{dV}{dx}\frac{\partial \rho}{\partial p} - \frac{p}{m}\frac{\partial \rho}{\partial x} + \beta \frac{\partial}{\partial p}\left(\rho p + mkT\frac{\partial \rho}{\partial p}\right) = 0 \tag{1.13.7.7}$$

may be represented in terms of position–energy coordinates $\{x, E\}$ using the transformations

$$\frac{\partial}{\partial p} f_{\mathrm{R,L}}(x,p) = \pm\sqrt{2[E - V(x)]/m}\,\frac{\partial}{\partial E} f_{\mathrm{R,L}}(x,E), \tag{1.13.7.8}$$

$$\frac{\partial}{\partial x} f_{\mathrm{R,L}}(x,p) = \frac{\partial}{\partial x} f_{\mathrm{R,L}}(x,E) + \frac{dV}{dx}\frac{\partial}{\partial E} f_{\mathrm{R,L}}(x,E), \tag{1.13.7.9}$$

where we define the distribution functions for the right- and left-going particles as

$$f_{\mathrm{R}} = \rho\left(x, \sqrt{2m[E - V(x)]}\right),$$

$$f_{\mathrm{L}} = \rho\left(x, -\sqrt{2m[E - V(x)]}\right).$$

Furthermore, we can set $E = 0$ in the relationship

$$p(x,E) = \pm\sqrt{2m[E - V(x)]} \approx p(x,0) = \pm\sqrt{-2mV(x)} \tag{1.13.7.10}$$

because we have chosen the separatrix trajectory to coincide with $E = 0$ (see Fig. 1.13.7.1) and we suppose that the leading contributions to the escape stem

only from particles in a *narrow* range of energy of order kT. Consider now the dissipative term in Eq. (1.13.7.7), namely

$$\beta\frac{\partial}{\partial p}\left(\rho p+mkT\frac{\partial\rho}{\partial p}\right)\approx\frac{\beta p^2(x,0)}{m}\frac{\partial}{\partial E}\left[\rho+kT\frac{\partial\rho}{\partial E}\right], \quad (1.13.7.11)$$

where we have used Eq. (1.13.7.10). Thus the quasi-stationary equation, Eq. (1.13.7.7), becomes

$$\frac{p}{m}\frac{\partial\rho}{\partial x}-\frac{dV}{dx}\frac{\partial\rho}{\partial p}=\frac{\beta}{m}p^2(x,0)\frac{\partial}{\partial E}\left(\rho+kT\frac{\partial\rho}{\partial E}\right) \quad (1.13.7.12)$$

or, in terms of $f_{\mathrm{R,L}}(x,E)$,

$$\frac{\partial f_{\mathrm{R,L}}}{\partial x}=\pm\beta\sqrt{-2mV(x)}\frac{\partial}{\partial E}\left(f_{\mathrm{R,L}}+kT\frac{\partial f_{\mathrm{R,L}}}{\partial E}\right). \quad (1.13.7.13)$$

Now we define the action $S(E)$ pertaining to librational motion in the well via

$$\frac{dS}{dx}=\pm\sqrt{2m\left[E-V(x)\right]}\approx\pm\sqrt{-2mV(x)}, \quad (1.13.7.14)$$

recalling that inside the well $V(x)$ is negative. Hence Eq. (1.13.7.12) can be compactly represented as the energy/action diffusion equation

$$\frac{\partial f_{\mathrm{R,L}}}{\partial S}=\beta\frac{\partial}{\partial E}\left(f_{\mathrm{R,L}}+kT\frac{\partial f_{\mathrm{R,L}}}{\partial E}\right), \quad (1.13.7.15)$$

describing diffusion and uniform drift in energy space in the separatrix region and so governing the noisy motion there.

The solution of Eq. (1.13.7.15) can be reduced to an integral equation using the principle of superposition, by first determining the Green function $g(E,S|E',S')=g(E-E',S-S')$ (the transition probability in energy space). The Green function g is the solution of the equation

$$\frac{\partial g}{\partial S}=\beta\frac{\partial}{\partial E}\left(g+kT\frac{\partial g}{\partial E}\right) \quad (1.13.7.16)$$

subject to the initial condition $g(E,0|E',0)=\delta(E-E')$; here we have dropped the subscripts R, L, writing $f_{\mathrm{R,L}}=g$. Defining the characteristic function $\tilde{g}(\lambda,S)$ of the change in energy per cycle $E-E'$ in a narrow range kT near the top of the barrier via

$$\tilde{g}(\lambda,S)=\int_{-\infty}^{\infty}g(E-E',S)e^{i\lambda(E-E')/(kT)}d(E-E'), \quad (1.13.7.17)$$

we have, as in Section 1.12,

$$\tilde{g}(\lambda, S) = e^{-(i\lambda\beta S + \lambda^2 \beta S)/(kT)} \tag{1.13.7.18}$$

which directly follows from the delta function initial condition. Furthermore,

$$\tilde{g}(\lambda, S) = e^{-\beta S\lambda(\lambda+i)/(kT)} \tag{1.13.7.19}$$

so that at $\lambda - i/2$, $\tilde{g}$ is real, viz.,

$$\tilde{g}\left(\lambda - i/2, S\right) = e^{-\beta S(\lambda^2 + 1/4)/(kT)}. \tag{1.13.7.20}$$

Clearly, Eq. (1.13.7.18) is the characteristic function of a Gaussian random variable with variance $\langle (E-E')^2 \rangle - \langle E-E' \rangle^2 = 2\beta kTS$ and mean $\langle E-E' \rangle = -\beta S$. Thus, the Green function g is

$$g(E-E', S) = \frac{1}{\sqrt{4\pi\beta kTS}} e^{-\frac{(E-E'+\beta S)^2}{4\beta kTS}}. \tag{1.13.7.21}$$

By superposition, the solution of Eq. (1.13.7.16) for an arbitrary initial distribution of energy $f(E', 0)$ is then given by the convolution integral

$$f(E, S) = \int_{-\infty}^{\infty} f(E', 0) g(E-E', S) dE'. \tag{1.13.7.22}$$

Integral equation for the distribution function $f(E)$

In order to derive a closed integral equation for the distribution function, we need additional information concerning $V(x)$ outside the barrier. Here, the particles, having surmounted the barrier, never return to the well. By hypothesis, in terms of the functions $f_{R,L}(E, x)$, we have outside the well (i.e., for $E > 0$ since $E = 0$ defines the boundary of the well),

$$f_L(E, 0) = 0. \tag{1.13.7.23}$$

Conversely, close to the barrier the flux of left-going particles is simply due to right-going particles with $E < 0$ reflected from the barrier, so that inside the well (i.e., for $E < 0$),

$$f_L[E, x(E)] = f_R[E, x(E)]. \tag{1.13.7.24}$$

Here $x(E)$ is the root of the equation $V(x) = E$, $x_1 < x < 0$ corresponding, of course, to the right-hand turning point at a given energy E. Equations (1.13.7.23) and (1.13.7.24) constitute boundary conditions because (a) they relate f_L to f_R for $E < 0$, (b) no left-going particles exist right at the barrier top. Clearly, particles with different values of E are reflected at different values of $x(E)$.

However, for $E \approx kT$ (the order of magnitude of a fluctuation), *the variation in the values of $x(E)$ is small in size compared to the overall extent of the well.* One may therefore assume that all such particles propagate along (boundary layer) trajectories very close to the separatrix $E = E_C = 0$. Thus they can be described by the Green function, Eq. (1.13.7.21), with $S = S(0)$ denoting the action of a particle librating in the well with energy equal to the barrier energy, viz.,

$$S(0) \approx \int_{E_C} \sqrt{-2mV(x)}dx = 2\int_{x_1}^{0} \sqrt{-2mV(x)}dx, \qquad (1.13.7.25)$$

where E_C now indicates that the line integral is to be taken along the separatrix (which of course constitutes [71] an *open* trajectory rather than the closed trajectories of the librational motion in the well). The action $S(0)$ is the basic parameter of the problem, and has already appeared in our discussion of the VLD result. The justification that $S(0)$ may be used can be given as follows. If $|E| << \Delta V$ (details in [44]), we have

$$S(0) - S(E) = |E/\omega_C| \ln|\Delta V / E|,$$

where ω_C is the barrier frequency. This expression tends to zero in the limit of small E.

We now return to the boundary conditions, Eqs. (1.13.7.23) and (1.13.7.24), and introduce, following Mel'nikov [66], the new function

$$f(E) = f_R(E, 0), \quad E > 0, \quad f(E) = f_R[E, x(E)], \quad E < 0 \qquad (1.13.7.26)$$

with $x(E)$ defined by the separatrix $E = E_C = 0$. Clearly, $f(E)$ governs the escape rate for $E > 0$ and the rate of reflection at the barrier for $E < 0$. Now the reflected particles constitute a distribution of left-going particles f_L. They flow to the left-hand boundary of the well and are then reflected; thus f_L becomes f_R. They then flow across the well once more and reproduce the distribution $f(E)$. This is the condition that must accompany the integral Eq. (1.13.7.22) in order that it should become a *closed* integral equation for $f(E)$. Clearly, the evolution of the energy distribution function in the *vicinity of the separatrix* is governed by the Green function

$$g(E - E', S) = (4\pi kT\delta)^{-1/2} e^{-(E-E'+\delta)^2/(4kT\delta)}, \qquad (1.13.7.27)$$

where $\delta = \beta S(0)$ is the mean energy loss in one cycle (i.e., per oscillation) of the librational motion in the well with energy equal to the barrier energy. We can now write down our fundamental integral equation for the energy distribution function $f(E)$ of particles with a possibility of escaping, in the form of the Wiener–Hopf equation [70]

$$f(E) = \int_{-\infty}^{0} g(E-E')f(E')dE', \tag{1.13.7.28}$$

where $g(E-E') = g(E-E', S)$. Note that, because the exponential factor in $g(E-E')$ decays so quickly, we suffer no great error in replacing the lower limit, which should be $E-\Delta V$ by $-\infty$. This is important: otherwise the problem could not be posed as a Wiener–Hopf equation. Furthermore, we have the boundary condition that, deep in the well the distribution, $f(E)$ must be the Maxwell–Boltzmann distribution, i.e.,

$$f(E) = f_0(E) = \frac{\omega_A}{2\pi kT} e^{-\frac{E+\Delta V}{kT}} \tag{1.13.7.29}$$

(here we have noted that $E \approx -\Delta V + \omega_A^2 (x-x_A)^2/2$ near the bottom of the well $(x \approx x_A)$. Solving Eq. (1.13.7.28) for $f(E)$ yields, from Eq. (1.13.7.6), the escape rate Γ, effectively reducing to the calculation of the depopulation factor $A[\delta/(kT)]$ expressing the fact that the density at the barrier is no longer zero.

In order to evaluate $A[\delta/(kT)]$, we consider the Fourier transforms $\varphi^+(\lambda)$ and $\varphi^-(\lambda)$ defined (so that λ is dimensionless) as

$$\varphi^{\pm}(\lambda) = (2\pi/\omega_A) e^{\frac{\Delta V}{kT}} \int_{-\infty}^{\infty} U(\pm E) f(E) e^{\frac{i\lambda E}{kT}} dE, \tag{1.13.7.30}$$

where $U(x)$ is Heaviside's theta or step function. The functions $\varphi^+(\lambda)$ and $\varphi^-(\lambda)$, which are the Fourier transforms of $f(E)$ for $E>0$ and $E<0$, are analytic in the upper and lower complex half-planes of λ, with the only exception being the pole of $\varphi^-(\lambda)$ at $\lambda = -i$. Using the boundary condition of a Maxwell–Boltzmann distribution deep in the well, i.e., Eq. (1.13.7.29), one may approximate $\varphi^-(\lambda)$ for $|\lambda+i| << 1$ as

$$\varphi^-(\lambda) \approx -i/(\lambda+i). \tag{1.13.7.31}$$

Clearly,

$$\varphi^+(0) = \frac{2\pi}{\omega_A} e^{\frac{\Delta V}{kT}} \int_0^{\infty} f(E)dE = \frac{2\pi}{\omega_A} \Gamma e^{\frac{\Delta V}{kT}} \tag{1.13.7.32}$$

while, by definition from Eq. (1.13.7.6), in the under-damped region where the prefactor $\Lambda \approx A$, the escape rate Γ is given by

$$\Gamma \approx A\omega_A e^{-\frac{\Delta V}{kT}}/(2\pi). \tag{1.13.7.33}$$

On comparing Eqs. (1.13.7.32) and (1.13.7.33), the prefactor A is

$$A = \varphi^+(0), \tag{1.13.7.34}$$

which shows how the depopulation factor may be determined from the characteristic function of the energy distribution in the upper half-plane.

Now, with Eqs. (1.13.7.28) and (1.13.7.30), writing the Green function explicitly and using the properties of Gaussian integrals, we have

$$\varphi^-(\lambda)+\varphi^+(\lambda)=\frac{2\pi}{\omega_A}e^{\frac{\Delta V}{kT}}\int_{-\infty}^{0}\int_{-\infty}^{\infty}\frac{f(E')}{\sqrt{4kT\beta s}}e^{-\frac{(E-E'+\beta s)^2}{4kT\beta s}}e^{\frac{i\lambda E}{kT}}dEdE'$$

$$=\frac{2\pi}{\omega_A}e^{\frac{\Delta V}{kT}}e^{-\frac{\lambda(\lambda+i)\beta s}{kT}}\int_{-\infty}^{0}f(E')e^{\frac{i\lambda E'}{kT}}dE'=\tilde{g}(\lambda)\varphi^-(\lambda), \qquad (1.13.7.35)$$

where $\tilde{g}(\lambda)$ is given by Eq. (1.13.7.19).

In order to illustrate [66] how the Wiener–Hopf method [70] may be used to determine $A=\varphi^+(0)$, we rewrite Eq. (1.13.7.35) as

$$\varphi^+(\lambda)+G(\lambda)\varphi^-(\lambda)=0, \qquad (1.13.7.36)$$

where $G(\lambda)=1-\tilde{g}(\lambda)$. The solution of Eq. (1.13.7.36) may now be determined in terms of $G(\lambda)$, as follows. From Eq. (1.13.7.36) we have

$$\ln[-\varphi^+(\lambda)]=\ln\varphi^-(\lambda)+\ln G(\lambda). \qquad (1.13.7.37)$$

Next, using Cauchy's integral formula, we define two functions $\ln G^+(\lambda)$ and $\ln G^-(\lambda)$ as

$$\ln G^{\pm}(\lambda)=\pm\frac{1}{2\pi i}\lim_{\varepsilon\to 0}\int_{-\infty}^{\infty}\frac{\ln G(\lambda')}{\lambda'-\lambda\mp i\varepsilon}d\lambda'. \qquad (1.13.7.38)$$

The functions $G^+(\lambda)$ and $G^-(\lambda)$ are entire functions which have no zeros in the corresponding half-planes $\mathrm{Im}\,\lambda>0$ and $\mathrm{Im}\,\lambda<0$. Both $G^+(\lambda)$ and $G^-(\lambda)$ $\to 1$ as $\lambda\to\infty$, and $G(\lambda)$ may be decomposed as

$$\ln G(\lambda)=\ln G^+(\lambda)+\ln G^-(\lambda) \qquad (1.13.7.39)$$

or $G(\lambda)=G^+(\lambda)G^-(\lambda)$, so Eq. (1.13.7.36) may be rewritten as

$$\ln[-\varphi^+(\lambda)/G^+(\lambda)]=\ln[\varphi^-(\lambda)G^-(\lambda)]. \qquad (1.13.7.40)$$

As the functions on both sides of Eq. (1.13.7.40) are analytic in the two *different* half-planes of λ, both sides must be equal to an *entire* function, which can be chosen to satisfy the boundary condition Eq. (1.13.7.31) and which may be taken in the form $\ln h(\lambda)$, so that

$$\varphi^+(\lambda)=-h(\lambda)G^+(\lambda) \text{ and } \varphi^-(\lambda)=h(\lambda)/G^-(\lambda). \qquad (1.13.7.41)$$

Now from Eq. (1.13.7.31), we have

$$h(\lambda)=-iG^-(-i)/(\lambda+i), \qquad (1.13.7.42)$$

yielding, with Eqs. (1.13.7.41), the solution of the Wiener–Hopf equation, Eq. (1.13.7.36), viz.,

$$\varphi^+(\lambda)=\frac{iG^+(\lambda)G^-(-i)}{\lambda+i} \text{ and } \varphi^-(\lambda)=-\frac{iG^-(-i)}{G^-(\lambda)(\lambda+i)}. \tag{1.13.7.43}$$

Thus the prefactor $A=\varphi^+(0)$ is given by

$$A=G^+(0)G^-(-i)=\left|G^+(0)\right|^2 \tag{1.13.7.44}$$

since

$$G^-(-i)=\left[G^+(0)\right]^*$$

(the asterisk denotes the complex conjugate). This can be verified by displacement of the contour of integration in Eq. (1.13.7.38) to the straight line $\operatorname{Im}\lambda=-i/2$. Thus, with the replacement $\lambda'\to\bar{\lambda}-i/2$ in Eq. (1.13.7.38), we have

$$\ln G^+(0)=\frac{1}{2\pi i}\int_{-\infty}^{\infty}\frac{\ln G\left(\bar{\lambda}-i/2\right)}{\bar{\lambda}-i/2}d\bar{\lambda}, \tag{1.13.7.45}$$

where the shifted function

$$G(\bar{\lambda}-i/2)=1-\tilde{g}(\bar{\lambda}-i/2)$$
$$=1-e^{-\Delta(\bar{\lambda}^2+1/4)}$$

is real; see Eq. (1.13.7.20). Using Eq. (1.13.7.45), we obtain the depopulation factor

$$A(\Delta)=\left|G^+(0)\right|^2=e^{\frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{\ln\{1-\exp[-\Delta(\lambda^2+1/4)]\}}{\lambda^2+1/4}d\lambda}. \tag{1.13.7.46}$$

One can show that for small Δ (details in [44]) $A(\Delta)\sim\Delta$ while for large Δ, $A(\Delta)\to 1$ so regaining the VLD and IHD results, respectively.

Kramers' VLD result

Before proceeding, it will be instructive to present one more method of regaining the VLD result, Eq. (1.13.6). In the VLD limit, the integral equation, Eq. (1.13.7.28), reduces to the differential equation [66]

$$\delta\,\partial_E(f+kT\partial_E f)=0,\quad \delta<<kT, \tag{1.13.7.47}$$

subject to the boundary condition $f(0)=0$. The reduction may be accomplished by noting that the derivative $\partial_E f$ satisfies the same integral equation, Eq.

(1.13.7.28), as $f(E)$ itself [80]. We now determine $f(E)$ from Eq. (1.13.7.47) and then use it to calculate the VLD escape rate. We have

$$f + kT\partial_E f = C', \tag{1.13.7.48}$$

where C' is a constant to be determined. Because, deep in the well, the distribution is given by the Maxwell–Boltzmann distribution (1.13.7.29), the complete solution of Eq. (1.13.7.48) is

$$f(E) = \frac{\omega_A}{2\pi kT} e^{-(E+\Delta V)/(kT)} + C'. \tag{1.13.7.49}$$

We now stipulate that the boundary condition at the top of the well is $f(0) = 0$. Thus $C' = -(\omega_A / 2\pi kT)\exp[-\Delta V / (kT)]$, yielding

$$f(E) = \frac{\omega_A}{2\pi kT}\left[e^{-E/(kT)} - 1\right] e^{-\Delta V/(kT)}. \tag{1.13.7.50}$$

The condition that the density of particles vanishes at the top of the barrier is tantamount (cf. [72]) to ignoring the time it takes to go from the critical or barrier energy trajectory to the separatrix. Put more succinctly, the 50/50 chance of the particle returning to the well is replaced, in VLD only, by zero chance of returning. Thus, in VLD *only*, all the particles are absorbed at the barrier. This condition of complete depopulation at the barrier is also used by Kramers when he explicitly imposes $(\rho e^{E/(kT)})_C \approx 0$. It must be justified rigorously, as shown by Mel'nikov [66] who, by calculating the average energy of the escaping particles, deduced that

$$f(0) \sim \omega_A \delta (kT)^{-2} e^{-\Delta V/(kT)}$$

which is negligible only in the VLD case. Now, in order to get the VLD escape rate from Eq. (1.13.7.47), we have to evaluate the current at the barrier J, which is defined as

$$f\delta + kT\delta\,\partial_E f = -J. \tag{1.13.7.51}$$

Now, at the barrier top, $E = 0$, $f(0) = 0$, so that $J = -kT\delta\,\partial_E f = \Gamma$, since we have normalized to one particle in the well. Thus, noting Eq. (1.13.7.50), we have the Kramers VLD result, Eq. (1.13.6), which is perhaps a more convincing derivation than that of Kramers.

1.14. Applications of the theory of Brownian movement in a potential

Amongst the physical phenomena to which the theory has been applied are:

(1) Current–voltage characteristics of the Josephson junction.

(2) Mobility of superionic conductors.
(3) Dielectric and Kerr-effect relaxation in nematic liquid crystals.
(4) Line widths in nuclear magnetic resonance.
(5) Incoherent scattering of slow neutrons.
(6) Cycle slips in second-order phase-locked loops.
(7) Quantum noise in ring-laser gyroscopes.
(8) Thermalization of neutrons in a heavy gas moderator.
(9) Photoelectromotive force in semiconductors.
(10) Rate coefficient in chemical reactions.
(11) Line shape of single-mode semiconductor lasers.
(12) Dynamics of a charged density wave condensate.
(13) Dynamic light scattering.
(14) Superparamagnetism (magnetization relaxation of nanoparticles).
(15) Magnetic relaxation in ferrofluids.
(16) Polymer dynamics.
(17) Fluorescence depolarization.
(18) Thermal noise in electrical circuits.
(19) Diffusion magnetic resonance imaging, etc.

The applications listed under headings 2, 4, 5, 8, 9, and 11–13 are summarized in the review article [5] and in Risken's book [21] in relation to the Fokker–Planck equation for Brownian motion in a periodic potential. Applications 1, 6 and 7 all rely on the same Langevin equations for Brownian motion in a tilted periodic potential, which is described in the context of the Josephson junction in Chapter 5 (see also [21]). Applications to laser spectroscopy are described in Refs. [21], [64], and [65]. The reader is also referred to Gardiner's *Quantum Optics* [81]. The various applications to radio engineering are described by Stratonovich [48] and Engberg and Larsen [82]. Fluorescence depolarization of molecules in solutions is discussed by Lakowicz [83]. The applications to polymer dynamics, dynamic light scattering, and nuclear magnetic relaxation in liquids are described by Doi and Edwards [84], Berne and Pecora [85], and McConnell [86], respectively. The application to chemical reactions is the escape-rate theory [21, 43, 50, 60, 61] (see also Section 1.13). The magnetization relaxation of single-domain ferromagnetic particles [87, 88] and the Kramers escape-rate theory are closely interlinked, so we shall summarize the application of the Kramers theory to superparamagnetism in Section 1.18. The application of the theory to dielectric and Kerr-effect relaxation in liquids and nematic liquid crystals is discussed in Chapters 3, 4, 7, 8, 10, and 11. One of the most interesting and useful applications of translational

Brownian motion is to phase diffusion in magnetic resonance imaging [89] which we summarize in more detail in Chapters 3 and 12. Yet another modern application is to stochastic resonance [90] which is illustrated in Section 1.21. For the details of the applications to incoherent scattering and the lifetime of the superconducting state in a Josephson junction, see Refs. [66], [91], and [92]).

The simplest example of rotational Brownian movement is the Debye theory of dielectric relaxation [10, 32, 59, 77], which we shall summarize before proceeding to our discussion of superparamagnetism.

1.15. Rotational Brownian motion: application to dielectric relaxation

The Debye theory of dielectric relaxation has, as its starting point, the Fokker–Planck equation for rotational Brownian motion in the space of a sphere, when the inertia of the sphere is neglected. A detailed derivation of this equation is given by Debye [32]. However, we shall give here a derivation of his equation based on the vector Euler–Langevin equation of Lewis *et al.* [93]. This method has the advantage that it can easily be extended to include the dipole–dipole interaction between the polar molecules as well as crystalline anisotropy, the latter of which is important in the application of the theory to nematic liquid crystals [62, 94] (see Chapters 7 and 8).

We study the rotational Brownian movement of a spherical body, which is presumed to be homogeneous, the motion being entirely due to random couples that have no preferential direction. The sphere contains a *rigid* electric dipole $\boldsymbol{\mu}$. Then the rate of change of $\boldsymbol{\mu}(t)$ is

$$\dot{\boldsymbol{\mu}}(t) = \boldsymbol{\omega}(t) \times \boldsymbol{\mu}(t), \tag{1.15.1}$$

where $\boldsymbol{\omega}(t)$ is the angular velocity of the body. We remark that Eq. (1.15.1) is a purely kinematic relation with no particular reference either to the Brownian movement or to the shape of the body. We make it specific to the Brownian rotation of a sphere by supposing that $\boldsymbol{\omega}(t)$ obeys the Euler–Langevin equation

$$I\dot{\boldsymbol{\omega}}(t) + \varsigma\boldsymbol{\omega}(t) = \boldsymbol{\mu}(t) \times \mathbf{E}(t) + \boldsymbol{\lambda}(t). \tag{1.15.2}$$

In Eq. (1.15.2), I is the moment of inertia of the sphere, $\varsigma\boldsymbol{\omega}$ is the damping torque due to Brownian movement, and $\boldsymbol{\lambda}(t)$ is the white noise driving torque, again due to Brownian movement so that $\boldsymbol{\lambda}(t)$ has the following properties:

$$\overline{\lambda_i(t)} = 0, \quad \overline{\lambda_i(t)\lambda_j(t')} = 2kT\varsigma\delta_{ij}\delta(t-t'), \tag{1.15.3}$$

where the indices $i, j = 1, 2, 3$ in Kronecker's delta δ_{ij} correspond to the Cartesian laboratory coordinate axes X, Y, Z. The term $\boldsymbol{\mu} \times \mathbf{E}(t)$ in Eq. (1.15.2) is the

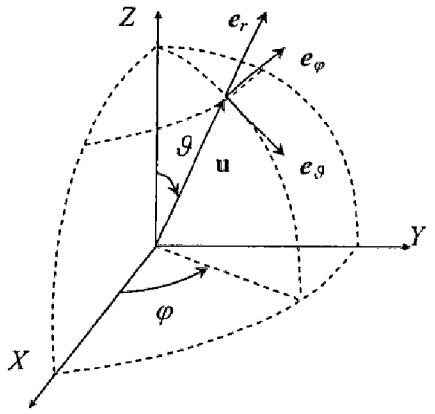


Fig. 1.15.1. Spherical polar coordinate system.

torque due to an externally applied electric field. The overbar means a statistical average over an ensemble of dipoles which, bearing in mind our interpretation of the Langevin equation as an integral equation, start at time t with the *same* angular velocity $\boldsymbol{\omega}$ and the *same* orientation $\boldsymbol{\mu}$.

Equation (1.15.2) includes the inertia of the sphere. The non-inertial limit is the limit when I tends to zero or when the friction coefficient ς becomes very large. In this limit, the angular velocity vector may immediately be written down from Eq. (1.15.2) as

$$\boldsymbol{\omega}(t) = \varsigma^{-1}[\boldsymbol{\lambda}(t) + \boldsymbol{\mu}(t) \times \mathbf{E}(t)]. \tag{1.15.4}$$

We combine this with the kinematic relation, Eq. (1.15.1), to obtain

$$\varsigma \dot{\boldsymbol{\mu}}(t) = \boldsymbol{\lambda}(t) \times \boldsymbol{\mu}(t) + [\boldsymbol{\mu}(t) \times \mathbf{E}(t)] \times \boldsymbol{\mu}(t), \tag{1.15.5}$$

This is the Langevin equation for the motion of $\boldsymbol{\mu}$ in the non-inertial limit.

Equation (1.15.5) refers to one selected dipole. We may use that equation to write down the Fokker–Planck equation in spherical polar coordinates (see Fig. 1.15.1) using the intuitive method presented above in Section 1.2. As we saw in that section, the current density $\mathbf{J}_d$ in the absence of thermal agitation is

$$\mathbf{J}_d = W\dot{\mathbf{u}}, \tag{1.15.6}$$

where $\mathbf{u}$ is a unit vector along $\boldsymbol{\mu}$ and $W(\vartheta, \varphi, t)$ is the density of dipole moment orientations on a sphere of unit radius. The orientation of the unit vector $\mathbf{u}$ is described by the polar angle ϑ and azimuth φ with $u_X = \sin\vartheta\cos\varphi$, $u_Y = \sin\vartheta\sin\varphi$, and $u_Z = \cos\vartheta$. The applied electric field $\mathbf{E}(t)$ is the negative gradient of a scalar potential V, so that

$$\mathbf{E}(t) = -\mu^{-1}\left(\frac{\partial V}{\partial u}\mathbf{e}_r + \frac{\partial V}{\partial \vartheta}\mathbf{e}_\vartheta + \frac{1}{\sin\vartheta}\frac{\partial V}{\partial \varphi}\mathbf{e}_\varphi\right), \tag{1.15.7}$$

where $\mathbf{e}_\vartheta$ is a unit vector in the direction of ϑ increasing, $\mathbf{e}_\varphi$ is a unit vector in the direction of φ increasing, and $\mathbf{e}_r$ is a unit vector in the direction of $\mathbf{u}$. The vector products in Eq. (1.15.5) are then in spherical coordinates

$$\boldsymbol{\mu}\times\mathbf{E}=\begin{vmatrix}\mathbf{e}_r & \mathbf{e}_\vartheta & \mathbf{e}_\varphi\\ 1 & 0 & 0\\ -\dfrac{\partial V}{\partial u} & -\dfrac{\partial V}{\partial\vartheta} & -\dfrac{1}{\sin\vartheta}\dfrac{\partial V}{\partial\varphi}\end{vmatrix}=\frac{1}{\sin\vartheta}\frac{\partial V}{\partial\varphi}\mathbf{e}_\vartheta-\frac{\partial V}{\partial\vartheta}\mathbf{e}_\varphi,$$

$$(\boldsymbol{\mu}\times\mathbf{E})\times\boldsymbol{\mu}=\begin{vmatrix}\mathbf{e}_r & \mathbf{e}_\vartheta & \mathbf{e}_\varphi\\ 0 & \dfrac{1}{\sin\vartheta}\dfrac{\partial V}{\partial\varphi} & -\dfrac{\partial V}{\partial\vartheta}\\ \mu & 0 & 0\end{vmatrix}=-\mu\left(\frac{\partial V}{\partial\vartheta}\mathbf{e}_\vartheta+\frac{1}{\sin\vartheta}\frac{\partial V}{\partial\varphi}\mathbf{e}_\varphi\right),$$

so that the drift current density, Eq. (1.15.6), is

$$\mathbf{J}_\mathrm{d}=-\frac{1}{\varsigma}\left[\mathbf{e}_\vartheta\frac{\partial V}{\partial\vartheta}+\mathbf{e}_\varphi\frac{1}{\sin\vartheta}\frac{\partial V}{\partial\varphi}\right]W. \tag{1.15.8}$$

Equation (1.15.8) refers to the current density in the absence of thermal agitation, which has been calculated from Eq. (1.15.6) neglecting the noise term. To include thermal agitation, we add to $\mathbf{J}_\mathrm{d}$ a diffusion term

$$\mathbf{J}_\mathrm{diff}=-D_\mathrm{R}\left[\mathbf{e}_\vartheta\frac{\partial}{\partial\vartheta}+\mathbf{e}_\varphi\frac{1}{\sin\vartheta}\frac{\partial}{\partial\varphi}\right]W, \tag{1.15.9}$$

the tendency of which is to spread the density of dipole moment orientations, i.e., to make them more uniform. Here D_R is the rotational diffusion coefficient. The continuity equation

$$\frac{\partial W}{\partial t}+\mathrm{div}\mathbf{J}=\frac{\partial W}{\partial t}+\frac{1}{\sin\vartheta}\left[\frac{\partial}{\partial\vartheta}(\sin\vartheta J_\vartheta)+\frac{\partial}{\partial\varphi}J_\varphi\right],$$

where $\mathbf{J}=\mathbf{J}_\mathrm{d}+\mathbf{J}_\mathrm{diff}$ is the total current density, so that

$$J_\vartheta=-\frac{W}{\varsigma}\frac{\partial V}{\partial\vartheta}-D_\mathrm{R}\frac{\partial W}{\partial\vartheta},$$

$$J_\varphi=-\frac{W}{\varsigma\sin\vartheta}\frac{\partial V}{\partial\varphi}-\frac{D_\mathrm{R}}{\sin\vartheta}\frac{\partial W}{\partial\varphi},$$

then yields the Fokker–Planck (here the Smoluchowski) equation

$$\frac{\partial W}{\partial t}=D_\mathrm{R}\Delta W+\frac{1}{\varsigma}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta W\frac{\partial V}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial}{\partial\varphi}\left(W\frac{\partial V}{\partial\varphi}\right)\right]. \tag{1.15.10}$$

Here the operator Δ is given by

$$\Delta = \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}, \tag{1.15.11}$$

i.e., the angular part of the Laplacian. Now, in equilibrium $\dot{W}=0$, so that W must reduce to the Boltzmann distribution $W_0 = Z^{-1}e^{-V(\vartheta,\varphi)/(kT)}$ (Z is the partition function). Substituting W_0 into Eq. (1.15.10), we then find the rotational diffusion coefficient $D_R = kT/\varsigma$. If we define the *Debye relaxation time* by $\tau_D = 1/(2D_R)$, the rotational Smoluchowski equation, Eq. (1.15.10), becomes

$$2\tau_D\frac{\partial W}{\partial t} = \Delta W + \frac{1}{kT}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta W\frac{\partial V}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial}{\partial\varphi}\left(W\frac{\partial V}{\partial\varphi}\right)\right]. \tag{1.15.12}$$

We shall now follow Debye [32], who specialized this equation to a d.c. field **E** applied along the polar axis (so that $V=-\mu E\cos\vartheta$). Eq. (1.15.12) then becomes

$$2\tau_D\frac{\partial W}{\partial t} = \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left[\sin\vartheta\left(\frac{\partial W}{\partial\vartheta}+\frac{\mu E}{kT}\sin\vartheta W\right)\right]. \tag{1.15.13}$$

This equation obtained by Debye [32] is simply the Smoluchowski equation written in spherical polar coordinates. We remark that Eq. (1.15.13) is also the correct form of the Smoluchowski equation for isotropic rotational diffusion of *prolate* or *oblate* spheroids.

The general solution of Eq. (1.15.13) is

$$W(\vartheta,t) = \sum_{n=0}^{\infty} a_n(t)P_n(\cos\vartheta), \tag{1.15.14}$$

where the $P_n(z)$ are the Legendre polynomials [95] and the $a_n(t)$ are functions to be determined. However, as far as dielectric relaxation is concerned, we are generally interested in the linear approximation in the applied field. Thus, for the after-effect solution in which the steady field $\mathbf{E}=\mathbf{E}_0$ is suddenly switched off at time $t=0$, we may assume that W has the form

$$W(\vartheta,t) = \frac{1}{4\pi}\left(1+\frac{\mu E_0}{kT}g(t)\cos\vartheta\right), \tag{1.15.15}$$

which, on substitution into Eq. (1.15.13), yields $g(t)=e^{-t/\tau_D}$. Thus the mean dipole moment $\mu\langle\cos\vartheta\rangle$ is, taking account of the azimuthal angle φ, given by

$$\mu\langle\cos\vartheta\rangle = \mu\int_0^{2\pi}\int_0^{\pi} W\cos\vartheta\sin\vartheta\,d\vartheta\,d\varphi = \frac{\mu^2 E_0}{3kT}e^{-t/\tau_D}. \tag{1.15.16}$$

Likewise we may deduce that, when the field $\mathbf{E}$ is alternating so that $\mathbf{E} = \mathbf{E}_m e^{i\omega t}$, the value of the mean dipole moment is

$$\mu\langle\cos\vartheta\rangle = \frac{\mu^2}{3kT}\frac{E_m e^{i\omega t}}{1+i\omega\tau_D}. \tag{1.15.17}$$

We see at once that there is a *difference* in phase $-\tan^{-1}(\omega\tau_D)$ between $\mu\langle\cos\vartheta\rangle$ and $\mathbf{E}$. This phase difference persists if, in place of $\mathbf{E}_m e^{i\omega t}$, we take its real and imaginary parts $\mathbf{E}_m \cos\omega t$ or $\mathbf{E}_m \sin\omega t$. Debye made an estimate of the relaxation time τ_D by assuming that the Stokes formula for the frictional torque on a rotating sphere, $\varsigma = 8\pi\eta a^3$, applies to the dipole molecule (η is the viscosity of the liquid, a is the radius of the sphere). For water at room temperature, where $\eta = 0.01$ Po, and assuming that $a = 2\times10^{-8}$ cm, he found ς to be 2×10^{-24} which yields a relaxation time τ_D of 0.25×10^{-10} s. Thus the maximum dielectric loss should occur in the microwave frequency region. This is the principle of operation of the microwave oven.

1.15.1. *Breakdown of the Debye theory at high frequencies*

As we have emphasized, the Debye theory of dielectric relaxation ignores the inertia of the rotating dipoles. Thus as has been said repeatedly, that theory breaks down at very short periods ~10^{-12} s. (The discussion is largely due to Sack [96]). In order to achieve maximum clarity in our presentation, we now summarize the main findings of the Debye theory. First of all, by the preceding discussion it is apparent that if a system is subject to an a.c. field $E_m \cos\omega t$, which is not so large as to cause nonlinear effects, then the steady-state response may be described by a complex susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ depending on the angular frequency ω, such that the longitudinal component of the time-dependent dipole moment $\langle M_z\rangle(t)$ of a dielectric sample is

$$\langle M_z\rangle(t) \propto E_m\left[\chi'(\omega)\cos\omega t + \chi''(\omega)\sin\omega t\right]. \tag{1.15.1.1}$$

The coefficient $\chi''(\omega)$ is a measure of the energy loss per cycle for a constant amplitude E_m. The susceptibility $\chi(\omega)$ is given by the Debye equation

$$\chi(\omega) = \frac{\chi'(0)}{1+i\omega\tau_D}. \tag{1.15.1.2}$$

The dielectric loss $\chi''(\omega)$ has a maximum for $\omega\tau_D = 1$. Experimental curves of $\chi''(\omega)$ vs. ω usually show a peak broader than that predicted by Eq. (1.15.1.2). This can be explained by a *distribution* $f(\tau)$ of relaxation times τ, so that we have

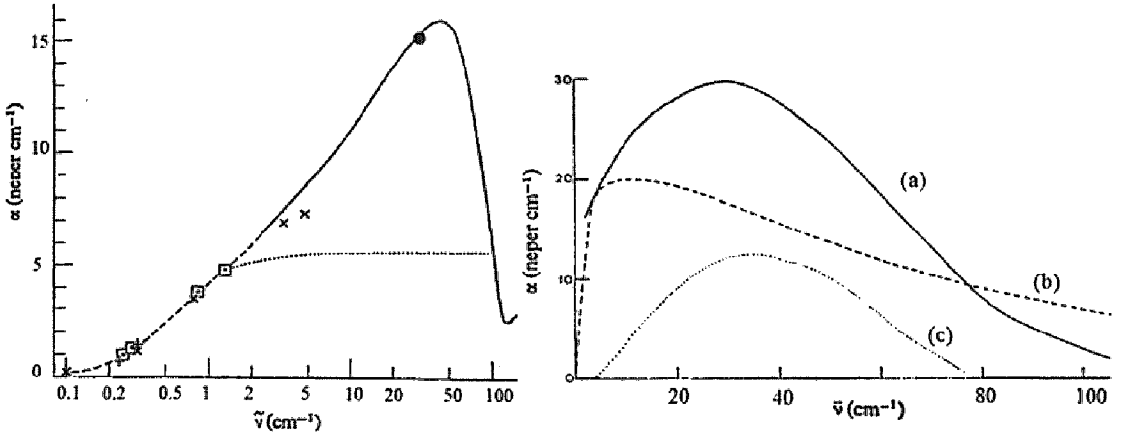


Figure 1.15.1.1. (Left) Absorption coefficient α vs. frequency $\tilde{\nu}$ [$\tilde{\nu} = \omega/(2\pi c)$] for liquid chlorobenzene at 20 °C. The solid line represents the far-infrared experimental data, the broken line links the microwave data (symbols), the dotted line represents α calculated from the Debye equation, Eq. (1.15.1.2). (Right) α vs. $\tilde{\nu}$ for liquid methyl chloroform at 20 °C. The solid line (a) represents the experimental data, the broken line (b) represents α calculated from the Rocard equation, Eq. (1.15.1.4), and (c): (a)–(b). Reproduced by permission of the Royal Society of Chemistry from Ref. [97].

$$\frac{\chi(\omega)}{\chi'(0)} = \int_0^\infty \frac{f(\tau)d\tau}{1+i\omega\tau}. \tag{1.15.1.3}$$

We shall illustrate in Section 1.22 how this distribution of relaxation times may arise naturally. Whatever the mechanism for the relaxation, however, Eqs. (1.15.1.2) and (1.15.1.3), break down at very high frequencies since the absorption coefficient $\alpha(\omega) \propto \omega\chi''(\omega) \rightarrow$ constant (the Debye plateau) as $\omega \rightarrow \infty$. They predict, for example, an infinite integral dipolar absorption [98] with *complete opacity* in some extreme cases such as water (*"Black Water"*) [96] and an *infinite rate* of energy loss for an electron travelling through the material. They are also unable to account for the resonance or Poley [97, 99–104] absorption peak occurring in the far-infrared or terahertz band of frequencies (see Fig. 1.15.1.1). This problem is discussed in Chapter 11.

Furthermore, in the time domain, the Debye equations imply that an abrupt change in the field **E** would produce an instantaneous finite alteration of the rate of change of the dipole moment ($\dot{\boldsymbol{\mu}}$), which is impossible in view of the finite rotational inertia of the dipoles. In general, the product $\omega\chi''(\omega)$ must tend to zero in the limit of high frequencies [100]; hence, in the frequency range in which $\chi(\omega)$ can be expanded in negative powers of ω, i.e.,

$$\chi(\omega) = a_0 + \frac{a_1}{i\omega} + \frac{a_2}{(i\omega)^2} + \cdots,$$

the coefficient a_1 must vanish. This is compatible with a distribution of relaxation times of the type given in Eq. (1.15.1.3), only if the function $\chi(\log\tau)$ can take on *negative* as well as positive values [96]. In the time domain, the stipulation that $\omega\chi''(\omega)$ must vanish means that the Taylor expansion of the after-effect function must not contain terms of order $|t|$. The above considerations show that, in dielectric relaxation processes, inertial effects become important at high frequencies. Consequently, there have been many attempts to include them in the Debye theory [40, 96]. The earliest attempt was that of Rocard in 1933, followed by Dimitriev and Gurevich (1946) and Powles (1948) [96]. Rocard derived the equation now known as the Rocard equation

$$\frac{\chi(\omega)}{\chi'(0)} = \frac{1}{1+i\omega\tau_D - \omega^2\tau_D I/\varsigma}, \qquad (1.15.1.4)$$

which shows the desired return to transparency at high frequencies (the second characteristic time I/ς is of the order 10^{-12}–10^{-13} s). The calculations were all based, in one way or another, on the inclusion of an extra term in the Smoluchowski equation, thus rendering them only partially correct. Indeed, inertial effects can be consistently treated only on the basis of the Klein–Kramers equation, which considers distributions in configuration–angular velocity space where *both* angular positions and angular momenta (or angular velocities) are taken as independent variables, or of the inertial Langevin equation. The first investigator to adopt the approach based on the Klein–Kramers equation was E.P. Gross in 1955 [105], who considered the behavior of rigid dipoles rotating about fixed axes in a viscous medium. The paper of Gross, however, does not include a detailed description of how his results were obtained; the reader is referred to the work of Sack [96] who gave a detailed derivation of these results and extended the theory to rotation in space. McConnell [40] has succinctly reviewed all the calculations described above.

We have formulated the Debye theory of dielectric relaxation, utilizing the vector method based on the kinematic relation of Eq. (1.15.1). This method has the advantage that it may be easily adapted to include the effects of a crystalline anisotropy potential, as is required in the theory of dielectric relaxation of nematic liquid crystals [94] (see Chapters 7 and 8 for a detailed treatment) and the effect of the electric dipole–dipole coupling between dipolar molecules. If both effects are included, the potential energy (in the case of uniaxial anisotropy for N similar dipoles with common anisotropy axis $\mathbf{n}$) would be

$$V = -\sum_{i=1}^{N} \boldsymbol{\mu}_i \cdot \mathbf{E}_i - \sum_{i=1}^{N} K\mu_i^{-2}(\boldsymbol{\mu}_i \cdot \mathbf{n})^2 + \sum_{i=1}^{N} \sum_{i<j(j\neq i)} \left[\frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{r_{ij}^3} - \frac{3(\boldsymbol{\mu}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\mu}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right],$$

where the first term arises from the external field, the second term is the uniaxial anisotropy energy, the third term is the dipole–dipole interaction energy, $\mathbf{r}_{ji}$ is the vector separation, and K is the anisotropy constant. Unless the dipole–dipole interaction energy is zero, it is impossible to make the assumption that each dipole of the assembly behaves in the same way as it does in the Debye theory, which ignores all intermolecular interactions. Another advantage of the vector formulation is that it facilitates comparison with the Langevin equations governing the magnetization kinetics of superparamagnetic nanoparticles such as the Landau–Lifshitz or Gilbert equations [58, 106], a topic which we shall now discuss.

1.16. Superparamagnetism: magnetic after-effect

In general, a particle of ferromagnetic material [35] below a certain critical size (typically 150 Å in radius) constitutes a *single-domain particle* meaning [107] that it is in a state of *uniform magnetization* for *any applied field*. If we denote the magnetic dipole moment of such a particle by $\boldsymbol{\mu}$ and ignore the anisotropy energy, and if we further suppose that an assembly of them has come to equilibrium at temperature T under the influence of an applied magnetic field $\mathbf{H}$, then we will have, for the mean dipole moment in the direction of the field,

$$\langle \boldsymbol{\mu} \cdot \mathbf{h} \rangle = \mu(\coth \xi - \xi^{-1}) = \mu L(\xi), \tag{1.16.1}$$

where $\mathbf{h} = \mathbf{H}/H$, $L(\xi)$ is the Langevin function [98, 108], and $\xi = \mu H/(kT)$ is a dimensionless field parameter. The behavior is exactly analogous to that of an electric dipole in the Debye theory of the static electric susceptibility [98] or the Langevin treatment of paramagnetism; the vital difference, however, is that the magnetic moment $\boldsymbol{\mu}$ is *not* that of a *single* atom but rather of a *single-domain particle* of volume v which may be of the order of 10^4–10^5 Bohr magnetons, so that *extremely large* moments and *large* susceptibilities are involved: hence the term *superparamagnetism*. The superparamagnetism, or *thermal instability* of the magnetization, occurs if the thermal energy kT is sufficient to change the orientation of $\boldsymbol{\mu}$ of the entire particle. Then the thermal agitation causes continual changes in the orientation of $\boldsymbol{\mu}$ and, in an ensemble of such particles, maintains a distribution of orientations characteristic of thermal equilibrium. Hence the number of particles with orientations of $\boldsymbol{\mu}$ within solid angle $d\Omega = \sin\vartheta\, d\vartheta\, d\varphi$ is proportional to $e^{-vV(\vartheta,\varphi)/(kT)}d\Omega$, where V is the free energy per unit volume and ϑ and φ are angular coordinates which describe the orientation of $\boldsymbol{\mu}$. Thus the overall behavior is just like assembly of paramagnetic atoms. There is no hysteresis, merely saturation behavior.

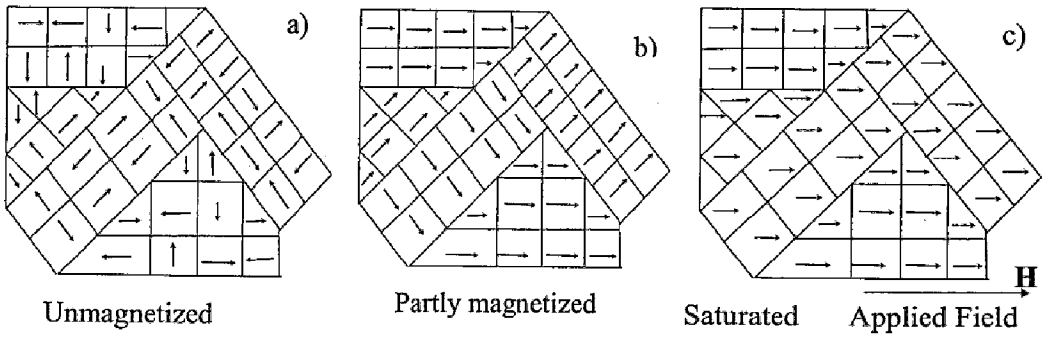


Figure 1.16.1. (a) A ferromagnetic material, where the domains of the material are magnetized in the directions of easy magnetization. The arrows indicate the direction of the magnetization of each domain, where adjacent domains have opposite directions of magnetization, so that the overall magnetization of the material is negligible. If we apply a uniform external magnetic field, in the direction shown, some of the domains, those with magnetic orientations perpendicular or opposite to the direction of the applied field, become unstable and quickly rotate to another direction of easy magnetization in the same direction as the applied field. This is illustrated in (b). If we were to increase the applied field to the point of saturation, we would have the situation of (c).

The theory that a ferromagnetic material consists (magnetically speaking) of elementary regions, each magnetized almost to saturation in some direction, was first proposed by Weiss [107] in 1907. He assumed that these regions coincided with the crystals of which the material was composed, an assumption which was subsequently refuted by Frenkel and Dorfman and by Heisenberg and Bloch [107], who realized that even a *single* crystal is comprised of these minute permanent magnets, now known as magnetic domains (Figure 1.16.1). However, the exact nature of domains remained under debate until 1935 when Landau and Lifshitz [107] discovered them to be in the form of elementary layers.

Single-domain particles will in general not be *isotropic*, as is assumed in deriving Eq. (1.16.1), above but will have *anisotropic* contributions to their total energy associated with the external shape of the particle, imposed stress or the crystalline structure itself. If we consider the simplest anisotropy energy, namely the uniaxial one, then the total free energy of the particle, vV, will be (if the applied field **H** is assumed parallel to the polar axis)

$$vV = Kv\sin^2\vartheta - \mu H\cos\vartheta, \tag{1.16.2}$$

so that the magnetization curve will no longer be the Langevin function. However, the dominant term governing the approach to saturation will still be $1-\xi^{-1}$ [107].

The discussion so far has been concerned with equilibrium behavior. We now have to consider *magnetic after-effect behavior*; i.e., under what conditions

an assembly of single-domain particles can achieve thermal equilibrium in a time that is *short* compared with the time of an experiment. One way of achieving equilibrium is by *physical rotation* of the particles; this can occur if they are suspended in a liquid carrier – this is a *ferrofluid*. Here [107] the factor determining the rate of approach to equilibrium is the *viscosity of the medium in which the particles are suspended* – this mechanism may be treated using the Debye theory, as illustrated above for electric dipoles. The mechanism is described in more detail in Section 1.19 below which deals with ferrofluids [109]. We remark that the conditions for the validity of the Debye theory are much better satisfied for a ferrofluid than for electric dipoles, because the ferrofluid particles, owing to their relatively large size, are a much closer approximation to idealized Brownian particles than are polar molecules. In addition, the dynamical behavior of the particles will manifest itself in the mid-radio frequency (medium wave) region rather than in the microwave band.

In a solid, physical rotation of the particles cannot take place. However, in 1949, Néel [110, 111] pointed out that, if a single-domain particle were *sufficiently small*, thermal fluctuations could cause its *direction of magnetization* to undergo a type of Brownian rotation, so that the stable magnetic behavior characteristic of a ferromagnet would be destroyed. Here, since the relaxing entity is the magnetic moment inside the particle, the inertia of the particle will of course play no role, because no physical rotation of the particle occurs, unlike in Debye relaxation of a polar molecule. An example given by Brown [112] of a tape recording is of interest: we expect that if we put this recording on a shelf that it will stay in the same magnetic state; we would be surprised if it suddenly jumped from being a recording of Beethoven to a recording of Brahms. In principle, however, [112] the *apparent stability* of the recording is only one of *many* local minima of the free energy: thermal agitation can cause spontaneous jumps from one such state to another. The apparent stability [112] (*ferromagnetic behavior*) arises because our tape or magnet cannot get from one magnetic state to another without passing over an energy barrier which is very large in comparison with kT. Thus, the probability per unit time of a jump over such a barrier is so small that the mean time we would have to wait for it to occur *far exceeds our own lifetime*; we perceive stable ferromagnetic behavior. However, if the barrier is neither very large nor very small in comparison with the noise strength kT (our case), then the specimen neither remains in a single stable state for a long time nor attains thermal equilibrium in a short time after a change in field: it instead undergoes a change of magnetization which is not completed instantaneously but lags behind the field. This is called *magnetic*

after-effect, or *magnetic viscosity*, or *Néel relaxation*, and occurs only for *sufficiently fine* ferromagnetic particles. In order to illustrate the Néel mechanism [107], consider an assembly of aligned uniaxial particles in the presence of a field **H**, whose potential energy is given by Eq. (1.16.2). Thus, the particles are fully magnetized along the polar axis, which is the axis of symmetry. A sufficiently long time after the field is switched off, the remanence will vanish as

$$M_r(t) = M_S e^{-t/\tau}, \tag{1.16.3}$$

which is the longest lived mode of the relaxation process. Here M_S is the mean magnetization of a non-relaxing particle, t is the time after the removal of the field, and τ is the superparamagnetic relaxation time. Néel [110, 111] then suggested that, from TST theory [61, 62], the relaxation time τ is given by

$$\tau^{-1} = f_0 e^{-vK/kT}, \tag{1.16.4}$$

where f_0 is roughly the frequency of the gyromagnetic precession [108] so that, by varying the volume or the temperature of the particles, τ can be made to vary from 10^{-9} s to *millions of years* (f_0^{-1} is often taken as small as 10^{-10}–10^{-11} s in practice). The presence of the exponential factor in Eq. (1.16.4) indicates that, in order to approach the zero remanence (corresponding to thermal equilibrium), a sufficient number of particles (magnetic moments) must be reversed by thermal activation over the energy barrier vK. The probability of such a process is proportional to $e^{-vK/kT}$ (compare the Kramers transition state method above). For example, when $\mathbf{H} = 0$, Eq. (1.16.2) is a symmetric bistable potential with minima at $\vartheta = 0$ and $\vartheta = \pi$ and a maximum at $\vartheta = \pi/2$.

Néel's calculation of τ was later criticized by Brown [106] on two counts (at this point, the subject matter of the book comes into play): (i) the system is not explicitly treated as a *gyromagnetic one*; and (ii) it relies on a *discrete orientation* approximation. Brown [106] suggested that both of these difficulties could be resolved by constructing the Fokker–Planck equation for the PDF of magnetic moment orientations on the unit sphere from the appropriate Langevin equation. He was then able to find, using the Kramers method, an approximate formula for τ in the high-barrier limit for the potential of Eq. (1.16.2) which agreed with Néel's formula except for the prefactor f_0. This is discussed in detail in Sections 1.17 and 1.18 below.

It is apparent from Eq. (1.16.4) that the Néel relaxation time τ depends *exponentially on the particle volume*; hence there is a fairly well-defined particle radius above which the magnetization will appear stable. We consider the figures given by Bean and Livingston [107] for a spherical iron particle with

uniaxial anisotropy $Kv\sin^2\vartheta$. A particle of radius 115 Å will have a relaxation time of 10^{-1} s at 300 K, so that the moment will relax almost instantaneously. A particle of radius 150 Å, on the other hand, will have a relaxation time of 10^9 s and so will be exceedingly stable (i.e., the moment will not reverse in this time; see the preceding example above). This situation corresponds to an energy barrier that is very large in comparison to kT where, for any reasonable measurement time [106], we may ignore thermal agitation and calculate the static magnetization by simply minimizing V with respect to the polar and azimuthal angles (ϑ, φ) for each value of an applied field $\mathbf{H}_0$. This is the well-known Stoner–Wohlfarth calculation [113]; it leads to hysteresis because in certain field ranges two or more minima exist and transitions between them are neglected. Here a typical potential would be [114]

$$vV(\vartheta,\varphi) = Kv\sin^2\vartheta - \mu H_0(\cos\vartheta\cos\psi + \sin\psi\sin\vartheta\cos\varphi). \qquad (1.16.5)$$

The polar axis **k** is the easy axis of magnetization; the field $\mathbf{H}_0$ is applied in the xz plane at an angle ψ to the easy axis. Thus, in general, there will be only a narrow range of particle sizes for which the relaxation time will be of the order of experimental times, and for which measurable "magnetic viscosity" effects, manifesting themselves as an *observable* change of magnetization, *lagging behind field changes*, would be expected. Bean and Livingston have given a rough measure of the size of the particle for transition to stable behavior, taking $\tau = 10^2$ s, they find that the energy is $25kT$. The temperature at which this occurs for a given particle is called the *blocking temperature*. They obtain sizes of 40 Å for h.c.p. cobalt, 125 Å for iron, 140 Å for f.c.c. cobalt. We mention that, in an assembly consisting *solely* of single-domain particles, the remanence at a given temperature should be a measure of the amount of material with particle volume greater than the volume that is just stable at this temperature. Thus [107], by following the increase of remanence with decreasing temperature, we can find out how much material lies in various ranges of volume, and so determine the particle size distribution.

It is interesting to recall that Néel [110] was led to his solid-state mechanism of relaxation, that is *rotation of the magnetic moment inside the particle due to thermal agitation*, through the study of *paleomagnetism*. Much work had been done on measuring the intensity and direction of the remanent magnetization in rocks, with the view that such data would yield information on the strength and direction of the earth's magnetic field at the time the rock was formed. As is well illustrated by the elegant exposition of Blackett [115],

> "The detailed study of the natural magnetization of rocks is likely to allow us to trace back to the beginning of geological time both the history of the earth's

> magnetic field and the motion of continental masses relative to each other and to the geographical pole. The ability of the magnetic rocks to "remember" an earlier magnetic field depends on their ability to exist in thermal equilibrium with the earth's field at a stage early in their formation but to be later "frozen" in a state of magnetization stable against later changes of the direction and strength of the field."

Thus [107] the establishment of thermal equilibrium of the rock magnetization may be accomplished by either the Debye or Néel mechanisms. The Debye-like mechanism occurs [107] in sedimentary rocks. There the particles align themselves with the direction of the earth's field by mechanical rotation, while the sediment is still wet and uncompressed. Later the sediment becomes relatively hard rock and this ferrofluid-like behavior is lost, so that Debye relaxation can no longer take place and the magnetization is thus stable against later changes in the earth's field, so preserving the direction of the earth's magnetic field from the epoch in which the sediment was laid down.

In igneous rocks, however, the material becomes magnetic by cooling through its Curie point [107], and there is no mechanical rotation of the particles. At high temperatures, however, the ratio of barrier height to thermal energy is such that Néel relaxation may occur. Clearly, this will be in the early stages of the formation of the rock (e.g., in mountain building periods). As the rocks cool, the magnetization will become stable: the particles will have cooled to a temperature below their blocking temperature and the magnetization will be thus stable against later changes in the earth's field, again preserving the direction of the earth's magnetic field from the epoch in which the rocks have formed. The relaxation times in this case are of the order of geological times. The rocks thus play the role of "magnetic fossils" (rocks from widely scattered parts of the world but of the same age showing the same magnetic patterns), giving evidence of a past reversal of the earth's magnetic field, records of a time when the northern magnetic pole resided where the southern magnetic pole is today. Reversals are believed to have occurred as many as 25 times during the last 5 million years, with the last such reversal having occurred about 730,000 years ago. In an apt phrase coined in a popular article by Dr. William Reville, "*the earth's magnetic chronicle is written in stone.*"

Another possible mechanism of magnetic relaxation over potential barriers, which is of much current interest, is macroscopic quantum tunneling of the magnetization ("macroscopic" because of the large number of spins involved), which was originally suggested by Bean and Livingston [107]. By this is meant the possibility of transitions of the magnetic moment at absolute zero from a state of complete alignment to a state of zero overall magnetization, owing to

quantum tunneling [116] of the magnetic moment through the anisotropy potential barrier (see [63] for a recent review of single-particle measurements).

Before we proceed to the more sophisticated treatment of Brown [106] based on the Langevin equation, we shall briefly describe the *discrete orientation model* for the calculation of the Néel relaxation time (this model is described in detail in Chapter 9, Section 9.4.2). We shall suppose that the energy barriers are so large in comparison with kT that the magnetization is always along one of the directions (ϑ_i, φ_i) of easy magnetization; nevertheless, the barriers are not so high as to preclude changes of orientation altogether. Thus, in orientation i, there is a probability ν_{ij} per unit time of a jump to orientation j. The ν_{ij} depend on K, H, and kT. Let us now suppose that we have only two orientations as for a uniaxial anisotropy given by Eq. (1.16.2). Let 1 and 2 refer to the positive and negative orientations, respectively. If we have a large number n of identical non-interacting particles, the number of particles n_i in orientation i then changes with time in accordance with the equations

$$\dot{n}_1 = -\dot{n}_2 = \nu_{21} n_2 - \nu_{12} n_1. \tag{1.16.6}$$

Hence, we have the evolution equation [117]

$$\frac{d}{dt}(n_2 - n_1) = -(\nu_{21} + \nu_{12})(n_2 - n_1) + (\nu_{12} - \nu_{21})n,$$

so that n_1 and n_2 approach their final values when ν_{12} and ν_{21} are constant according to the factor $e^{-(\nu_{12}+\nu_{21})t}$, that is, with time constant

$$\tau = (\nu_{12} + \nu_{21})^{-1}. \tag{1.16.7}$$

If ν_{ij}^0 is the frequency of oscillation of a particle in a potential well, the probability per second for the flip of a particle from orientation i to orientation j is given by

$$\nu_{ij} = \nu_{ij}^0 e^{-v[V_m - V_i]/(kT)}, \quad (i = 1, j = 2 \text{ or } i = 2, j = 1), \tag{1.16.8}$$

where V_i is the free energy density in orientation i, and V_m is the free energy density at the top of the barrier between the orientations i and j; v is, as usual, the particle volume. The frequencies ν_{ij}^0, if they vary with temperature, are assumed to do so slowly in comparison with the exponential factor, and are often taken to be constant, although Néel [110] has calculated them explicitly (see Refs. [106, 111, 112]). We reiterate that, regardless of the precise form of ν_{ij}^0, if the ratio v/T changes by a factor of less than three in a certain critical part of its range, the time constant, Eq. (1.16.7), changes from 10^{-1} to 10^9 s. Thus, to a good approximation [112], we may reaffirm that a *critical volume* v_c exists such that particles with $v < v_c$ are *superparamagnetic*. We remark that the discrete

orientation model of overbarrier relaxation was originally proposed for dielectric relaxation in polar crystals by Debye [32] and extensively developed by Fröhlich [117].

1.17. Brown's treatment of Néel relaxation

The starting point of Brown's treatment [106, 112] of the dynamical behavior of the magnetization **M** for a single-domain particle is Gilbert's equation which, without thermal agitation, is

$$\dot{\mathbf{M}} = \gamma \mathbf{M} \times \left(\mathbf{H} - \eta \dot{\mathbf{M}} \right). \tag{1.17.1}$$

In Eq. (1.17.1), γ is the ratio of magnetic moment to angular momentum (gyromagnetic ratio), η is a phenomenological damping constant,

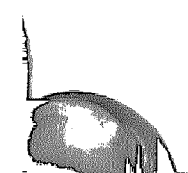
$$\mathbf{H} = -\frac{\partial V}{\partial \mathbf{M}}, \quad \frac{\partial V}{\partial \mathbf{M}} = \mathbf{i}\frac{\partial V}{\partial M_X} + \mathbf{j}\frac{\partial V}{\partial M_Y} + \mathbf{k}\frac{\partial V}{\partial M_Z}, \tag{1.17.2}$$

and V is the Gibbs free energy density (the total free energy is vV). In general, **H** represents the *conservative* part and $-\eta\dot{\mathbf{M}}$ the *dissipative* part of an "effective field." Brown now supposes that, in the presence of thermal agitation, the dissipative "effective field" $-\eta\dot{\mathbf{M}}$ describes only the statistical average of the rapidly fluctuating random field due to thermal agitation, and that this term must become $-\eta\dot{\mathbf{M}} + \mathbf{h}(t)$, where the Gaussian random field $\mathbf{h}(t)$ has the properties

$$\overline{h_i(t)} = 0, \quad \overline{h_i(t_1)h_j(t_2)} = (2kT\eta / v)\delta_{ij}\delta(t_1 - t_2). \tag{1.17.3}$$

Here the indices $i, j = 1, 2, 3$ correspond to the Cartesian axes X, Y, Z of the laboratory coordinate system. The overbars denote statistical averages over a large number of moments, which have all started with the same orientation (ϑ, φ) (here we use spherical polar coordinates; see Fig. 1.15.1). On assuming that the $h_i(t)$ obey Isserlis's theorem (Section 1.3), Brown [106] was then able to derive, after a long and tedious calculation using the methods of Wang and Uhlenbeck [13, 58], the Fokker–Planck equation for the density of magnetization orientations $W(\vartheta, \varphi, t)$ on the sphere of radius M_S. This procedure may be circumvented, however, by using an alternative approach given by Brown which appears to be based on the argument of Einstein given in Section 1.2.

In order to illustrate this, we first write (cross-multiplying vectorially by **M** and using the triple vector product formula) Gilbert's equation in the absence of thermal agitation (noiseless equation) as an explicit equation for $\dot{\mathbf{M}}$ (see Chapter 9, Section 9.2.1), namely



$$\dot{\mathbf{M}} = \alpha^{-1} h' M_S (\mathbf{M} \times \mathbf{H}) + h' (\mathbf{M} \times \mathbf{H}) \times \mathbf{M}, \tag{1.17.4}$$

where $\alpha = \eta\gamma M_S$ is a dimensionless damping coefficient and

$$h' = \frac{\alpha\gamma}{(1+\alpha^2)M_S}.$$

Equation (1.17.4) has the mathematical form of the earlier Landau–Lifshitz equation, namely

$$\dot{\mathbf{M}} = \gamma (\mathbf{M} \times \mathbf{H}) + \frac{\alpha\gamma}{M_S} (\mathbf{M} \times \mathbf{H}) \times \mathbf{M}, \tag{1.17.5}$$

which may be written from Eq. (1.17.4) by taking the low-damping limit, $\alpha << 1$ (usually, α lies in the range 0.01 to 1). On writing $\mathbf{M} = \mathbf{u}M_S$, Eq. (1.17.4) becomes

$$\dot{\mathbf{u}} = -\frac{h'}{\alpha}\left(\mathbf{u} \times \frac{\partial}{\partial \mathbf{u}} V\right) + h' \mathbf{u} \times \left(\mathbf{u} \times \frac{\partial}{\partial \mathbf{u}} V\right). \tag{1.17.6}$$

Here, instead of $\mathbf{M}$ we use the unit vector $\mathbf{u}$, where the Cartesian coordinates are the direction cosines u_i of $\mathbf{M}$ so that $\partial / \partial \mathbf{M}$ may be replaced by $M_S^{-1} \partial / \partial \mathbf{u}$, where $\partial / \partial \mathbf{u}$ means the gradient on the surface of the unit sphere [106] so that, in the spherical coordinate system (Fig. 1.15.1), the operator $\partial / \partial \mathbf{u}$ is

$$\frac{\partial}{\partial \mathbf{u}} = \frac{\partial}{\partial \vartheta} \mathbf{e}_\vartheta + \frac{1}{\sin \vartheta} \frac{\partial}{\partial \varphi} \mathbf{e}_\varphi. \tag{1.17.7}$$

The instantaneous orientation (ϑ, φ) of the magnetization $\mathbf{M}$ of a particle may be represented by a point on the unit sphere $(1, \vartheta, \varphi)$. As the magnetization changes its direction, the representative point moves over the surface of the sphere. Following [112], consider now a statistical ensemble of identical particles and let $W(\vartheta, \varphi, t) d\Omega$ be the probability that $\mathbf{M}$ has orientation (ϑ, φ) within solid angle $d\Omega = \sin \vartheta d\vartheta d\varphi$. The PDF $W(\vartheta, \varphi, t)$ is then related to the probability current $\mathbf{J}$ of such representative points swarming over the surface S of the sphere by the continuity equation

$$\dot{W} + \mathrm{div}\mathbf{J} = 0. \tag{1.17.8}$$

Equation (1.17.8) states that the swarming representative points are neither created nor destroyed, merely moving to new positions on the surface of the sphere [112]. Now in the absence of thermal agitation, we have $\mathbf{J} = W\dot{\mathbf{u}}$, where $\dot{\mathbf{u}}$ is given by Eq. (1.17.6). Let us again (as in Section 1.2) add to this $\mathbf{J}$ a diffusion term $-k' \partial_{\mathbf{u}} W$ (k' is a proportionality constant to be determined later), which represents the effect of thermal agitation; its tendency is to smooth out the

distribution, i.e., to make it more uniform. This intuitive procedure, just as with the dielectric problem of Section 1.15, gives for the components of **J** (on evaluating $\mathbf{u}\times\partial V/\partial\mathbf{u}$, etc. in spherical polar coordinates)

$$\mathbf{J}_\vartheta = -h'\left[\left(\frac{\partial V}{\partial\vartheta}-\frac{1}{\alpha\sin\vartheta}\frac{\partial V}{\partial\varphi}\right)W+\frac{k'}{h'}\frac{\partial W}{\partial\vartheta}\right], \tag{1.17.9}$$

$$\mathbf{J}_\varphi = -h'\left[\left(\frac{1}{\alpha}\frac{\partial V}{\partial\vartheta}+\frac{1}{\sin\vartheta}\frac{\partial V}{\partial\varphi}\right)W+\frac{k'}{h'\sin\vartheta}\frac{\partial W}{\partial\varphi}\right]. \tag{1.17.10}$$

Equations (1.17.9) and (1.17.10), when substituted into the continuity Eq. (1.17.8), now yield Brown's Fokker–Planck equation, namely

$$\frac{\partial W}{\partial t}=k'\Delta W+\frac{h'}{\sin\vartheta}\left\{\frac{\partial}{\partial\vartheta}\left[\left(\sin\vartheta\frac{\partial V}{\partial\vartheta}-\frac{1}{\alpha}\frac{\partial V}{\partial\varphi}\right)W\right]+\frac{\partial}{\partial\varphi}\left[\left(\frac{1}{\alpha}\frac{\partial V}{\partial\vartheta}+\frac{1}{\sin\vartheta}\frac{\partial V}{\partial\varphi}\right)W\right]\right\}, \tag{1.17.11}$$

which may be written in compact vector form as

$$\frac{\partial W}{\partial t}=k'\Delta W+\frac{h'}{\alpha}\mathbf{u}\cdot\left(\frac{\partial}{\partial\mathbf{u}}V\times\frac{\partial}{\partial\mathbf{u}}W\right)+h'\frac{\partial}{\partial\mathbf{u}}\cdot\left(W\frac{\partial}{\partial\mathbf{u}}V\right), \tag{1.17.12}$$

the angular part of the Laplacian Δ being as defined by Eq. (1.15.11). The terms in $h'\alpha^{-1}$ and h' are the *precessional* (gyromagnetic) term, giving rise to ferromagnetic resonance (usually in the GHz range), and the *alignment* term, respectively. The constant k' is evaluated by requiring that the Boltzmann distribution $W_0(\vartheta,\varphi)=Ae^{-vV(\vartheta,\varphi)/(kT)}$ of orientations (A is a normalizing constant) should be the stationary (equilibrium) solution of Eq. (1.17.11). The imposition of the Boltzmann distribution of orientations yields

$$k'=\frac{kTh'}{v}=\frac{1}{2\tau_{\mathrm{N}}}, \tag{1.17.13}$$

where

$$\tau_{\mathrm{N}}=\frac{vM_{\mathrm{S}}(1+\alpha^2)}{2kT\gamma\alpha} \tag{1.17.14}$$

is a characteristic (diffusion) relaxation time (τ_{N} is of the order of 10^{-10}–10^{-8} s). When $\alpha\to\infty$ (i.e., ignoring the gyromagnetic terms) Brown's equation, Eq. (1.17.11), has the same mathematical form as the rotational diffusion equation, Eq. (1.15.10).

Early studies of the magnetization relaxation process [58, 106] were mainly confined to the axially symmetric solutions of Eq. (1.17.11), i.e., when $V=V(\vartheta)$ and $W=W(\vartheta,t)$ (where the gyromagnetic terms automatically drop

out of the Fokker–Planck equation). An example is the calculation of the Néel superparamagnetic relaxation time (the time required to surmount the potential barrier) τ for uniaxial anisotropy for an applied field parallel to the easy axis. In this case the Néel relaxation time is determined by assuming that the process is dominated by a single relaxation mode (the barrier-crossing or Néel mode), i.e.,

$$\tau = 1/\lambda_1, \tag{1.17.15}$$

where λ_1 is the smallest non-vanishing eigenvalue of the Fokker–Planck operator in Eq. (1.17.11) when it is converted to a Sturm–Liouville problem [58, 106]. For axial symmetry, it is easy to convert Eq. (1.17.11) to a set of differential-recurrence relations [58, 106] by expanding the distribution function $W(\vartheta, t)$ as a series of zonal harmonics (Legendre polynomials). These may be arranged as an infinite set of linear equations [58]

$$\dot{\mathbf{X}}(t) = \mathbf{A}\mathbf{X}(t), \tag{1.17.16}$$

whence λ_1 may be determined as the smallest non-vanishing root of the characteristic equation

$$\det(\lambda\mathbf{I} - \mathbf{A}) = 0 \tag{1.17.17}$$

by taking a sufficiently large number of equations. The restriction to axial symmetry, so that only the zonal harmonics are involved, simplifies the problem of solving Eq. (1.17.11) in two important ways. (1) It radically simplifies the intricate manipulations of the spherical harmonics $Y_{l,m}(\vartheta,\varphi)$ [95] (see Chapter 7, Section 7.2.2), which are required in order to obtain the set of differential-recurrence relations. After simplification only one index l, the order of the spherical harmonics, is involved. (2) The restriction to the single index l reduces the number of equations to be solved in Eq. (1.17.16), thereby eliminating the loss of precision in floating-point calculations which so bedevils numerical calculations associated with the non-axially symmetric solutions [78, 112].

The two important problems, involving non-axially symmetric potentials, are: (i) *uniaxial anisotropy*, where the assumption that the applied field and anisotropy vector are collinear is abandoned (the potential of Eq. (1.16.5) is a special case of this, where the external magnetic field $\mathbf{H}_0$ is assumed to be applied along a line of longitude); and (ii) *cubic anisotropy*, in which V becomes

$$V(\vartheta,\varphi) = \frac{K}{4}(\sin^2 2\vartheta + \sin^4\vartheta\sin^2 2\varphi). \tag{1.17.18}$$

Here, the direction of the magnetization of a particle is always defined by the two polar angles ϑ and φ measured from one of the easy axes. Equation (1.17.18) is written for cubic anisotropy in zero applied field with {100} as the

easy axis where $K>0$. If the easy axis is $\{111\}$, the same expression can be used with $K<0$ [112]. For particles with cubic anisotropy, the energy barrier between adjacent easy directions of magnetization will appear in the exponent; the barrier is $Kv/4$ for $K>0$ and $|Kv|/12$ for $K<0$. We shall treat these non-axially symmetric problems in detail in Chapter 9.

1.18. Asymptotic expressions for the Néel relaxation time

At the time Brown was writing (1963), the lack of advanced computing facilities, without which λ_1 cannot be calculated from Eq. (1.17.17), compelled him to seek simple analytic formulas for λ_1 in the high-energy barrier approximation. This was accomplished by utilizing the Kramers escape-rate theory of Section 1.13, suitably modified for rotation in space and for a non-separable Hamiltonian (as we shall see in Section 1.18.2), as the Kramers theory had originally been formulated for translational Brownian motion of point particles.

1.18.1. *Magnetization reversal time in a uniaxial superparamagnet: application of Kramers' method*

The solution for the escape rate for an arbitrary potential of the magneto-crystalline anisotropy will be given in Section 1.18.2 using Langer's method. It is instructive, however, to first give the solution for the particular case of axially symmetric potentials, as this illustrates the application of Kramers' theory to the magnetic problem. Here, the escape rate has the interesting particular property that it is valid for all values of the damping parameter α, unlike the mechanical problem treated in Section 1.13. This is a consequence of the fact that in an axially symmetric potential $V(\vartheta)$, the Fokker–Planck equation (1.17.12) for the distribution function $W(\vartheta,t)$ is effectively a one-space-variable equation, viz.,

$$2\tau_N \frac{\partial W}{\partial t} = \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left[\sin\vartheta\left(\frac{\partial W}{\partial\vartheta}+W\frac{\partial V}{\partial\vartheta}\right)\right] \qquad (1.18.1.1)$$

(here the abbreviation $vV(\vartheta)/(kT)\rightarrow V(\vartheta)$ will be used). In Kramers' mechanical problem, on the other hand, the governing equation, namely the Klein–Kramers equation, is always an equation in a two-dimensional state space, and can only be converted to a one-dimensional equation in the limiting cases (VLD and IHD). We remark that the IHD case is only quasi one-dimensional, by virtue of the introduction of the variable $u=p-ax'$. In

magnetic relaxation, the three friction regimes of Kramers' problem, namely VLD, the crossover region, and IHD, will only appear when non-axially symmetric potentials are involved.

For an axially symmetric potential $V(\vartheta)$ with two wells at $\vartheta_1 = 0$ and $\vartheta_2 = \pi$ separated by a potential barrier at ϑ_m, we have $\partial J_\varphi / \partial \varphi = 0$ since $W = W(\vartheta)$. Hence referring to Eq. (1.17.9), and recalling that, in the quasi-stationary case $\dot{W} = 0$, the total current over the barrier $J = 2\pi J_\vartheta \sin\vartheta$ is constant. Thus, with Eq. (1.17.9) we obtain

$$\frac{\partial W}{\partial \vartheta} + \frac{\partial V}{\partial \vartheta} W = e^{-V} \frac{\partial}{\partial \vartheta}\left(e^{V} W\right) = -\frac{2\tau_{\mathrm{N}} J}{2\pi \sin\vartheta},$$

and so

$$e^{V(\vartheta)} W(\vartheta) = -\frac{\tau_{\mathrm{N}} J}{\pi} \int_{\vartheta}^{\vartheta_m} \csc\vartheta' e^{V(\vartheta')} d\vartheta'. \tag{1.18.1.2}$$

Suppose now that W vanishes at the barrier angle $\vartheta = \vartheta_m$ (i.e., particles which arrive at this boundary are no longer counted), so that $W(\vartheta_m) = 0$, i.e., all the particles are absorbed. Then

$$W(\vartheta) = -\frac{\tau_{\mathrm{N}} J}{\pi} e^{-V(\vartheta)} \int_{\vartheta}^{\vartheta_m} \csc\vartheta' e^{V(\vartheta')} d\vartheta' \tag{1.18.1.3}$$

and the number of particles N_i in the well i is

$$N_i = 2\pi \int_{\vartheta_i}^{\vartheta_m} W \sin\vartheta d\vartheta = -2\tau_{\mathrm{N}} J \int_{\vartheta_i}^{\vartheta_m} e^{-V(\vartheta)} \sin\vartheta \int_{\vartheta}^{\vartheta_m} \csc\vartheta' e^{V(\vartheta')} d\vartheta' d\vartheta. \tag{1.18.1.4}$$

Thus, the characteristic escape (mean first-passage) time $\tau(\vartheta_i)$ from the well i is, via the flux-over-population method [21,118],

$$\tau(\vartheta_i) \sim \frac{N_i}{J} = -2\tau_{\mathrm{N}} \int_{\vartheta_i}^{\vartheta_m} e^{-V(\vartheta)} \sin\vartheta \int_{\vartheta}^{\vartheta_m} \csc\vartheta' e^{V(\vartheta')} d\vartheta' d\vartheta.$$

On integrating by parts, we obtain

$$\tau(\vartheta_i) = 2\tau_{\mathrm{N}} \int_{\vartheta_i}^{\vartheta_m} \csc\vartheta' e^{V(\vartheta')} \int_{\vartheta_i}^{\vartheta'} e^{-V(\vartheta)} \sin\vartheta d\vartheta d\vartheta'. \tag{1.18.1.5}$$

This is the time to reach the top of the barrier, provided that all particles there are absorbed, which is the boundary condition that W vanishes at $\vartheta = \vartheta_m$. Equation (1.8.1.5) can also be derived using the mean first-passage time (MFPT) approach [21,118] (see also Chapter 12, Section 12.4.1) by solving the equation

$$L_{\mathrm{FP}}^{\dagger}\tau(\vartheta)=\frac{1}{2\tau_{\mathrm{N}}\sin\vartheta}\frac{\partial}{\partial\vartheta}\left[e^{V}\sin\vartheta\frac{\partial}{\partial\vartheta}e^{-V}\tau(\vartheta)\right]=-1$$

for $\tau(\vartheta)$ with appropriate boundary conditions; here $L_{\mathrm{FP}}^{\dagger}$ is the adjoint Fokker–Planck operator.

In practice, a particle has a 50:50 chance of crossing, which means that the corresponding Kramers escape rate Γ_i from the well i is given by

$$\Gamma_i \approx [2\tau(\vartheta_i)]^{-1}. \tag{1.18.1.6}$$

The integrals in Eq. (1.18.1.5) may be approximately evaluated using steepest descents [106, 118]. In order to accomplish this, we note that, for the exact time to go from the well at $\vartheta_1 = 0$ to the top of the barrier at $\vartheta = \vartheta_m$, we have

$$\tau(0)=2\tau_{\mathrm{N}}\int_0^{\vartheta_m}\csc\vartheta' e^{V(\vartheta')}\int_0^{\vartheta'}e^{-V(\vartheta)}\sin\vartheta d\vartheta d\vartheta'. \tag{1.18.1.7}$$

Employing Kramers' argument in the manner described in Refs. [106] and [118], the integral is now evaluated in the limit of very high potential barriers. Since almost all the particles (i.e., the population) are situated near the minimum at $\vartheta_1 = 0$, then ϑ is a very small angle. The well (inner) integral in Eq. (1.18.1.7) may then be evaluated using steepest descents, yielding the well population as

$$\int_{\text{near }\vartheta_i} e^{-V(\vartheta)}\sin\vartheta d\vartheta \approx \int_0^{\infty}\vartheta e^{-[V(0)+V''_{\vartheta\vartheta}(0)\vartheta^2/2]}d\vartheta \sim \frac{e^{-V(0)}}{V''_{\vartheta\vartheta}(0)}. \tag{1.18.1.8}$$

The integral may be extended to infinity without significant error, since the particles are almost all at the origin. Likewise, near the barrier ϑ_m, the Taylor series in $V(\vartheta)$ can be approximated by its first two non-vanishing terms $V(\vartheta)\approx V(\vartheta_m)-\left|V''_{\vartheta\vartheta}(\vartheta_m)\right|(\vartheta-\vartheta_m)^2/2$. Hence, we have for the outer integral

$$\int_{\text{near }\vartheta_m}\csc\vartheta' e^{V(\vartheta')}d\vartheta' \approx \frac{e^{V(\vartheta_m)}}{\sin\vartheta_m}\int_{-\infty}^{\vartheta_m} e^{-\left|V''_{\vartheta\vartheta}(\vartheta_m)\right|[\vartheta'-\vartheta_m]^2/2}d\vartheta' \tag{1.18.1.9}$$

(here the range of integration in Eq. (1.18.1.9) may be extended to $-\infty$ since the integral has its main contribution from values near to ϑ_m and almost no contribution lying outside these values). Because

$$\int_{-\infty}^{\mu} e^{-(x-\mu)^2/(2\sigma^2)}dx = \sigma\sqrt{\frac{\pi}{2}}, \tag{1.18.1.10}$$

we have

$$\int_{\text{near }\vartheta_m}\csc\vartheta' e^{V(\vartheta')}d\vartheta' \sim \frac{\sqrt{\pi}}{\sin\vartheta_m\sqrt{2\left|V''_{\vartheta\vartheta}(\vartheta_m)\right|}}e^{-V(\vartheta_m)}.$$

Hence, in the *high-barrier limit*, the mean first-passage time $\tau(0)$ for transitions from the point domain ($\vartheta = 0$) is

$$\tau(0) \sim \frac{\tau_N}{V''_{\vartheta\vartheta}(0)} \frac{\sqrt{2\pi}}{\sqrt{|V''_{\vartheta\vartheta}(\vartheta_m)|}} \frac{e^{V(\vartheta_m)-V(0)}}{\sin\vartheta_m}. \tag{1.18.1.11}$$

Likewise, the time to go from the minimum at $\vartheta_2 = \pi$ to ϑ_m is

$$\tau(\pi) = 2\tau_N \int_{\vartheta_m}^{\pi} \frac{1}{\sin\vartheta'} e^{V(\vartheta')} d\vartheta' \int_{\vartheta'}^{\pi} e^{-V} \sin\vartheta d\vartheta, \tag{1.18.1.12}$$

which can be estimated in the high-barrier approximation as

$$\tau(\pi) \sim \frac{\tau_N}{V''_{\vartheta\vartheta}(\pi)} \frac{\sqrt{2\pi}}{\sqrt{|V''_{\vartheta\vartheta}(\vartheta_m)|}} \frac{e^{V(\vartheta_m)-V(\pi)}}{\sin\vartheta_m}. \tag{1.18.1.13}$$

These are the times to reach the barrier from the debth of the well. According to Eq. (1.16.7), the corresponding reversal time of the magnetization τ is, in the high-barrier limit, given by

$$\tau \approx (\Gamma_1 + \Gamma_2)^{-1} = \left(\frac{1}{2\tau(0)} + \frac{1}{2\tau(\pi)}\right)^{-1} = \frac{2\tau(0)\tau(\pi)}{\tau(0)+\tau(\pi)}. \tag{1.18.1.14}$$

For example, for the axially symmetric potential $V = \sigma(\sin^2\vartheta - 2h\cos\vartheta)$, cf. Eq. (1.16.2), we have, from Eqs. (1.18.11)–(1.18.14) (details in [118]),

$$\tau \sim \frac{\tau_N\sqrt{\pi}}{\sigma^{3/2}(1-h^2)}\left[(1+h)e^{-\sigma(1+h)^2} + (1-h)e^{-\sigma(1-h)^2}\right]^{-1}, \tag{1.18.1.15}$$

[$\sigma = vK/(kT)$ and $h = M_S H/(2K)$], which in the limit $h \to 0$, reduces to

$$\tau = \frac{\tau_N\sqrt{\pi}e^{\sigma}}{2\sigma^{3/2}}. \tag{1.18.1.16}$$

Equation (1.18.1.16) is Brown's asymptotic formula [106] for the reversal time of the magnetization for uniaxial superparamagnets. For arbitrary barrier heights, the mean first-passage time, Eq. (1.18.1.14), yields [118]

$$\tau_{\mathrm{MFPT}}^{-1} = \frac{1}{4\tau_N}\left[\left(\int_{-1}^{-h} \frac{e^{-\sigma(z^2+2hz)}}{1-z^2} \int_{-1}^{z} e^{\sigma(z'^2+2hz')} dz'dz\right)^{-1}\right.$$
$$\left. + \left(\int_{-h}^{1} \frac{e^{-\sigma(z^2+2hz)}}{1-z^2} \int_{z}^{1} e^{e^{\sigma(z'^2+2hz')}} dz'dz\right)^{-1}\right]. \tag{1.18.1.17}$$

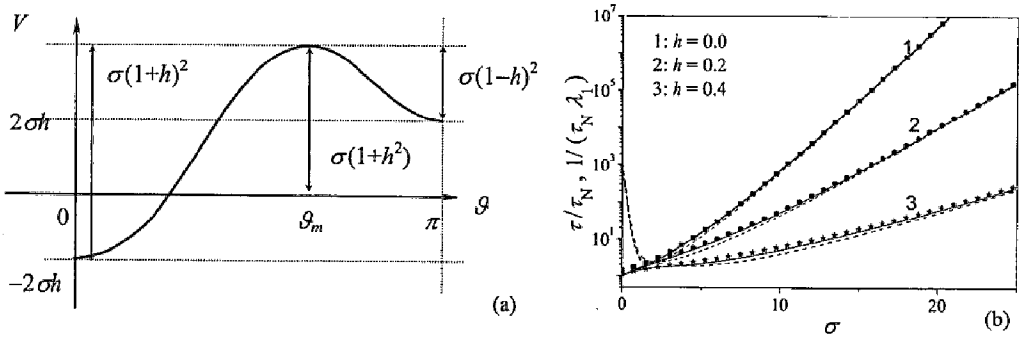


Figure 1.18.1.1. (a) The profile of the uniaxial potential $V = \sigma(\sin^2\vartheta - 2h\cos\vartheta)$, showing a maximum at $\vartheta = \vartheta_m = \arccos(-h)$ and minima at $\vartheta = 0$ and π. Particles in the shallower well are inhibited from crossing into the deeper well by the potential barrier of height $\sigma(1-h)^2$. The particles populating the deeper of the two wells, however, must possess greater thermal energy to be able to cross over into the shallower well, owing to the elevated potential barrier height denoted by $\sigma(1+h)^2$. (b) Reversal time of the magnetization τ vs. σ (inverse temperature parameter) for $h = 0$, 0.2, and 0.4. Solid lines: numerical calculation of the inverse of the smallest non-vanishing eigenvalue of the Fokker–Planck operator λ_1 (see Chapter 9, Section 9.3). Dashed lines: Brown's asymptotic equation, Eq. (1.18.1.15). Symbols: the MFPT equation, Eq. (1.8.1.17).

As can be seen in Fig. 1.18.1.1, Eq. (1.18.1.17) provides a good approximation for the reversal time $\tau \approx \lambda_1^{-1}$ for any barrier height, while Eq. (1.18.1.15) allows one to estimate τ for $\sigma \geq 3$. We shall return to Eqs. (1.18.1.15) and (1.18.1.17) later, in Chapter 9.

We now consider non-axially symmetric problems, so that the various cases (IHD, VLD, etc.) of the Kramers calculation will appear.

1.18.2. *Escape rate formulas for superparamagnets*

The application of Kramers' escape theory to superparamagnetic relaxation in the IHD limit has been given in detail by Smith and de Rozario [119], Brown [112], Klik and Gunther [120], and Geoghegan *et al.* [78] (all this work is described in Ref. [44]). Klik and Gunther [120] used Langer's method (described in Section 1.13) and realized that the various Kramers damping regimes also applied to magnetic relaxation of single-domain ferromagnetic particles.

In this section, we show in detail how Langer's method may be used to solve this problem. Again, we deal with an energy (or Hamiltonian) function, $E = V(\vartheta, \varphi)$, with minima at points A and B separated by a barrier (saddle point) at C (see Fig. 1.13.1). We use spherical polar coordinates (ϑ, φ), where ϑ

is the polar angle and φ is the azimuthal angle as usual. The noiseless Gilbert equation, Eq. (1.17.6), takes the form in the coordinates $(p = \cos\vartheta, \varphi)$ [112]

$$\dot{p} = -h'(1-p^2)\partial_p V - h'\alpha^{-1}\partial_\varphi V, \tag{1.18.2.1}$$

$$\dot{\varphi} = h'\alpha^{-1}\partial_p V - h'(1-p^2)^{-1}\partial_\varphi V, \tag{1.18.2.2}$$

where subscripts denote the partial derivatives. We linearize these equations about the saddle point and determine λ_+ from the transition matrix as in the Klein–Kramers case of Section 1.13.6. Thus, expanding the Hamiltonian $V(p,\varphi)$ as a Taylor series about the saddle point $(p_C = \cos\vartheta_C, \varphi_C)$, we obtain

$$V = V_0 + \frac{1}{2}\left[V_{pp}^{(0)}(p-p_C)^2 + 2V_{p\varphi}^{(0)}(p-p_C)(\varphi-\varphi_C) + V_{\varphi\varphi}^{(0)}(\varphi-\varphi_C)^2\right], \tag{1.18.2.3}$$

with the superscript (0) denoting evaluation at the saddle point. We remark, following Klik and Gunther [120], that the Hamiltonian is defined on a phase space which is a closed manifold (the space (ϑ, φ) is the surface of a unit sphere) and that a local energy minimum is thus surrounded by two or more saddle points, depending on the symmetry of the problem. The total probability flux away from the metastable minimum equals the sum of the fluxes through all the saddle points. In asymmetric cases, e.g., when an external field is applied, some of these fluxes become exponentially small and may safely be neglected. The total flux away from the metastable minimum is then dominated by the energetically most favorable path. Now, if the coordinates of the saddle point are (φ_C, p_C), we have

$$\frac{\partial V}{\partial p} = (p-p_C)V_{pp}^{(0)} + (\varphi-\varphi_C)V_{p\varphi}^{(0)}, \tag{1.18.2.4}$$

$$\frac{\partial V}{\partial \varphi} = (p-p_C)V_{p\varphi}^{(0)} + (\varphi-\varphi_C)V_{p\varphi}^{(0)}. \tag{1.18.2.5}$$

Now, let the saddle point C of interest lie on the equator $p = 0$ and make the transformation $\varphi - \varphi_C \to \varphi$. Equations (1.18.2.1) and (1.18.2.2) then become in matrix notation

$$\begin{pmatrix}\dot{\varphi}\\ \dot{p}\end{pmatrix} = h'\begin{pmatrix}-1 & \alpha^{-1}\\ -\alpha^{-1} & -1\end{pmatrix}\begin{pmatrix}\dfrac{\partial V}{\partial \varphi}\\ \dfrac{\partial V}{\partial p}\end{pmatrix}. \tag{1.18.2.6}$$

Thus, the linearized Eq. (1.18.2.6) has the form of the canonical Eqs. (1.13.5.4), and so Langer's equation, Eq. (1.13.5.29), may be used to calculate the IHD

escape rate. In particular, the transport matrix $\mathbf{M}$ and the matrix $\tilde{\mathbf{M}}$ (see Section 1.13.5) are given by

$$\mathbf{M} = h'\begin{pmatrix} 1 & -\alpha^{-1} \\ \alpha^{-1} & 1 \end{pmatrix}, \qquad \tilde{\mathbf{M}} = h'\begin{pmatrix} -1 & -\alpha^{-1} \\ \alpha^{-1} & -1 \end{pmatrix}.$$

The equations of motion (1.18.2.6) linearized at the saddle point become [120]

$$\begin{pmatrix} \dot{\varphi} \\ \dot{p} \end{pmatrix} = h'\begin{pmatrix} \alpha^{-1}V_{p\varphi}^{(0)} - V_{\varphi\varphi}^{(0)} & \alpha^{-1}V_{pp}^{(0)} - V_{p\varphi}^{(0)} \\ -V_{p\varphi}^{(0)} - \alpha^{-1}V_{\varphi\varphi}^{(0)} & -V_{pp}^{(0)} - \alpha^{-1}V_{p\varphi}^{(0)} \end{pmatrix}\begin{pmatrix} \varphi \\ p \end{pmatrix}. \qquad (1.18.2.7)$$

Equations (1.18.2.7) are the noiseless Langevin equations given by Klik and Gunther; see Ref. [120], Eq. (3.2). The secular equation of Eq. (1.18.2.7) then (as in Section 1.13.6) yields

$$\lambda_{\pm} = h'\left\{-\frac{V_{pp}^{(0)} + V_{\varphi\varphi}^{(0)}}{2} \pm \sqrt{\left(\frac{V_{pp}^{(0)} + V_{\varphi\varphi}^{(0)}}{2}\right)^2 - \frac{1+\alpha^2}{\alpha^2}\left[V_{pp}^{(0)}V_{\varphi\varphi}^{(0)} - \left(V_{p\varphi}^{(0)}\right)^2\right]}\right\}. \qquad (1.18.2.8)$$

The Hessian matrix of the system is

$$\begin{pmatrix} V_{\varphi\varphi} & V_{p\varphi} \\ V_{p\varphi} & V_{pp} \end{pmatrix}, \qquad (1.18.2.9)$$

and the Hessian itself is *negative* at the saddle point. Thus, to ensure a growing disturbance at the saddle point, we must again take the positive sign in Eq. (1.18.2.8). Now the well angular frequency is defined as

$$\omega_i = \frac{\gamma}{M_S}\sqrt{V_{pp}^{(i)}V_{\varphi\varphi}^{(i)} - (V_{p\varphi}^{(i)})^2}, \qquad (1.18.2.10)$$

the superscript (i) denoting evaluation at the minimum of well i, while the saddle angular frequency is

$$\omega_0 = \frac{\gamma}{M_S}\sqrt{\left|V_{pp}^{(0)}V_{\varphi\varphi}^{(0)} - (V_{p\varphi}^{(0)})^2\right|}, \qquad (1.18.2.11)$$

which, with Eq. (1.13.5.29), leads to the Klik and Gunther result [120]

$$\Gamma = \frac{\lambda_+\omega_i}{2\pi\omega_0}e^{-\frac{v(V_0 - V_i)}{kT}}. \qquad (1.18.2.12)$$

This formula demonstrates the wide-ranging uses of Langer's method and shows clearly how, once the potential landscape is known, the IHD escape rate may be

calculated. If we now choose a local coordinate system (φ, p) at the saddle point, where $V_{p\varphi}=0$, then we obtain a more compact expression for λ_+, namely

$$\lambda_+ = \frac{h'}{2}\left\{ -\left[V_{pp}^{(0)} + V_{\varphi\varphi}^{(0)}\right] + \sqrt{[V_{pp}^{(0)} - V_{\varphi\varphi}^{(0)}]^2 - 4\alpha^{-2} V_{pp}^{(0)} V_{\varphi\varphi}^{(0)}} \right\}, \quad (1.18.2.13)$$

where we observe that the α^{-2} term represents the effect of the precessional term in the Gilbert equation on the longitudinal relaxation. This *mode coupling effect* is always present in a non-axially symmetric potential, as the smallest eigenvalue of the Fokker–Planck equation will always *intrinsically* depend on the damping. This is unlike axial symmetry, where the damping only enters via the free diffusion time.

Equations (1.18.2.12) and (1.18.2.13) were also derived from first principles directly using Kramers' escape-rate theory, without recourse to Langer's work, by Smith and de Rozario [119] and Brown [112], and have been reviewed by Geoghegan *et al.* [78]. In Brown's calculation [112], the free energy density is diagonalized so that, in the vicinity of the saddle point and minimum, respectively, we have [78]

$$V = V_0 + \frac{1}{2}\left(c_1^{(0)}\varphi^2 + c_2^{(0)} p^2\right) \text{ and } V = V_i + \frac{1}{2}\left(c_1^{(i)}\varphi^2 + c_2^{(i)} p^2\right), \quad (1.18.2.14)$$

where $c_1^{(0)}$ and $c_2^{(0)}$ are the coefficients of the second-order term of the Taylor series of the expansion of H at the saddle point, and $c_1^{(i)}$ and $c_2^{(i)}$ are the coefficients of the second-order term in the Taylor series expansion of the energy in the well. Thus Brown's IHD result for the escape rate [112] reads

$$\Gamma_i = \frac{\Omega_0 \omega_i}{2\pi\omega_0} e^{-v(V_0 - V_i)/kT}, \quad (1.18.2.15)$$

where

$$\Omega_0 = \frac{h'}{2}\left[-c_1^{(0)} - c_2^{(0)} + \sqrt{(c_2^{(0)} - c_1^{(0)})^2 - 4\alpha^{-2} c_1^{(0)} c_2^{(0)}}\right] \quad (1.18.2.16)$$

is the damped saddle angular frequency (see Eq. (5.60) of Geoghegan *et al.* [78], where a detailed derivation is given). Obviously Brown's equation, Eq. (1.18.2.15), coincides with Eq. (1.18.2.12).

We remark that the magnetization reversal time problem differs fundamentally from that of point particles, because: (i) the magnetic system has two degrees of freedom, the polar ϑ and azimuthal φ angles, (ii) the undamped equation of motion of the magnetization of a single-domain ferromagnetic particle is the gyromagnetic equation, (iii) the Hamiltonian is non-separable, and (iv) the inertial effects play no role. Notwithstanding these differences, the role

of inertia in the mechanical system is essentially mimicked in the magnetic system for non-axially symmetric potentials by the gyromagnetic term, causing *coupling* or *entanglement* of the transverse and longitudinal modes. Hence, in order to derive escape-rate formulas for superparamagnetic particles equivalent to those for mechanical particles, one has to consider, in Brown's Fokker–Planck equation, a non-axially symmetric free energy density $V(\vartheta,\varphi)$, where explicit coupling between the two degrees of freedom exists. Thus both regimes of damping (IHD and VLD) can now occur, reflecting the fact that the dynamics of the transverse response affect the dynamics of the longitudinal response, and vice versa. This was first realized in 1990 by Klik and Gunther [120]. They showed that the various Kramers damping regimes also apply to the magnetic relaxation of single-domain ferromagnetic particles, and derived the corresponding VLD formula. Furthermore, they also realized that the magnetic IHD calculations [112, 119] are, as described above, a special case of Langer's general treatment of the decay of metastable states of systems with many degrees of freedom [73]. They therefore understand why Eq. (1.18.2.15), which is derived for a *non-separable* Hamiltonian and is the free energy, behaves like the *separable* Hamiltonian result, Eq. (1.13.1.18), when the energy loss per cycle of the almost-periodic, noise-perturbed motion at the saddle point energy $\alpha S_i >> 1$. If $\alpha S_i << 1$, one may prove, using first-passage times (details in [44]), that for the escape from a single well

$$\Gamma_i = \Gamma_i^{\mathrm{VLD}} \sim \frac{\alpha S_i \omega_i}{2\pi} e^{-\frac{v(V_0 - V_i)}{kT}}, \qquad (1.18.2.17)$$

where

$$S_i = \frac{v}{kT} \oint_{E_C} \left[\left(1-p^2\right) \partial_p V d\varphi - \left(1-p^2\right)^{-1} \partial_\varphi V dp \right] \qquad (1.18.2.18)$$

is the dimensionless action. Equation (1.18.2.17) is effectively the same as the corresponding Kramers result for point particles, Eq. (1.13.2.13). The conditions of applicability of the IHD and VLD solutions for superparamagnets are defined by $\alpha \gtrsim 1$ and $\alpha << 1$, respectively.

Later, Coffey *at al.* [44, 121] have shown that the Mel'nikov–Meshkov formalism, connecting the VLD and IHD Kramers escape rates as a function of the dissipation parameter for mechanical particles (Section 1.13.7), can be extended to include the magnetization relaxation of single-domain ferromagnetic particles having non-axially symmetric potentials of the magnetocrystalline anisotropy. The equation bridging the VLD and IHD escape rates is given by [44, 121]

$$\Gamma_i = A(\alpha S_i)\Gamma_i^{\mathrm{IHD}}, \tag{1.18.2.19}$$

where $A(\Delta)$ is the depopulation factor, Eq. (1.13.7.46), which interpolates between the VLD and ID regimes. Noting that

$$A(\Delta) \to 1 \text{ as } \Delta \to \infty \text{ and } A(\Delta)/\Delta \to 1 \text{ as } \Delta \to 0, \tag{1.18.2.20}$$

one may show that Eq. (1.18.2.19) reduces, in the IHD and VLD limits, to Eqs. (1.18.2.15) and (1.18.2.17), respectively.

We remark that Eqs. (1.18.2.15), (1.18.2.17), and (1.18.2.19) may be used to verify experimentally the Kramers theory for magnetic particles. This has been accomplished using the sophisticated single-particle measurement techniques developed by Wernsdorfer [63]. We further remark that a second interpolation problem arises in the magnetic version of the Kramers escape rate, namely how to join axially asymmetric and non-axially symmetric asymptotic expressions for the greatest relaxation time, in the limit of small departures from axial symmetry. This problem has been described in detail in Refs. [44, 122] by considering the asymptotes generated by Eq. (1.16.5) for $\psi = 0$ and $\psi \neq 0$. We emphasize that, in the derivation of all these formulas, it is assumed that the potential is non-axially symmetric. If the departures from axial symmetry become small, the non-axially symmetric asymptotic formulas for the escape rate may be smoothly connected to the axially symmetric formulas, by means of suitable interpolation integrals [44].

We shall also return, in Sections 1.20 and 1.21, to the Kramers theory in connection with two important effects which occur in bistable potentials. These are: (i) the effect of a uniform bias force on the relaxation time, and (ii) the stochastic resonance phenomenon. In the meantime, we shall briefly indicate how the formulas we developed in Sections 1.15 and 1.18 may be applied to ferrofluids.

1.19. Ferrofluids

Ferrofluids are [109] *stable colloidal suspensions* of *single-domain* magnetic particles in a *liquid carrier*. These liquids are composed of small (~150 Å) particles of ferromagnetic material, coated with a molecular layer of a surfactant, and suspended in an ordinary liquid. The coatings prevent the particles from sticking to each other, and thermal agitation keeps them suspended because of the ensuing Brownian motion.

The simplest model of a magnetic fluid is considered as a gas of non-interacting ferroparticles suspended in a liquid carrier. The magnetic properties

of such a system are analogous to those of a paramagnetic gas, i.e., the magnetization curve is described by the Langevin function, the static susceptibility, χ, by Curie's law $\chi \sim T^{-1}$, and its dispersion by the Debye formula

$$\frac{\chi(\omega)}{\chi} = \frac{1}{1+i\omega\tau_c},$$

where τ_c is a characteristic relaxation time. In ferrofluids, both Debye relaxation with the Debye relaxation time τ_D (due to mechanical rotation of the fluid particles; cf. Section 1.15) and Néel relaxation with a characteristic time τ (due to rotation of the magnetic moment inside the particle) may occur. Theoretical studies have assumed [109] for the most part that the Debye and Néel mechanisms may be treated *separately*, i.e., one has two extreme types of behavior: (a) the Debye relaxation mechanism, where the Néel relaxation mechanism is *blocked* or *frozen* in the particle, and (b) where the *mechanical rotation* of the particles is *frozen* and only the Néel mechanism is operative. The overall characteristic relaxation time τ_c is then supposed to obey the equation

$$\tau_c = \frac{\tau\tau_D}{\tau+\tau_D}. \tag{1.19.1}$$

A popular formula used in analysis, for example, is Brown's axially symmetric formula for the superparamagnetic relaxation time τ, Eq. (1.18.1.16), combined with the Debye time τ_D. The relaxation process has been described succinctly in Ref. [109] as follows:

> "There is a finite coupling between the orientation of the magnetic moment $\boldsymbol{\mu}$ of a ferroparticle and the position of the particle itself (orientation of its crystal axes). Without this coupling the moment $\boldsymbol{\mu}$ would be similar to a compass needle, where rotation of the instrument frame does not influence the behavior. Because of the above coupling, the reorientation of the vector $\boldsymbol{\mu}$ may take place in two different ways: (1) rotation of $\boldsymbol{\mu}$ within the particle with respect to its crystal axes, and (2) rotation of $\boldsymbol{\mu}$ together with the particle with respect to the liquid matrix. Both processes – they proceed simultaneously – are of the rotary diffusion type. The efficiency of the internal (Néel) diffusion of the magnetic moment strongly depends on particle size, but that of the external one (the Brownian) depends strongly on the viscosity of the liquid carrier."

Along with these processes, two other factors are of great importance:

- *Polydispersedness of ferrofluids.* The actual distribution of the particle size in colloids results in a moderate (1–2 orders of magnitude) extension of the Debye relaxation spectrum, and an enormous (up to 13–15 orders!) extension of the Néel relaxation spectrum. Averaging with a particle-size

distribution function may change the low-frequency Debye susceptibility $\chi(\omega)$ unrecognizably.

- *Blocking of the rotational degrees of freedom of the particles on solidification of a carrier liquid.* As the liquid matrix freezes, the suspended particles lose their mechanical mobility. The Debye relaxation mechanism thus becomes ineffective.

We reiterate that one of the outstanding advantages of the ferrofluid system, as opposed to polar molecules, as a test of the Debye theory of relaxation, is that unlike electric dipoles, the ferrofluid particles closely approximate in size to actual Brownian particles. Thus the conditions for the validity of the Debye theory are more closely satisfied by the ferrofluid particles.

Thus, a major development in the theory of ferrofluids would be a model of particle reorientation which avoids the two extremes of a *frozen* Debye or a *frozen* Néel mechanism, instead taking account of both mechanisms *simultaneously*. Such a development has been inspired [123] by the discoveries of Fannin *et al.* [124, 125], which suggests that both relaxation and ferromagnetic resonance behavior appear in magnetic fluids. The "egg" model of magnetic fluids [109, 123], which is a form of the itinerant oscillator model (and is treated in Chapter 11), represents an attempt to consider the composite behavior.

1.20. Depletion effect in a biased bistable potential

If we have a random variable, the quantities of interest are its expectation value and its variance, and, as far as the dynamics are concerned, the autocorrelation function (ACF) (Section 1.6). The ACF measures the correlation between the value of a random variable at time $t_1 = 0$, and its value at time $t_2 = t$. It may be shown from linear response theory [59] (see Chapter 2, Section 2.8) that the decay of the magnetization of a superparamagnet following a small change ΔH in the applied field directed along the easy axis is $M_{\|}(t) = M_0 C(t)$, where $M_0 = v\Delta H M_S / (kT)$ and

$$C(t) = \langle \cos \vartheta(0) \cos \vartheta(t) \rangle_0 - \langle \cos \vartheta(0) \rangle_0^2 \qquad (1.20.1)$$

is the ACF of the longitudinal component of the magnetization. The zeros on the angular braces represent the averages in the absence of the small perturbation ΔH. Clearly, if we set $t = 0$, we have

$$C(0) = \langle \cos^2 \vartheta(0) \rangle_0 - \langle \cos \vartheta(0) \rangle_0^2 . \qquad (1.20.2)$$

This is the variance of the magnetization. Moreover, the process is assumed to be stationary, which means that the statistics describing the process do not change over the course of time.

The pertinent property of the ACF is the integral relaxation time τ_{int} defined as the normalized area under the curve of $C(t)$, viz.,

$$\tau_{\text{int}} = \frac{1}{C(0)} \int_0^\infty C(t)dt, \tag{1.20.3}$$

which is identical with the correlation time of linear response theory (see Chapter 2, Section 2.9). The integral relaxation time includes the contributions of all the modes of the decay of the magnetization, and so is a *global* characteristic of the relaxation process. In order to evaluate τ_{int}, we would in principle have to determine all the eigenvalues λ_k $(k = 1, 2, ...)$ of the Fokker–Planck operator (or, equivalently, the eigenvalues of the hierarchy of recurrence relations generated by the Langevin equation averaged over its realizations), which may be accomplished by solving the recurrence relations generated by the Fokker–Planck or averaged Langevin equations. However, in Section 1.18.1, we have shown how the escape time $\tau = \lambda_1^{-1}$ associated with the longest-lived mode (λ_1 is the smallest non-vanishing eigenvalue) may be derived using the method of mean first-passage times. Moreover, the integral relaxation time τ_{int} is virtually identical with the escape time τ if the configuration of the system is such that the contributions of all the other modes, save the longest lived one, are negligible. In other cases, however, τ_{int} may differ exponentially from τ, and so may not be used to estimate the escape time. The two characteristic times, τ and τ_{int} have been extensively discussed in Refs. [44, 118, 126–129], and will be described in more detail later.

Here, it will be sufficient to consider the integral relaxation time in a biased bistable potential

$$V(\vartheta) = -\sigma(\cos^2 \vartheta + 2h \cos \vartheta) = -\sigma \cos^2 \vartheta - \xi \cos \vartheta \tag{1.20.4}$$

shown in Fig. 1.18.1, as we now describe. Now the population in the shallower of the two potential wells may be substantially decreased by the application of the uniform bias force. This has a profound effect on τ_{int} because, at a certain critical value of the bias force (which is much less than that required to destroy the bistable character of the potential), a switchover of τ_{int} from Arrhenius to non-Arrhenius behavior will take place. The effect was originally discovered for magnetic relaxation in 1995 by Coffey *et al.* [127] (see Chapter 9, Section 9.3.2) for the biased uniaxial anisotropy potential Eq. (1.20.4) by numerical solution of the Fokker–Planck equation (1.18.1.1). The solution of that equation for τ_{int}

indicated that, at fields well below the critical field at which the bistable character of the potential is destroyed, the integral relaxation time ceases to be dominated by the smallest non-vanishing eigenvalue λ_1. Thus, the escape time τ no longer dominates τ_{int} for bias fields in excess of a certain critical field. Hence, the *contribution of relaxation modes to* τ_{int}, *other than the barrier-crossing mode, becomes significant.* The effect was later explained by Garanin [126]. It appears to be a universal feature of the relaxation in biased bistable potentials [127, 128] (see also [118] for a review). In the analysis which follows, however, we shall demonstrate, using the magnetic anisotropy potential of Eq. (1.20.4), that the effect, while *dependent on* the potential shape, is essentially *independent of* the precise nature of the prefactor in the Kramers escape rate, and may be predicted by the transition-state theory coupled with the definition of the integral relaxation time and the partition function.

Following the elegant exposition of Garanin [126], we begin our approximate calculation of τ_{int} by recalling that escape over the barrier in an asymmetric bistable potential is a very slow process, and the time dependence of the PDF is exponentially slow. This quasi-stationary behavior (to all extents and purposes, the behavior of the system appears stationary) allows us to make use of the partition function to calculate the dynamical quantities pertaining to the overbarrier relaxation process, and ultimately to characterize the depletion effect. If the barrier is high, we may suppose [126, 128] that $C(t)$ is the sum of the fast relaxation processes in the deep well plus the slow overbarrier process from the shallower well into the deep well, so that $C(t)$ may be approximated as (see Chapter 2, Section 2.13)

$$C(t) \approx \Delta_{\text{W}} e^{-t/\tau_{\text{W}}} + \Delta_{\text{B}} e^{-\lambda_1 t}, \tag{1.20.5}$$

where Δ_{W} is the population of particles in the deep well and Δ_{B} arises from the population of particles crossing over the barrier. The relaxation time τ_{W} is associated with the fast relaxation processes in the well. The inverse of the well time τ_{W}^{-1} is approximately equal to [126]

$$2\sigma\tau_{\text{N}}^{-1}(1+h).$$

This equation holds because all the intra-well modes have approximately the same relaxation time, which is just the diffusion time divided by the effective barrier height while λ_1 is essentially proportional to $e^{-\sigma(1-h)^2}$; see Eq. (1.18.1.15). It represents the escape rate over the barrier from the shallower of the two wells.

The simple analytical expression Eq. (1.20.5) may be used to determine the integral relaxation time, whence the depletion effect may be explained using

approximate expressions for the partition function. We proceed as follows. We have, from Eqs. (1.20.4) and (1.20.5),

$$\tau_{\text{int}} \approx \frac{1}{C(0)} \int_0^\infty \left(\Delta_{\text{W}} e^{-t/\tau_{\text{W}}} + \Delta_{\text{B}} e^{-\lambda_1 t} \right) dt = \frac{\tau_{\text{W}} \Delta_{\text{W}} + \Delta_{\text{B}} / \lambda_1}{\Delta_{\text{W}} + \Delta_{\text{B}}}. \tag{1.20.6}$$

Because escape over a barrier is a slow process, i.e., few particles escape due to the height of the barrier, it follows that $\Delta_{\text{B}} >> \Delta_{\text{W}}$; thus we can write

$$\tau_{\text{int}} = \tau_{\text{W}} + (\Delta_{\text{B}} / \Delta_{\text{W}}) \lambda_1^{-1}. \tag{1.20.7}$$

Since λ_1^{-1} is exponentially large in the high-barrier limit, one would expect that τ_{int} would be dominated by the second term, unless $\Delta_{\text{B}} / \Delta_{\text{W}}$ has negative exponential type behavior so that τ_{int} would be dominated by the fast relaxation time τ_{W}. We shall show that this is indeed the case if the reduced field h exceeds a critical value [126, 128], and we shall further show that the behavior is *independent* of the precise nature of the prefactor.

To illustrate this, we will derive an expression for the total population $\Delta_{\text{W}} + \Delta_{\text{B}}$ based on our analysis of the ensemble averages using the partition function. We have, from Eqs. (1.20.3) and (1.20.5),

$$\Delta_{\text{W}} + \Delta_{\text{B}} = \langle z^2 \rangle_0 - \langle z \rangle_0^2 \tag{1.20.8}$$

with $z = \cos \vartheta$. We can evaluate $\langle z \rangle_0$ and $\langle z^2 \rangle_0$ in terms of the partition function Z given by

$$Z = \int_{-1}^{1} e^{\sigma z^2 + \xi z} dz. \tag{1.20.9}$$

We have [126]

$$\langle z \rangle = \frac{1}{Z} \frac{\partial Z}{\partial \xi} = \frac{Z'}{Z} \text{ and } \langle z^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \xi^2} = \frac{Z''}{Z}. \tag{1.20.10}$$

Substituting these expressions in Eq. (1.20.8), we have the total population

$$\Delta_{\text{W}} + \Delta_{\text{B}} = Z'' / Z - (Z' / Z)^2. \tag{1.20.11}$$

The right-hand side of this equation is formally an exact expression for the variance.

Thus, the vital quantity in calculating averages (and hence the integral relaxation time), is the partition function Z from Eq. (1.20.9). We shall now indicate, using the asymptotic results, how approximate expressions for Z may be calculated for the biased uniaxial potential, Eq. (1.20.1), expressions which of course hold for potential barrier heights well in excess of kT. We have, from Eq. (1.20.10) evaluated at the i^{th} minimum, $i = 1, 2$, (see Eq. (1.18.1.8))

$$Z(\vartheta_i) \sim e^{-V(\vartheta_i)} / \partial^2_{\vartheta\vartheta} V(\vartheta_i). \tag{1.20.12}$$

We now take the second derivative of the potential, and make the appropriate substitutions for the numerator and denominator. Thus we can express Z in terms of the dimensionless anisotropy and external field parameters σ and ξ, respectively. Because (following Ref. [126])

$$\partial^2_{\vartheta\vartheta} V = 2\sigma \cos 2\vartheta + \xi \cos \vartheta,$$

evaluating Eq. (1.20.12) at $\vartheta = 0$ will yield an expression for the portion of the overall partition function (population) corresponding to the deeper well, which we call $Z_+ = e^{\sigma+\xi} / (2\sigma + \xi)$. If we evaluate Eq. (1.20.12) at $\vartheta = \pi$, where the particles are located in the shallower well, we will find the portion of the overall partition function corresponding to the shallower well, which we call $Z_- = e^{\sigma-\xi} / (2\sigma - \xi)$. The overall partition function, however, is effectively the sum of these two individual contributions, i.e., $Z \approx Z_+ + Z_-$. The asymptotic method which we have employed is useful since it is difficult to evaluate the integrals exactly when anisotropy is included, because they are not expressible as elementary functions. (The exact solution for Z can be expressed in terms of the error functions of imaginary argument [118]).

The *total* population $\Delta_B + \Delta_W$ can now be evaluated using our high-barrier approximation for Z,

$$\Delta_W + \Delta_B = \frac{Z_+'' + Z_-''}{Z_+ + Z_-} - \left(\frac{Z_+' + Z_-'}{Z_+ + Z_-} \right)^2. \tag{1.20.13}$$

The essence of our calculation is also to evaluate $\Delta_B + \Delta_W$ from our *separate* expressions for Z_+ and Z_-. It is important that we are mindful of the fact that very few particles cross over the barrier once the relaxation process has been initiated. Therefore, the variance may also be approximately estimated as being *the sum of the variances in each well if it were isolated.* The terms in this expression would not, however, contain any exponentials, as they will always cancel in a formula such as y'/y or y''/y, if y is given by a single exponential term, as is so, for each isolated well. Therefore, the *difference* between the variance of the *overall* process calculated by using the exact $Z = Z_+ + Z_-$ and the variance calculated by using Z_+ and Z_- *separately* gives Δ_B. Thus, by determining which terms correspond to Δ_W, and which correspond to Δ_B, we can calculate τ_{int}, as expressed by Eq. (1.20.6). E.g., consider $Z_\pm = A_\pm e^{\sigma \pm \xi}$, where $A_+ = (2\sigma + \xi)^{-1}$ and $A_- = (2\sigma - \xi)^{-1}$ represent the prefactors of this particular system. It is obvious that $Z^{-1}Z'$ contains exponential factors while the isolated

well moments $Z_{\pm}^{-1}Z_{\pm}'$ do not. We need not be concerned with the precise form of A_1 and A_2, as they will simply be algebraic prefactors for any given system.

We now reach our final result by considering the second term on the right of Eq. (1.20.13). The relevant representation is

$$\frac{Z_+' + Z_-'}{Z_+ + Z_-} = \frac{Z_+'/Z_+}{1 + Z_-/Z_+} + \frac{Z_-'/Z_-}{1 + Z_+/Z_-}. \tag{1.20.14}$$

If we ignore the irrelevant algebraic prefactors, then it is obvious that

$$Z_-/Z_+ \cong e^{-2\xi} \text{ and } Z_+/Z_- \cong e^{2\xi}.$$

By using these approximations, we can rewrite Eq. (1.20.14) as

$$\frac{Z_+' + Z_-'}{Z_+ + Z_-} \cong \frac{Z_+'}{Z_+} + e^{-2\xi}\frac{Z_-'}{Z_-}.$$

Clearly, if we apply the same method to $(Z_+'' + Z_-'')/(Z_+ + Z_-)$, we obtain

$$\frac{Z_+'' + Z_-''}{Z_+ + Z_-} \cong \frac{Z_+''}{Z_+} + e^{-2\xi}\frac{Z_-''}{Z_-}.$$

By substituting these two equations into Eq. (1.20.13), we have our final expression for $\Delta_W + \Delta_B$, which is

$$\Delta_W + \Delta_B \cong \frac{Z_+''}{Z_+} - \left(\frac{Z_+'}{Z_+}\right)^2 + \frac{Z_-''}{Z_-}e^{-2\xi} - 2\frac{Z_+'}{Z_+}\frac{Z_-'}{Z_-}e^{-2\xi}. \tag{1.20.15}$$

We remark that in writing this equation, we have declared an $e^{-4\xi}$ term small and irrelevant. Equation (1.20.15) now yields, by inspection, the terms corresponding to Δ_W and Δ_B. Clearly, the first two terms on the right-hand side correspond to the variance in the deeper well, and must then correspond to Δ_W. The third and fourth terms of Eq. (1.20.15) must correspond to Δ_B because, from our initial reasoning, they can only have their origin in the partition function Z of the *entire* system and so must be due to the combined effect of the two wells.

We can thus infer that $\Delta_B/\Delta_W \approx e^{-2\xi} = e^{-4\sigma h}$, while $\lambda_1^{-1} \sim e^{\sigma(1-2h)}$ (see Eq. (1.18.1.15)), so that the overall contribution of the second term is $\lambda_1^{-1}\Delta_B/\Delta_W \sim e^{\sigma(1-6h)}$, which verifies the analytical result first given by Garanin [126] in 1996 and confirmed by earlier (1994) [127] numerical calculations of the integral relaxation time. Thus, the relaxation time can change its sign from *positive exponential* behavior to *negative exponential* behavior if $h_c = 1/6 \approx 0.17$. Hence, the overall relaxation time switches from growing exponential behavior ($h < 0.17$), to being dominated by the (algebraic) first term pertaining to

relaxation in the deep well. Such behavior, with h_c dependent on the precise form of the potential, appears to be a universal feature of bistable potentials subjected to a bias force; see Refs. [118, 128]. Another method of evaluation of the parameters Δ_W, Δ_B, and τ_W will be given in Chapter 2, Section 2.13.

The depletion effect we have just described is an example of a particular effect, which arises as a result of the bistable nature of the considered potential. Yet another effect, which may arise in systems which possess bistable or multistable states, is the phenomenon of *stochastic resonance* [130].

1.21. Stochastic resonance

The mechanism of stochastic resonance, which is intimately bound up with the Kramers escape rate, being rooted in a physical synchronization between the inter-well (Kramers escape) timescale and the periodic time of the weak a.c. modulation which acts as an external clock, is relatively easy to explain [130]. We consider a Brownian particle moving in a symmetric double-well potential $V(x)$ (see Fig. 1.21.1). The thermal forces from the bath cause transitions between the neighboring potential wells with the escape rate from one well to the other given, in the heavily damped case (where the energy loss per cycle of a particle at the saddle point energy is much greater than kT), by Eq. (1.13.5), viz.,

$$\Gamma = \frac{\omega_A \omega_C}{2\pi\beta} e^{-\Delta V/(kT)}. \tag{1.21.1}$$

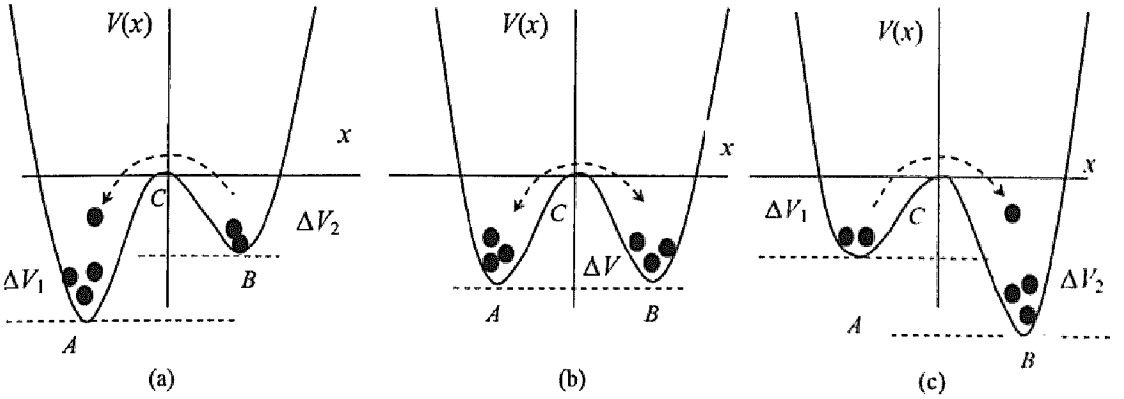


Figure 1.21.1. Double-well potential as used in stochastic resonance [130]. The minima are located at A and B. These two minima are separated by a potential barrier In the absence of a periodic forcing function (b), the barrier heights ΔV_1 and ΔV_2 are equal to ΔV, so that the potential is symmetric. The periodic forcing function causes the double-well potential to tilt back and forth, thereby raising and lowering the potential barriers of the right and left wells, respectively, in an antisymmetric cyclic fashion (a and c).

If we now apply a weak periodic forcing $f_0 \cos \Omega t$ of frequency Ω, the double-well potential will be tilted up and down, periodically raising and lowering the potential barriers ΔV [130]. The periodic forcing is too weak to let particles *roll periodically* from one potential well into the other one, but *noise-induced hopping between potential wells may become synchronized with the weak periodic forcing* [130]. This statistical synchronization takes place when the averaged waiting (escape) time (cf. Section 1.18.1 above)

$$\tau_e(kT) = 1/\Gamma \tag{1.21.2}$$

between two noise-induced transitions is comparable with *half* the period $\tau_\Omega = 2\pi/\Omega$ of the periodic forcing. This yields [130] the *timescale matching condition* for stochastic resonance, namely

$$2\tau_e(kT) = \tau_\Omega. \tag{1.21.3}$$

Thus, stochastic resonance in a symmetric double-well potential manifests itself in a *synchronization of activated hopping events*, with a reaction rate described by Eq. (1.21.1) in the heavily damped case *with the weak periodic forcing* [130]. For a given period $\tau_\Omega = 2\pi/\Omega$ of the periodic forcing, the timescale matching condition can be fulfilled by altering the noise level $kT_{\max}$ (see Chapter 6, Section 6.5).

An attractive account of the discovery of stochastic resonance was given by Gammaitoni *et al.* in Ref. [130]. According to Gammaitoni *et al.*, the stochastic resonance phenomenon was first noted by C. Nicolis and G. Nicolis [131] and Benzi *et al.* [132] (details in Ref. [130]) in a discussion of the problem of the periodically recurrent ice ages. In the model of Benzi *et al.* [132] formulated in 1981, the global climate is represented by a double-well potential, where one minimum represents a well temperature corresponding to a largely ice-covered earth. The small modulation of the earth's orbital eccentricity (the orbits of the minor planets are nearly circular) is represented by a weak periodic forcing. Short-term climatic fluctuations, such as the annual fluctuations in solar radiation, are modeled by Gaussian white noise. If the noise is tuned according to Eq. (1.21.3), *synchronized hopping* between the cold and warm temperatures (i.e., the other potential well) could significantly advance the response of the earth's climate to the weak perturbations caused by the earth's orbital eccentricity, according to Benzi *et al.* [132]. A thorough account of stochastic resonance phenomena in physical and biological systems is given in Ref. [130]. For example, stochastic resonance has been observed in bistable ring lasers, analog electronic simulators, in neurophysiology, where the firing of

periodically stimulated neurons appears to exhibit stochastic resonance [130], in single-domain ferromagnetic particles [133], etc.

For single-domain ferromagnetic particles with bistable uniaxial anisotropy potential $Kv\sin^2\vartheta$, the basic concept of stochastic resonance has been well described by Raikher and Stepanov [133]. In such a potential in the presence of noise, a weak alternating spatially uniform field of frequency Ω favoring the transitions between the equilibrium positions at $\vartheta = 0, \pi$ is applied. Under these conditions the signal-to-noise ratio determined from the spectral density $\bar{\phi}_M(\omega)$ of the magnetization (i.e., the frequency response to the applied field) evaluated at the frequency Ω of the weak applied a.c. field, first *increases* with increasing noise strength kT, then passes through a *pronounced maximum*, and then *decreases* again. This is the *stochastic resonance effect*, whereby the periodic response in both amplitude and phase may be manipulated by altering the noise strength. For example, on decreasing the driving frequency Ω, the peak amplitude of the periodic component of the response of a system moves to smaller noise strengths [130]. Later (Chapter 9, Section 9.3.3), we shall illustrate this phenomenon in detail by describing the calculations for such single-domain particles. The fact that the phenomenon occurs for these particles also indicates that one would expect stochastic resonance to be exhibited by nematic liquid crystals, since Néel or longitudinal relaxation of single-domain ferromagnetic particles in axially symmetric potentials is analogous to dielectric relaxation of nematics [134].

1.22. Anomalous diffusion

The theory of Brownian motion, which we have described above, is distinguished by a characteristic feature, namely the concept of a *collision rate* which is the inverse of the time interval between successive elementary jumps in the random walk of the Brownian particle owing to its surroundings; we recall the words of Einstein [3]:

> "We introduce a time interval τ in our discussion, which is to be very small compared with the observed interval of time, but, nevertheless of such a magnitude that the movements executed by a particle in two consecutive intervals of time τ are to be considered as mutually independent phenomena."

This concept, which is based on a random walk with a *well-defined characteristic waiting time* (thus called a discrete time random walk), and which applies when collisions are frequent but weak, leads to the Smoluchowski equation for the evolution of the concentration of Brownian particles in

configuration space. If inertial effects are included (see Note (8) of Ref. [3], due to Fürth), we obtain the Klein–Kramers equation for the evolution of the distribution function in phase space, which describes normal diffusion.

The random walk considered by Einstein [3] is a walk in which the elementary steps are taken at *uniform* intervals in time, and so is called a discrete time random walk. The concept of collisions which are frequent but weak can be clarified by remarking that, in the discrete time random walk, the problem [5] is always to find the probability that the system will be in a state m at some time t given that it was in a state n at some earlier time. Referring to the Smoluchowski integral, Eq. (1.9.1), viz.,

$$P_2(x_3,t_3 \mid x_1,t_1) = \int_{-\infty}^{\infty} P_2(x_2,t_2 \mid x_1,t_1) P_2(x_3,t_3 \mid x_2,t_2)\, dx_2, \qquad (1.22.1)$$

x_1 and x_3 can only have *discrete* values n and m, and the time t can only have discrete values $s\tau$ with $s = 1, 2, 3, \ldots$. The discrete form of the Smoluchowski equation is thus [13]

$$P(m, s\tau \mid n, \tau) = \sum_k P\left[k, (s-1)\tau \mid n\right] Q(m,k),$$

where $Q(m,n) = P(m,\tau \mid n)$. It is usual to drop the τ and just write the equation as

$$P(m,s \mid n) = \sum_k P(k, s-1 \mid n) Q(m,k), \qquad (1.22.2)$$

Now

$$\sum_m Q(m,k) = 1,$$

thus

$$Q(k,k) + \sum{}'_m Q(m,k) = 1, \qquad (1.22.3)$$

where the prime means that the value $m = k$ must be omitted from the summation. If we use this in Eq. (1.22.2) and drop the initial value n, we can write Eq. (1.22.2) in the form of the master equation

$$P(m,s) - P(m,s-1) = -P(m,s-1) \sum{}'_k Q(k,m) + \sum{}'_k P(k,s-1) Q(m,k). \qquad (1.22.4)$$

According to Wang and Uhlenbeck [13], one may interpret this by saying that the rate of change of $P(m,s)$ with time (where time is given by s) arises from the "gains" of P due to transitions from k to m, minus the "losses" of P due to transitions from m to all possible k. This provides a complete analog of the Boltzmann equation when the molecules of the gas can collide only against

fixed centers or against other molecules that have a *given* velocity distribution. Equation (1.22.4) must be solved for P given an initial distribution for P. Also, a "mechanism" or "physical cause" (*Stosszahlansatz*) for the random process must be given, that is, Q must be specified. The initial condition for Eq. (1.22.4) is

$$P(m,0\,|\,n)=P(m,0)=\delta_{mn}. \tag{1.22.5}$$

This is just the mathematical statement of the fact that the particle was *certainly* in state n at the start of the process.

We consider the random walk problem in one dimension. We imagine a particle that moves along the x-axis in such a way that, in each step, it can move either Δ to the right or Δ to the left, the duration of each step being τ. We wish to evaluate

$$P(m\Delta, s\tau\,|\,n\Delta)=P(m,s\,|\,n), \tag{1.22.6}$$

which is the probability that the particle is at $m\Delta$ at time $s\tau$ if, at the beginning, it was at $n\Delta$. The fact that the particle is free is now introduced by writing the transition probability Q as

$$Q(m,k)=\frac{1}{2}\left(\delta_{mk-1}+\delta_{mk+1}\right). \tag{1.22.7}$$

If we substitute Eq. (1.22.7) into Eq. (1.22.2), we find that $P(m,s)$ satisfies the difference equation (dropping the initial state n)

$$P(m,s)=\frac{1}{2}\left[P(m+1,s-1)+P(m-1,s-1)\right]. \tag{1.22.8}$$

This must be solved subject to the initial condition Eq. (1.22.5). The solution is [13]

$$P(m,s\,|\,n)=\frac{s!}{2^s\left[\left(|\,n-m\,|+s\right)/2\right]!\,\left[\left(|\,n-m\,|-s\right)/2\right]!}. \tag{1.22.9}$$

Equation (1.22.9) is readily verified by substitution into Eq. (1.22.4). Now, referring to Eq. (1.22.8), if Δ is the step length and τ the duration of the step,

$$P(m\Delta, s\tau\,|\,n\Delta)=\frac{1}{2}P\left[(m+1)\Delta,(s-1)\tau\,|\,n\Delta\right]+\frac{1}{2}P\left[(m-1)\Delta,(s-1)\tau\,|\,n\Delta\right].$$

Subtract $P[m\Delta,(s-1)\tau\,|\,n\Delta]$ from both sides of this equation, so it becomes

$$\begin{aligned}P\left(m\Delta,s\tau\,|\,n\Delta\right)-P\left[m\Delta,(s-1)\tau\,|\,n\Delta\right]&=\frac{1}{2}\left\{P\left[(m-1)\Delta,(s-1)\tau\,|\,n\Delta\right]\right.\\&\left.+P\left[(m+1)\Delta,(s-1)\tau\,|\,n\Delta\right]-2P\left[m\Delta,(s-1)\tau\,|\,n\Delta\right]\right\}.\end{aligned} \tag{1.22.10}$$

Equation (1.22.10) may be written in the equivalent form

$$\frac{P[m\Delta, s\tau \mid n\Delta] - P[m\Delta, (s-1)\tau \mid n\Delta]}{\tau} = \frac{\Delta^2}{2\tau}\{P[(m+1)\Delta, (s-1)\tau \mid n\Delta]$$

$$-2P[m\Delta, (s-1)\tau \mid n\Delta] + P[(m-1)\Delta, (s-1)\tau \mid n\Delta]\}\frac{1}{\Delta^2}. \qquad (1.22.11)$$

Consider a *large* number of *small* steps of *short* duration. More precisely, we suppose that Δ and τ approach zero in such a way that

$$\frac{\Delta^2}{2\tau} = D,\ n\Delta \to x_0,\ m\Delta \to x,\ s\tau = t.$$

Then Eq. (1.22.11) (by the definition of the derivative) goes over formally into the partial differential equation

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2}, \qquad (1.22.12)$$

where P is now written as $P(x,t \mid x_0,t_0)$. This equation is the basis of Einstein's theory of Brownian movement. It shows how, in a certain limit, the solution of the random-walk problem may be reduced to solving a diffusion equation like Eq. (1.22.12). The conditions imposed on P, the probability density, are

$$\int_{-\infty}^{\infty} P(x,t \mid x_0)\,dx = 1$$

and

$$\lim_{t\to 0} P(x,t \mid x_0) = \delta(x - x_0). \qquad (1.22.13)$$

For convenience, we have taken $t_0 = 0$. The first condition (1.22.13) is the usual one that a probability density function must satisfy. The second condition (1.22.13) expresses the *certainty* that at $t = 0$ the particle was at x_0. These conditions imply that

$$P(x,t \mid x_0) = \frac{1}{2\sqrt{\pi Dt}} e^{-(x-x_0)^2/(4Dt)}. \qquad (1.22.14)$$

Thus the position $x(t)$ of the Brownian particle is a Gaussian random variable with mean value $x_0 = \langle x(t)\rangle$ and variance

$$\sigma^2 = \langle [x(t) - x_0]^2 \rangle = 2D|t|$$

(for a detailed discussion of random walks see Ref. [135]).

If the foregoing random-walk approach is applied to the orientational motion of dipoles, as described in Section 1.15, we have seen that the theory describes

normal relaxation, with the mean dipole moment given by Eqs. (1.15.16) and (1.15.17), and the complex susceptibility given by Eq. (1.15.1.2). The τ_D in these equations means the Debye relaxation time and not the duration of a step. Thus, the complex permittivity $\varepsilon = \varepsilon'(\omega) - i\varepsilon''(\omega)$ is given by the Debye equation

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau_D}, \tag{1.22.15}$$

where ε_∞ is the relative permittivity at very high frequencies and ε_s is the static permittivity. Moreover, a (Cole–Cole) plot [100] of $\varepsilon''(\omega)$ versus $\varepsilon'(\omega)$ is a semicircle with radius

$$\frac{\varepsilon_s - \varepsilon_\infty}{2}$$

and center on the ε' axis at

$$\varepsilon' = \frac{\varepsilon_s + \varepsilon_\infty}{2},$$

with a maximum when $\omega\tau_D = 1$. Thus, τ_D may be determined by measuring the angular frequency when $\varepsilon''(\omega)$ is a maximum. In practice, however, many disordered substances such as glass-forming liquids, polymers, and amorphous semiconductors [136] show very significant departures from Debye behavior. In addition, the mean-square displacements or angular displacements associated with such transport phenomena are always proportional to a fractional power of the time, resulting in anomalous relaxation behavior. Such behavior has led to the description of these anomalous phenomena in the language of *continuous-time random walks* (CTRW) (originally [16, 137] introduced by Montroll and Weiss in 1965) which we will very briefly summarize.

First, we reiterate that that the random walk on which the theory of Brownian motion is based, is one in which the successive jumps in position of the particle are later at *uniform* intervals τ in time. In the CTRW on the other hand, the *times between the successive steps are themselves random variables* [16]. Hence, the prediction of position at the following step at any *given* time requires not only a knowledge of the *location* (as in the discrete-time random walk) of the random walk at that time, but also the *time* at which the last step occurred. This dependence on the state of the system and its past history means that the CTRW is, in general, *not a Markov process* [16]. Thus, referring to the quotation of Karl Pearson given in Section 1.2, the probability that after n stretches a random walker is at distance between r and $r + dr$ from his initial point $r = 0$ is a function

not only of r but also [16] of the intervals $T_n = t_n - t_{n-1}$ between successive steps of the walk. The concept of the CTRW is essential in the explanation of the various types of anomalous relaxation behavior of $\varepsilon(\omega)$ which we now describe. (A more detailed discussion of the CTRW is given in Chapter 12; see also [10, 18, 39]).

1.22.1. *Empirical formulas for the complex dielectric permittivity*

From almost the earliest days of dielectric relaxation measurements [100], marked departures from the form of $\varepsilon(\omega)$ predicted by the Debye equation have been observed. The best-known empirical formulas, which have been used to describe such experimental data, are (a) the Cole–Cole equation [100]:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + (i\omega\tau_D)^\sigma}, \qquad (0 < \sigma \leq 1), \tag{1.22.1.1}$$

which again produces a circular arc (however, the center lies below the horizontal axis), (b) the Davidson–Cole equation [100]:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{(1 + i\omega\tau_D)^\nu}, \qquad (0 < \nu \leq 1), \tag{1.22.1.2}$$

which produces a skewed arc, and (c) the Havriliak–Negami formula, which is a combination of the Cole–Cole and Davidson–Cole equations [100]:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{[1 + (i\omega\tau_D)^\sigma]^\nu}. \tag{1.22.1.3}$$

Each of these empirical formulas exhibit *anomalous relaxation* (i.e., departures from the Debye pattern) behavior. Just as in the Debye case, our task is to provide a theoretical justification for them. Before illustrating this using an approach based on the CTRW, we demonstrate how the above equations naturally give rise to a distribution of relaxation mechanisms. This idea, originally advanced by von Schweidler and later by Wagner [100], is in the notation of Fröhlich [117]

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_S - \varepsilon_\infty} = \int_0^\infty \frac{f(\tau)}{1 + i\omega\tau} d\tau. \tag{1.22.1.4}$$

This is a superposition integral and embodies the idea [100] that the dielectric behaves as if it were a collection of individual Debye time mechanisms with relaxation time τ and distribution function $f(\tau)$. One may show [100] that, for the Debye equation, Eq. (1.22.15),

$$f_{\mathrm{D}}(\tau)=\delta(\tau-\tau_{\mathrm{D}}). \tag{1.22.1.5}$$

Thus only one relaxation mechanism is involved, as is obvious by definition, while for the Cole–Cole equation, Eq. (1.22.1.1),

$$f_{\mathrm{CC}}(\tau)=\frac{\sin\pi\sigma}{\pi\tau[(\tau/\tau_{\mathrm{D}})^{\sigma}+(\tau/\tau_{\mathrm{D}})^{-\sigma}+2\cos\pi\sigma]}, \tag{1.22.1.6}$$

and for the Davidson–Cole equation, Eq. (1.22.1.2),

$$f_{\mathrm{DC}}(\tau)=\begin{cases}(\pi\tau)^{-1}(\tau_{\mathrm{D}}/\tau-1)^{-\nu}\sin\pi\nu, & \tau<\tau_{\mathrm{D}},\\ 0, & \tau>\tau_{\mathrm{D}},\end{cases} \tag{1.22.1.7}$$

and for the Havriliak–Negami equation, Eq. (1.22.1.3),

$$f_{\mathrm{HN}}(\tau)=\frac{(\tau/\tau_{\mathrm{D}})^{\nu\sigma}\left|\sin\left(\nu\arctan\left\{[(\tau/\tau_{\mathrm{D}})^{\sigma}+\cos\pi\sigma]^{-1}\sin\pi\sigma\right\}\right)\right|}{\pi\tau[(\tau/\tau_{\mathrm{D}})^{2\sigma}+2(\tau/\tau_{\mathrm{D}})^{\sigma}\cos\pi\sigma+1]^{\nu/2}}. \tag{1.22.1.8}$$

Thus, the anomalous relaxation behavior may be characterized by a *superposition* of an *infinite* number of Debye-like relaxation mechanisms, with the relaxation time distribution functions given by Eqs. (1.22.1.6)–(1.22.1.8). For the cases considered, these empirical equations take no account of high-frequency effects such as those due to the inertia of the molecules. These will be considered later in the context of inertia corrected anomalous relaxation [138]. We shall now illustrate how the empirical anomalous relaxation equations described above may be theoretically explained [139] by invoking a CTRW description, in which each step of the random walk occurs at a *random* time, chosen from a random distribution of waiting times (replacing the fixed uniform waiting time τ of the Einstein theory) *so broad that it does not possess a characteristic timescale.* In other words, the mean waiting time is *divergent.* The origin of the phenomenological parameter σ, taking the Cole–Cole equation, Eq. (1.22.1.1), as an example, must be sought in this "fractal time" waiting-time distribution.

1.22.2. *Theoretical justification for anomalous relaxation behavior*

The fact that the temporal occurrence of the motion events performed by the random walker is so broadly distributed that no characteristic waiting time exists, has often been exploited [139] in order to generalize the various diffusion equations of Brownian dynamics to explain anomalous relaxation phenomena. The resulting diffusion equations are called *fractional* diffusion equations, because in general they will involve *fractional derivatives* of the PDF with

respect to time. For example, in fractional diffusion, the simple Einstein equation for the Brownian motion of a free particle, Eq. (1.4.8), becomes (see Chapter 12, Section 12.2)

$$\frac{\partial P}{\partial t} = \left(\frac{kT}{\zeta}\right)^{\sigma} \frac{\partial^2}{\partial x^2}\, {}_0D_t^{1-\sigma} P, \tag{1.22.2.1}$$

where σ is the anomalous exponent, the fractional derivative ${}_0D_t^{1-\sigma}$ is given (the Riemann–Liouville definition) by [139, 140, 141]

$${}_0D_t^{1-\sigma} = \frac{\partial}{\partial t}\, {}_0D_t^{-\sigma} \tag{1.22.2.2}$$

in terms of the convolution (recall Cauchy's integral formula [142])

$${}_0D_t^{-\sigma} P(x,t \mid x_0) = \frac{1}{\Gamma(\sigma)} \int_0^t \frac{P(x,t' \mid x_0)\, dt'}{(t-t')^{1-\sigma}}, \tag{1.22.2.3}$$

$\Gamma(z)$ denoting the gamma function [143]. Equation (1.22.2.1) with $0 < \sigma < 1$ describes *slow diffusion* or *subdiffusion*, and with $1 < \sigma < 2$ describes *enhanced diffusion* or *superdiffusion* ($\sigma = 2$ defines the ballistic limit); *normal diffusion* occurs when $\sigma = 1$ (see Chapter 12).

The derivation of fractional diffusion equations such as Eq. (1.22.2.1) hinges on the observation (cf. Ref. [141], p. 118) that fractional diffusion is equivalent to a CTRW with waiting time density $w(t)$ given by a generalized Mittag–Leffler function (see Section 1.22.3 below and also Refs. [139] and [141]). The fact that $w(t)$ is given by a generalized Mittag–Leffler function amounts to assuming an asymptotic (long-time) power law form for the waiting time PDF, i.e., considering slow diffusion,

$$w(t) \sim A_\sigma \tau^\sigma t^{-1-\sigma}, \quad (0 < \sigma < 1), \tag{1.22.2.4}$$

(A_σ is a constant). The characteristic (mean) waiting time

$$\langle T_{\mathrm{W}} \rangle = \int_0^\infty t w(t) dt \tag{1.22.2.5}$$

then always tends to ∞ except in the limit $\sigma \to 1$ (the classical Brownian motion), where

$$w(t) = \delta(t - \tau),$$

so that the mean waiting time $\langle T_{\mathrm{W}} \rangle = \tau$.

A famous example [18] of a distribution function with a long-time tail like Eq. (1.22.2.4) is the Cauchy distribution

$$w(t) = \frac{a}{\pi} \frac{1}{a^2 + t^2} \tag{1.22.2.6}$$

with infinite second moment. This distribution is just one example of a whole class of distributions which, if applied to a sum of random variables, do not converge to the Gaussian distribution as the number of random variables tends to infinity. Thus, the central limit theorem, on which the theory of Brownian motion rests, is not obeyed because the long-time tails preclude convergence to the Gaussian distribution. Nevertheless, limiting distributions (now called Lévy distributions; see Ref. [18], Chapter 4) may exist (see also Chapter 12).

The divergence of the waiting time associated with the long-time-tailed nature of the waiting time PDF, Eq. (1.22.2.4), is, according to Metzler and Klafter [139] a manifestation of the *self-similar* nature of the waiting-time process. This has prompted many investigators to use, in the present context, the term *fractal time processes* to describe anomalous relaxation. Returning to the fractional diffusion equation, Eq. (1.22.2.1), that equation will now follow from Eq. (1.22.2.4) and CTRW theory. This is so because (see Ref. [141], p. 118) the integral equation for the PDF $f(x,t)$ for a continuous-time random walker to be in a position x at time t, starting from $x = 0$ at $t = 0$ with waiting time density given by Eq. (1.22.2.4), is equivalent in the diffusion limit to the fractional diffusion equation, Eq. (1.22.2.1). We illustrate this in Chapter 12.

We remark that postulating $w(t)$ as a generalized Mittag–Leffler function with long-time behavior given by Eq. (1.22.2.4), so that fractional diffusion may be described as a CTRW, is (just as with the postulate of the existence of a discrete time τ, the duration of an elementary jump in the Einstein theory of Brownian movement) equivalent to a *Stosszahlansatz* for the Boltzmann equation, which must of necessity underpin the entire theory. In other words, the *transition probability* or "mechanism" of the fractional diffusion process is that of the CTRW. In Chapter 12, we shall see in detail how a waiting-time PDF of the form of Eq. (1.22.2.4) allows one to generalize the Klein–Kramers equation of normal diffusion to fractional diffusion. We shall also demonstrate how the anomalous diffusion problem may be treated within the framework of the generalized Langevin equation or memory function formalism due to Mori, reviewed in Ref. [98]. The memory function formalism is attractive in the context of fractional diffusion, as it quite clearly underlines its non-Markovian nature. Furthermore, the CTRW provides a microscopic model, justifying the introduction of particular memory functions into the Mori theory, which may describe anomalous diffusion. In the meantime, we will confine ourselves to the fractional diffusion equation in configuration space (here a generalized

Smoluchowski equation) for an assembly of rigid non-interacting dipoles. Moreover, we shall demonstrate how that equation yields [144] the Cole–Cole equation, Eq. (1.22.1.1).

1.22.3. *Anomalous dielectric relaxation of an assembly of dipolar molecules*

In the fixed-axis rotation model of dielectric relaxation of polar molecules, a typical member of the assembly is a rigid dipole of moment $\boldsymbol{\mu}$ rotating about a fixed axis through its center. The dipole has moment of inertia I and is specified by the angular coordinate θ (the azimuth), so that it constitutes a system of one (rotational) degree of freedom. The fractional diffusion equation for the time evolution of the PDF $W(\theta,t)$ in configuration space is then the same as that previously written, Eq. (1.22.2.1), for a particle of one translational degree of freedom. However, rotational quantities replace translational ones and a potential energy term $V(\theta)$ is added, so that

$$\frac{\partial W}{\partial t} = \tau_{\mathrm{D}}^{-\sigma}\left[\frac{1}{kT}\frac{\partial}{\partial\theta}\left(\frac{\partial V}{\partial\theta}\right)+\frac{\partial^2}{\partial\theta^2}\right]{}_0D_t^{1-\sigma}W. \qquad (1.22.3.1)$$

Here $\tau_{\mathrm{D}} = \varsigma/(kT)$ is the Debye relaxation time, which is identified with the *inter-trapping* time, and $V(\theta) = -\mu E_0\cos\theta$ is the potential arising from an external d.c. electric field $\mathbf{E}_0$. The operator ${}_0D_t^{1-\sigma}$ is given, as before, by the Riemann–Liouville definition, Eq. (1.22.2.3), meaning that Eq. (1.22.3.1) now contains a slowly decaying memory function with a power law kernel, so that the process is no longer Markovian and so depends on the history of the system. We consider the after-effect solution of Eq. (1.22.3.1), where a d.c. field $\mathbf{E}_0$, having been applied to the assembly at a time $t=-\infty$ so that equilibrium conditions prevail by the time $t=0$, is switched off at $t=0$. In addition, it is supposed that the field is weak ($\mu E_0 << kT$). Thus, Eq. (1.22.3.1) becomes, for $t>0$

$$\frac{\partial W}{\partial t} = \tau_{\mathrm{D}}^{-\sigma}\frac{\partial^2}{\partial\theta^2}\left({}_0D_t^{1-\sigma}W\right). \qquad (1.22.3.2)$$

Equation (1.22.3.2) must be solved subject to the initial condition

$$W(\theta,0) = \frac{1}{2\pi}\left(1+\frac{\mu E_0}{kT}\cos\theta\right), \qquad (1.22.3.3)$$

where 2π is the normalizing constant. Just as with normal diffusion, the form of the initial condition, Eq. (1.22.3.3), suggests that the time-dependent solution should be

$$W(\theta,t)=\frac{1}{2\pi}\left(1+g(t)\frac{\mu E_0}{kT}\cos\theta\right), \tag{1.22.3.4}$$

yielding the fractional differential equation for $g(t)$, viz.,

$$\frac{d}{dt}g(t)=-\tau_{\mathrm{D}}^{-\sigma}\ {}_0D_t^{1-\sigma}g(t) \tag{1.22.3.5}$$

with solution [139]

$$g(t)=E_\sigma[-(t/\tau_{\mathrm{D}})^\sigma], \tag{1.22.3.6}$$

where $E_\sigma(z)$ is the Mittag–Leffler function defined by [139, 141]

$$E_\sigma(z)=\sum_{n=0}^{\infty}\frac{z^n}{\Gamma(1+\sigma n)}. \tag{1.22.3.7}$$

The Mittag–Leffler function interpolates between the initial stretched exponential form [139]

$$E_\sigma[-(t/\tau_{\mathrm{D}})^\sigma]\sim e^{-(t/\tau_{\mathrm{D}})^\sigma/\Gamma(1+\sigma)} \tag{1.22.3.8}$$

and the long-time inverse power-law behavior [139, 141]

$$E_\sigma[-(t/\tau_{\mathrm{D}})^\sigma]\sim(t/\tau_{\mathrm{D}})^{-\sigma}/\Gamma(1-\sigma). \tag{1.22.3.9}$$

The Debye result for $g(t)$ corresponds to $\sigma=1$, viz.,

$$E_1(-t/\tau_{\mathrm{D}})=e^{-t/\tau_{\mathrm{D}}}. \tag{1.22.3.10}$$

Now the mean moment due to orientation alone is given at any time $t>0$ by

$$\langle\boldsymbol{\mu}\cdot\mathbf{e}\rangle(t)=\int_0^{2\pi}\mu\cos\theta W(\theta,t)d\theta \tag{1.22.3.11}$$

($\mathbf{e}$ is a unit vector in the direction of $\mathbf{E}_0$), so that with Eq. (1.22.3.4) we have

$$\langle\boldsymbol{\mu}\cdot\mathbf{e}\rangle(t)=\frac{\mu^2E_0}{2kT}E_\sigma[-(t/\tau_{\mathrm{D}})^\sigma], \tag{1.22.3.12}$$

in contrast to the Debye result embodied in Eq. (1.15.16).

A practically much more important result than that treated above is the stationary response to a weak periodic field $\mathbf{E}(t)=\mathbf{E}_0e^{i\omega t}$ [144]. This response is characterized by the complex susceptibility $\chi(\omega)$, which may be obtained from the after-effect solution, Eq. (1.22.3.12), using linear response theory (see Chapter 2, Section 2.8). Hence

$$\chi(\omega)=\chi'(0)-i\omega\int_0^{\infty}b(t)e^{-i\omega t}dt, \tag{1.22.3.13}$$

where $b(t) = N_0 \langle \boldsymbol{\mu} \cdot \mathbf{e} \rangle (t)$ is the after-effect function and N_0 is the concentration of the dipoles. (In using this theorem, we note [39] the non-stationary nature of the *Stosszahlansatz* or mechanism, underlying the fractional dynamics). Equation (1.22.3.13), with the after-effect function $b(t)$ given by Eq. (1.22.3.12), yields

$$\chi(\omega) = \frac{\mu^2 N_0}{2kT}\left[1 - i\omega\int_0^\infty E_\sigma[-(t/\tau_D)^\sigma]e^{-i\omega t}dt\right]$$
$$= \frac{\mu^2 N_0}{2kT}\frac{1}{1+(i\omega\tau_D)^\sigma}, \qquad (1.22.3.14)$$

because the one-sided Fourier transform of the Mittag–Leffler function $E_\sigma[-(t/\tau_D)^\sigma]$ is [139,141]

$$\frac{1}{i\omega + \tau_D^{-\sigma}(i\omega)^{1-\sigma}}.$$

The calculation may be carried over to rotation in space [144]. Here, the space coordinate is ϑ (the colatitude) and the fractional diffusion equation for the PDF $W(\vartheta, t)$ becomes (see Eq. (1.15.13))

$$\frac{\partial W}{\partial t} = \tau_D^{-\sigma}\frac{1}{2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left[\sin\vartheta\frac{\partial}{\partial\vartheta}\right]{}_0D_t^{1-\sigma}W, \qquad (1.22.3.15)$$

where $\tau_D = \varsigma/2kT$ is the Debye relaxation time for rotation in space. It is now apparent that Eq. (1.22.3.15) may be solved, just as Eqs. (1.22.3.2), for rotation about a fixed axis, yielding

$$\langle \boldsymbol{\mu} \cdot \mathbf{e} \rangle (t) = \frac{\mu^2 E_0}{3kT} E_\sigma\left[-(t/\tau_D)^\sigma\right], \qquad (1.22.3.16)$$

$$\chi(\omega) = \frac{\mu^2 N_0}{3kT}\frac{1}{1+(i\omega\tau_D)^\sigma}. \qquad (1.22.3.17)$$

As in normal diffusion, Eqs. (1.22.3.16) and (1.22.3.17) differ from the corresponding one-dimensional analogs, Eqs. (1.22.3.12) and (1.22.3.14), only by a factor 2/3 and the appropriate definition of τ_D. Hence, the Debye theory of dielectric relaxation based on *normal* diffusion may be generalized to *anomalous* diffusion.

This concludes our long discussion of the various applications of the theory of Brownian movement, serving as both an introduction to and as a motivation for the study of its various detailed aspects.

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CHAPTER 3

BROWNIAN MOTION OF A FREE PARTICLE AND A HARMONIC OSCILLATOR

3.1. Introduction

In this chapter, we treat the translational Brownian motion of both a free particle and an oscillator. The appropriate Langevin equations are

$$m\ddot{x}(t) + \zeta \dot{x}(t) = F(t) \tag{3.1.1}$$

for a free particle, and

$$m\ddot{x}(t) + \zeta \dot{x}(t) + m\omega_0^2 x(t) = F(t) \tag{3.1.2}$$

for a Brownian oscillator, where $x(t)$ specifies the position of the particle or oscillator at time t, m is the mass, $\zeta \dot{x}$ is the viscous drag experienced by the particle, ω_0 is the oscillator frequency, and $F(t)$ is the white-noise driving force. We also consider the rotational analogs of these two models, namely, a free single-axis rotator and a torsional oscillator. The corresponding Langevin equations are

$$I\ddot{\theta}(t) + \varsigma \dot{\theta}(t) = \lambda(t) \tag{3.1.3}$$

for a free rotator, and

$$I\ddot{\theta}(t) + \varsigma \dot{\theta}(t) + I\omega_0^2 \theta(t) = \lambda(t) \tag{3.1.4}$$

for a torsional oscillator, where θ is the angle of rotation, I is the moment of inertia, while $\varsigma \dot{\theta}(t)$ and $\lambda(t)$ are the viscous drag and white-noise driving torques, respectively.

The common feature of all these models is that the Langevin equations (3.1.1)–(3.1.4) are *linear*, so that the calculation of observables is relatively simple. Detailed treatments of various aspects of the models are given, e.g., in Refs. [1]–[6] and [6]–[10] for both the translational and rotational Brownian motion. Some properties have already been considered in Chapter 1 (see Sections 1.3 and 1.11).

We now show how observables may be calculated from the Langevin equations, Eqs. (3.1.1)–(3.1.4). Applications of the models to the phase diffusion

in magnetic resonance imaging [11] and to dielectric relaxation [12] are also discussed.

3.2. Ornstein–Uhlenbeck theory of Brownian motion

The formula for the mean-square displacement $\langle(\Delta x)^2\rangle$ of a Brownian particle in a time interval t derived by Langevin [1] and Einstein [4], namely,

$$\langle(\Delta x)^2\rangle = 2kT\,|\,t\,|\,/\zeta, \tag{3.2.1}$$

has (as we discussed in detail in Chapter 1) the fundamental flaw that it is not *root-mean-square differentiable* at $t = 0$. We have also seen that this is a direct consequence of ignoring the inertia of the particles. In 1930, Uhlenbeck and Ornstein [2] derived, by including the inertia, the famous formula for $\langle(\Delta x)^2\rangle$ originally given by Ornstein and Fürth in 1918 [4] (cf. Eq. (1.5.10.5))

$$\langle(\Delta x)^2\rangle = \frac{2kTm}{\zeta^2}\left(\frac{\zeta}{m}\,|\,t\,| - 1 + e^{-\zeta|t|/m}\right), \tag{3.2.2}$$

which, for times $t >> m/\zeta$, reduces to Eq. (3.2.1), and for short times becomes

$$\langle(\Delta x)^2\rangle = (kT/m)t^2.$$

Thus $\langle(\Delta x)^2\rangle$ is now mean-square differentiable.

In this section, we show how Eq. (3.2.2) may be derived from the point of view of the Ornstein–Uhlenbeck theory. Thus we follow the method of Section 1.7, writing the Langevin equation in phase space (x, v), as

$$\dot{x}(t) = v(t), \quad m\dot{v}(t) = -\zeta v(t) + F(t), \tag{3.2.3}$$

where we designate the white-noise driving force as $F(t)$ with

$$\overline{F(t_1)} = 0, \quad \overline{F(t_1)F(t_2)} = 2\zeta kT\delta(t_1 - t_2). \tag{3.2.4}$$

It is again assumed that the particle starts off at a *definite* phase point (x_0, v_0), so that the state vector has components

$$x(t) = x_0 + \frac{v_0}{\beta}\left(1 - e^{-\beta t}\right) + \frac{1}{m\beta}\int_0^t \left(1 - e^{-\beta(t-t')}\right)F(t')dt', \tag{3.2.5}$$

$$v(t) = \dot{x}(t) = v_0 e^{-\beta t} + \frac{1}{m}\int_0^t e^{-\beta(t-t')}F(t')dt' \tag{3.2.6}$$

(here $\beta = \zeta/m$). Hence

$$\Delta x = x(t) - x_0 = \frac{v_0}{\beta}\left(1 - e^{-\beta t}\right) + \frac{1}{m\beta}\int_0^t \left[1 - e^{-\beta(t-t')}\right]F(t')dt'.$$

Now

$$\overline{\Delta x} = \frac{v_0}{\beta}\left(1 - e^{-\beta t}\right), \tag{3.2.7}$$

$$\overline{(\Delta x)^2} = \frac{v_0^2}{\beta^2}\left(1 - e^{-\beta t}\right)^2 + \frac{1}{m^2\beta^2}\int_0^t\int_0^t \left[1 - e^{-\beta(t-t')}\right]\left[1 - e^{-\beta(t-t'')}\right]\overline{F(t')F(t'')}\,dt'dt''$$

$$= \frac{v_0^2}{\beta^2}\left(1 - e^{-\beta t}\right)^2 + \frac{2kT}{m\beta}\int_0^t\int_0^t \left[1 - e^{-\beta(t-t')}\right]\left[1 - e^{-\beta(t-t'')}\right]\delta(t'' - t')\,dt'dt''. \tag{3.2.8}$$

Since

$$\int_0^t \delta(t'' - t')\left[1 - e^{-\beta(t-t'')}\right]dt'' = 1 - e^{-\beta(t-t')}, \tag{3.2.9}$$

we have, from Eq. (3.2.8),

$$\overline{(\Delta x)^2} = \frac{v_0^2}{\beta^2}\left(1 - e^{-\beta t}\right)^2 + \frac{2\zeta kT}{m\beta}\int_0^t \left[1 - 2e^{-\beta(t-t')} + e^{-2\beta(t-t')}\right]dt'$$

$$= \frac{v_0^2}{\beta^2}\left(1 - e^{-\beta t}\right)^2 + \frac{2kTt}{m\beta} + \frac{kT}{m\beta^2}\left[-3 + 4e^{-\beta t} - e^{-2\beta t}\right]. \tag{3.2.10}$$

This is the solution in the case where the collection of particles started off with the *definite* velocity v_0. If we have a Maxwellian distribution of initial velocities v_0, i.e., $m\langle v_0^2\rangle/2 = kT/2$, we find from Eq. (3.2.10) that

$$\langle(\Delta x)^2\rangle = \frac{2kT}{m\beta^2}\left(\beta t - 1 + e^{-\beta t}\right), \tag{3.2.11}$$

which is the Ornstein–Fürth formula, Eq. (3.2.2) [2]. For long times, the term in t is the only significant one, so that we obtain the result of Langevin [1] and Einstein [4], Eq. (3.2.1). We reiterate that $\langle(\Delta x)^2\rangle^{1/2}$ from Eq. (3.2.11) is *non-differentiable* at $t = 0$, so that in the non-inertial approximation, the *velocity* does not exist. If inertia is included, however, $\langle(\Delta x)^2\rangle^{1/2}$ is *differentiable* at $t = 0$ and the velocity exists. This question, first emphasized by Doob [13], was discussed in Chapter 2.

3.3. Stationary solution of the Langevin equation: the Wiener–Khinchin theorem

We have illustrated the calculation of the averages from the Langevin equation for *sharp* initial conditions. The solution of the Langevin equation for a free

particle subject to a *Maxwellian* distribution of velocities is called the stationary solution. Clearly, for the stationary solution

$$\langle v^2 \rangle = \frac{kT}{m}, \tag{3.3.1}$$

as the velocities are in thermal equilibrium. The relevant quantity is the velocity correlation function. The stationary solution may be found by extending the lower limit of integration to $-\infty$ and discarding the term in v_0 in Eq. (3.2.6). Thus, for distinct times t_1 and t_2, we have

$$v(t_1) = m^{-1} \int_{-\infty}^{t_1} e^{-\beta(t_1 - t')} F(t') dt', \quad v(t_2) = m^{-1} \int_{-\infty}^{t_2} e^{-\beta(t_2 - t'')} F(t'') dt'' \tag{3.3.2}$$

so that

$$\begin{aligned} \langle v(t_1) v(t_2) \rangle &= \frac{1}{m^2} \int_{-\infty}^{t_1} \int_{-\infty}^{t_2} e^{-\beta(t_1 - t' + t_2 - t'')} \langle F(t') F(t'') \rangle dt' dt'' \\ &= \frac{2\zeta kT}{m^2} \int_{-\infty}^{t_1} \int_{-\infty}^{t_2} e^{-\beta(t_1 - t' + t_2 - t'')} \delta(t'' - t') dt' dt'' = \frac{kT}{m} e^{-\beta|t_1 - t_2|}. \end{aligned} \tag{3.3.3}$$

The modulus bars must be inserted in order to ensure a decaying covariance. This is the velocity autocorrelation function (ACF) of a free Brownian particle. Noting that

$$\frac{d}{dt}(\Delta x)^2 = 2\Delta x(t) v(t), \qquad \Delta x(t) = \int_0^t v(u) du, \tag{3.3.4}$$

the mean-square displacement $\langle (\Delta x)^2 \rangle$ may be found using the formula

$$\langle (\Delta x)^2 \rangle = 2 \int_0^t \int_0^{t'} \langle v(t') v(u) \rangle du\, dt' = 2 \int_0^t (t - u) \langle v(0) v(u) \rangle du \tag{3.3.5}$$

yielding the same result as before, Eq. (3.2.11).

Now the velocity ACF may also be computed using the Wiener–Khinchin theorem. Following Ref. [3] closely, consider, for a very long time T', a wide-sense *stationary* random process; that is, a process in which the average of the product $\xi(t)\xi(t \pm \tau)$ depends only on τ (> 0), where we specify the process by the real-valued random variable $\xi(t)$ which is a causal function of the time t (see examples in Ref. [14]). We now form

$$\overline{\xi(t)} = \lim_{T' \to \infty} \frac{1}{T'} \int_{-T'/2}^{T'/2} \xi(t) dt, \tag{3.3.6}$$

i.e., the time average of $\xi(t)$ over an infinitely long time period. We may also define the ACF $C_\xi(\tau)$ as

$$C_\xi(\tau) = \overline{\xi(t)\xi(t+\tau)} = \lim_{T'\to\infty} \frac{1}{T'} \int_{-T'/2}^{T'/2} \xi(t)\xi(t+\tau)dt. \tag{3.3.7}$$

However, the ensemble averages (i.e., the average behavior of a huge ensemble of such stochastic systems observed *simultaneously*) and time averages are now equal (ergodic theorem), viz.,

$$C_\xi(\tau) = \langle \xi(t)\xi(t+\tau) \rangle = \overline{\xi(t)\xi(t+\tau)}. \tag{3.3.8}$$

Since

$$\xi(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{\xi}(\omega) e^{i\omega t} d\omega \text{ and } \tilde{\xi}(\omega) = \int_{-\infty}^{\infty} \xi(t) e^{-i\omega t} dt, \tag{3.3.9}$$

we have, using the shift theorem for Fourier transforms,

$$C_\xi(\tau) = \lim_{T'\to\infty} \frac{1}{T'} \int_{-T'/2}^{T'/2} \int_{-\infty}^{\infty} \tilde{\xi}(\omega) e^{i\omega t} \frac{d\omega}{2\pi} \int_{-\infty}^{\infty} e^{i\omega_1(t+\tau)} \tilde{\xi}(\omega_1) \frac{d\omega_1}{2\pi} dt. \tag{3.3.10}$$

Because

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{\pm ixy} dy = \delta(x), \tag{3.3.11}$$

on performing the integration over the t and ω_1 variables, we obtain

$$\begin{aligned} C_\xi(\tau) &= \lim_{T'\to\infty} \frac{1}{T'} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\tilde{\xi}(\omega)\tilde{\xi}(\omega_1)}{2\pi} e^{i\omega_1\tau} \delta(\omega_1 + \omega) d\omega\, d\omega_1 \\ &= \lim_{T'\to\infty} \frac{1}{T'} \int_{-\infty}^{\infty} \tilde{\xi}(\omega)\tilde{\xi}(-\omega) e^{-i\omega\tau} d\omega. \end{aligned} \tag{3.3.12}$$

Finally, since $\xi(t)$ is a real causal function of t, so that $\tilde{\xi}(-\omega) = \tilde{\xi}^*(\omega)$, we have

$$C_\xi(\tau) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \Phi_\xi(\omega) e^{-i\omega\tau} d\omega, \tag{3.3.13}$$

where

$$\Phi_\xi(\omega) = \lim_{T'\to\infty} \left|\tilde{\xi}(\omega)\right|^2 / T' \tag{3.3.14}$$

is the *spectral density* of the random variable $\xi(t)$. Since $\Phi_\xi(\omega)$ is an *even* function of ω, we will also have

$$C_\xi(\tau) = \frac{1}{\pi} \int_0^{\infty} \Phi_\xi(\omega) \cos\omega\tau\, d\omega. \tag{3.3.15}$$

By Fourier's integral theorem we also have

$$\Phi_\xi(\omega) = \int_{-\infty}^{\infty} C_\xi(\tau) e^{i\omega\tau} d\tau = 2\int_0^{\infty} C_\xi(\tau) \cos\omega\tau d\tau. \tag{3.3.16}$$

This is the Wiener–Khinchin theorem [11], namely, for a wide-sense stationary stochastic process the spectral density is the Fourier cosine-transform of $C_\xi(\tau)$.

We illustrate the use of the theorem by evaluating the velocity ACF of a free Brownian particle from the spectral density of the velocity $v(t)$. The velocity $v(t)$ in the Langevin equation, Eq. (3.2.3), is a Markov process. Since the Fourier transforms of $v(t)$ and the random force $F(t)$ are

$$\tilde{v}(\omega) = \int_{-\infty}^{\infty} v(t) e^{i\omega t} dt \quad \text{and} \quad \tilde{F}(\omega) = \int_{-\infty}^{\infty} F(t) e^{i\omega t} dt, \tag{3.3.17}$$

we have, from Eq. (3.2.3),

$$\tilde{v}(\omega) = \frac{1}{m} \chi(\omega) \tilde{F}(\omega), \tag{3.3.18}$$

where $\chi(\omega) = (\beta + i\omega)^{-1}$ is the transfer function of the system [14]. Now the spectral density of the velocity $v(t)$ is

$$\Phi_v(\omega) = \lim_{T'\to\infty} \tilde{v}(\omega)\tilde{v}^*(\omega)/T',$$

so that, with Eq. (3.3.18), we have

$$\Phi_v(\omega) = \chi(\omega)\chi^*(\omega)\frac{\Phi_F(\omega)}{m^2} = \frac{\Phi_F(\omega)}{m^2(\beta^2+\omega^2)}. \tag{3.3.19}$$

Since the spectral density of the random force $F(t)$ is given by

$$\Phi_F(\omega) = 2\zeta kT \int_{-\infty}^{\infty} \delta(\tau) e^{i\omega\tau} d\tau = 2\zeta kT,$$

we obtain

$$\Phi_v(\omega) = \frac{2\zeta kT}{m^2} \frac{1}{\beta^2+\omega^2}. \tag{3.3.20}$$

Substituting Eq. (3.3.20) into Eq. (3.3.13), we then have

$$\langle v(t)v(t+\tau)\rangle = \frac{\zeta kT}{\pi m^2} \int_{-\infty}^{\infty} \frac{e^{i\omega\tau} d\omega}{\beta^2+\omega^2} = \frac{2\beta kT}{\pi m} \int_0^{\infty} \frac{\cos\omega\tau}{\beta^2+\omega^2} d\omega.$$

Using

$$\int_0^{\infty} \frac{\cos mx}{1+x^2} dx = \frac{\pi}{2} e^{-|m|},$$

we finally have

$$\langle v(t)v(t+\tau)\rangle = \frac{kT}{m}e^{-\beta|\tau|}. \tag{3.3.21}$$

This is the velocity ACF as obtained by the Wiener–Khinchin theorem. The calculation of correlation functions based on this theorem is often known as Rice's method [3].

An example of applications of the free Brownian particle model is the incoherent scattering of slow neutrons in liquids [15, 16]. Another important application is diffusion magnetic resonance imaging (MRI) [11], which we discuss briefly in the following section.

3.4. Application to phase diffusion in MRI

The clinical applications of diffusion MRI are numerous. Changes in water diffusion in tissues have been associated with alterations in physiological and pathological states [17]. During signal acquisition in MRI, nuclear magnetic moments are manipulated via a combination of static, gradient, and radiofrequency magnetic fields. These fields and their relative timing (or pulse sequences) can be varied in many ways in order to create image contrast based on characteristics of the medium, tissue or pathology. In addition to varying tissue contrast, flowing, diffusing and perfusing spins can be encoded in the image signal.

The precession and relaxation of the net magnetization, due to the spin manipulation, is described by the phenomenological Bloch equations [18]. Bloch proposed, in his phenomenological treatment of nuclear induction, the differential equation for the time dependence of the nuclear magnetization $\mathbf{M}(t)$ under the influence of an external magnetic field $\mathbf{H}(t)$, viz.,

$$\dot{\mathbf{M}} = \gamma\mathbf{M}\times\mathbf{H} - \mathbf{i}\frac{M_X}{T_2} - \mathbf{j}\frac{M_Y}{T_2} - \mathbf{k}\frac{M_Z - M_0}{T_1}, \tag{3.4.1}$$

where γ is the gyromagnetic ratio of the nuclei under consideration, and $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are the usual triad of unit vectors along the Cartesian axes. The external field $\mathbf{H}(t)$ has the form

$$\mathbf{H}(t) = \mathbf{k}H_0 + \mathbf{H}_1(t), \tag{3.4.2}$$

where H_0 is strong and constant while $\mathbf{H}_1$ is relatively weak and an arbitrary function of time. M_0 is the equilibrium magnetization in the field H_0 and the establishment of thermal equilibrium is in Eq. (3.4.1), described by two relaxation time constants T_1 and T_2, the longitudinal and transverse relaxation

times, respectively, meaning that in the absence of the transverse field H_1, the X and Y components will vanish with a time constant T_2, while the equilibrium magnetization will be attained with a time constant T_1. To study relaxation, we suppose that H_1 is zero while H_0 is slightly altered in order to induce relaxation. The Bloch equations then become

$$\dot{\mathbf{M}} = \gamma(\mathbf{i}M_Y H_0 - \mathbf{j}M_X H_0) - \mathbf{i}\frac{M_X}{T_2} - \mathbf{j}\frac{M_Y}{T_2} - \mathbf{k}\frac{M_Z - M_0}{T_1}. \tag{3.4.3}$$

Clearly, the transverse (M_X, M_Y) and longitudinal (M_Z) components of $\mathbf{M}$ decouple in the absence of H_1. Thus, forming the complex variable

$$M_\perp(t) = M_X(t) + iM_Y(t),$$

we then have

$$\dot{M}_\perp = -i\gamma M_\perp H_0 - \frac{M_\perp}{T_2}. \tag{3.4.4}$$

The solution of this differential equation, following perturbation of the constant field H_0, is simply

$$M_\perp(t) = M_\perp(0)e^{-(i\omega_0 + 1/T_2)t}, \tag{3.4.5}$$

where $\omega_0 = \gamma H_0$ is the Larmor precessional frequency. Equation (3.4.5) represents a decaying oscillation. In practice, H_0 is not *constant* in space, and so it has a *field gradient* defining the magnitude of the field at the site of a nucleus which is represented by the position vector $\mathbf{r}(t)$,

$$H(\mathbf{r},t) = \mathbf{r}(t)\cdot\nabla H(z,t) = \mathbf{r}(t)\cdot\mathbf{G}(z,t). \tag{3.4.6}$$

Hence the solution, Eq. (3.4.5), alters to

$$M_\perp(\mathbf{r},t) = M_\perp(\mathbf{r},0)e^{-t/T_2 - i\gamma\int_0^t \mathbf{r}(t')\cdot\mathbf{G}(z,t')dt'}. \tag{3.4.7}$$

Clearly, the transverse magnetization is now a function of the position of the nucleus.

Equation (3.4.7), however, omits the Brownian motion of the particles in the liquid, which carry the nuclei. This must be taken account of in resonant imaging. In liquids, the positions of the molecules $\mathbf{r}$ fluctuate as a result of Brownian motion (*Schwankung*), so that the Larmor precession is affected, causing dephasing of the resonance signal. Thus if $\mathbf{r}(t)$ is a stochastic process, Eq. (3.4.4) becomes the stochastic differential equation,

$$\dot{M}_\perp(t) = -\left[i\gamma\mathbf{r}(t)\cdot\mathbf{G}(t) + 1/T_2\right]M_\perp(t), \tag{3.4.8}$$

which now represents the Langevin equation of the process. Thus, the time-varying field $\mathbf{r}(t)\cdot\mathbf{G}(t)$ at the site of a nucleus must now also constitute a stochastic process, because of the haphazard nature of the position vector $\mathbf{r}$. This causes phase fluctuations, viz.,

$$\Delta\Phi(t) = \int_0^t \omega(t')\,dt' = \gamma\int_0^t \mathbf{r}(t')\cdot\mathbf{G}(t')dt'. \tag{3.4.9}$$

Thus the dephasing $\Delta\Phi(t)$, owing to the thermal motion of the nuclei bearing the magnetic moments, is obtained by calculating the mean value of the functional $\left\langle e^{i\Delta\Phi}\right\rangle$, where

$$\Delta\Phi = -\gamma\int_0^t \dot{\mathbf{r}}(t_1)\int_0^{t_1}\mathbf{G}(t')dt'dt_1. \tag{3.4.10}$$

Equation (3.4.10) is obtained by integration by parts from Eq. (3.4.9), by imposing the so-called "rephasing condition"

$$\int_0^t \mathbf{G}(t')dt' = 0.$$

Dephasing due to random modulation of the Larmor frequency, $\omega(t)$, was first observed by Hahn [19], who noted the attenuation of the observed transient signals in NMR experiments as a result of the self-diffusion of "spin-containing liquid molecules." Clearly, the calculation of $\left\langle e^{i\Delta\Phi}\right\rangle$ merely amounts to determining the characteristic function of the centered random variable $\Delta\Phi$. This is particularly easy for centered Gaussian processes, because then one may write, following Sections 1.6.3 and 3.6 (below),

$$\left\langle e^{i\Delta\Phi}\right\rangle = e^{-\left\langle\Delta\Phi^2\right\rangle/2}. \tag{3.4.11}$$

Thus, if we regard the particles carrying the nuclei as free Brownian particles, we can determine the dephasing by means of Eq. (3.4.11).

Numerous attempts have been made to incorporate the Brownian motion of the liquid nuclei, e.g., [19, 20, 21]. The treatment of Carr and Purcell [21] (effectively Einstein's theory, as in Chapter 1, Section 1.4, adapted for phase fluctuations) assumes that a nucleus in a liquid executes a discrete-time random walk, owing to the cumulative effect of very large numbers of impacts from the surrounding particles, so that the phase is a sum of random variables each having arbitrary distributions. The only random variable is the position of the walker, i.e., the direction of the jump-length vector (Chapter 1, Section 1.4), as (a) it has finite variance and (b) the waiting time between jumps has finite mean.

The problem is always to find the probability that the walker will be in state n at some time t, given that it was in a state m at some earlier time; this gives rise in general to a difference equation ([3, 22]; see also Chapter 1, Section 1.22). However, by the central limit theorem (Chapter 1, Section 1.6.4), the dephasing effect may be calculated explicitly in the continuum limit of extremely small mean square displacements in infinitesimally short times. The above analysis was later much simplified by Torrey [23]. He avoided the problem of explicitly passing to the continuum limit by simply adding a magnetization diffusion term to the transverse magnetization in the Bloch equations (following Einstein, as in Chapter 1, Section 1.2), resulting in a partial differential equation, now called the Bloch–Torrey equation [24, 25]. Moreover, by the introduction of appropriate boundary conditions, this equation is ideally suited to describing restricted diffusion in a confining domain [25]. The Bloch–Torrey equation may be solved for nuclei diffusing freely in an infinite reservoir. Thus Torrey [23] obtained for the dephasing, following the application of a step gradient of magnitude G in a liquid characterized by a diffusion coefficient D,

$$\left\langle e^{i\Delta\Phi} \right\rangle = A(t) / A(0) = e^{-D\gamma^2 G^2 t^3/3}. \tag{3.4.12}$$

Moreover, for a simple bipolar gradient-echo experiment, with gradients of strength G and duration τ,

$$\left\langle e^{i\Delta\Phi} \right\rangle_{\mathrm{GE}} = A(2\tau) / A(0) = e^{-2D\gamma^2 G^2 \tau^3/3}. \tag{3.4.13}$$

The spin-echo diffusion experiment case is slightly different [26]; the calculations are considerably more involved than in the gradient echo case, where the second gradient pulse has the effect of resetting the dephasing caused by the first pulse. By applying the 180° pulse in the spin-echo experiment, the phase is reset by double the extent to which it was advanced [26], so that

$$\left\langle e^{i\Delta\Phi} \right\rangle_{\mathrm{SE}} = e^{-D\gamma^2 G^2 \delta^2 (\Delta - \delta/3)}, \tag{3.4.14}$$

where δ is the gradient spacing and Δ is the time interval from the starting time of the first gradient to the starting time of the rephasing gradient. *It follows that the diffusion coefficient D can then be measured via the amplitude of the echo signal from nuclear spins, subject to an appropriate sequence of magnetic field pulses.* Now Eqs. (3.4.9)–(3.4.14) describe the signal loss due to the translational motion of the magnetic moments in unrestricted (free) water in a magnetic resonance experiment. The equations have their origin in the work of Bloch [18], which is the starting point of our treatment of dephasing.

In order to illustrate the calculation of the dephasing from the Langevin equation, we consider for simplicity the Brownian motion of a free particle along the x-axis. We first derive Eq. (3.4.12) for the phase diffusion which corresponds to the non-inertial limit, where the inertia of the particle may be ignored. Here the Langevin equation is simply

$$\zeta \dot{x}(t) = F(t), \tag{3.4.15}$$

where $x(t)$ is the coordinate of the Brownian particle (nucleus), and $F(t)$ is the usual random force with white-noise properties. Equation (3.4.15) follows from the inertial Langevin equation, Eq. (3.2.3), for the velocity $v(t) = \dot{x}(t)$ of the Brownian particle of mass m by neglecting the inertial term.

According to Eq. (3.4.10) the non-inertial Langevin equation for the phase $\Phi(t)$ is

$$\dot{\Phi}(t) = -\gamma \dot{x}(t) \int_0^t G(t')dt' = -\gamma \zeta^{-1} F(t) \int_0^t G(t')\, dt'. \tag{3.4.16}$$

These equations simply state that the only way the phase can change is via the equation of motion of $x(t)$. In the Brownian motion of a free particle, the phase $\Phi(t)$ is a centered Gaussian random variable with variance $\sigma^2 = \langle \Delta\Phi^2 \rangle = \langle \Phi^2 \rangle$ since $\langle \Phi \rangle = 0$ and $t_0 = 0$. Noting that

$$\Phi^2(t) = 2\int_0^t \Phi(t_1)\dot{\Phi}(t_1)dt_1, \tag{3.4.17}$$

because we may take $\Phi(0) = 0$, we have for a step field gradient

$$\begin{aligned} \left\langle \Delta\Phi^2 \right\rangle &= 2\gamma^2 \zeta^{-2} \int_0^t \int_0^{t_1} \int_0^{t_1} G(t')\, dt' \int_0^{t_2} G(t'')\, dt'' \left\langle F(t_1)F(t_2) \right\rangle dt_1 dt_2 \\ &= 2D\gamma^2 \int_0^t \left[\int_0^{t_1} G(t'')dt'' \right]^2 dt_1 = \frac{2}{3} D\gamma^2 G^2 t^3, \end{aligned} \tag{3.4.18}$$

where $D = kT/\zeta$ is the diffusion coefficient which is, as usual, defined via the mean-square displacement of the Brownian particle in a time interval t. Hence, from Eq. (3.4.11) we have the known result Eq. (3.4.12) for the dephasing following the application of a step gradient.

The gradient-echo result Eq. (3.4.13) may be obtained in a similar way. For the spin-echo case, Eq. (3.4.14) may be obtained by writing the left-hand side of Eq. (3.4.18) as [26]

$$\left\langle \Delta\Phi^2 \right\rangle = 2D\gamma^2 \int_0^{2\tau} [R^2(t_1) + 2(\xi - 1)\mathbf{f} \cdot \mathbf{R}(t_1) + f^2]dt_1 \tag{3.4.19}$$

with $\xi = +1$ for $t < \tau$ and $\xi = -1$ for $t > \tau$, where $\mathbf{R}(t)$ is defined by

$$\mathbf{R}(t) = \int_0^t \mathbf{G}(t')dt' \tag{3.4.20}$$

and $\mathbf{f} = \mathbf{R}(\tau)$, where τ is the time of application of the 180° pulse.

The above analysis ignores the inertia of the Brownian particles. If inertial effects are included, the translational process, $x(t)$, now possesses *two* characteristic times. One time characterizes the slow diffusion associated with the non-inertial motion, which we have already analyzed. The other time is the correlation time $\tau_v = m/\zeta$ of the velocity ACF. It is of interest to show how one can include these characteristic times in the phase diffusion. Therefore we show how the calculation using the non-inertial Langevin equation may be extended to a free particle of mass m. In the inertial motion of a Brownian particle, the velocity ACF is given by Eq. (3.3.21), which we rewrite as

$$\langle \dot{x}(t_1)\dot{x}(t_2)\rangle = \frac{kT}{m} e^{-\beta|t_1 - t_2|}. \tag{3.4.21}$$

Now for a step field gradient we again have

$$\dot{\Phi}(t) = -\gamma G t \dot{x}(t) \text{ and } \Phi(t) = -\gamma G \int_0^t t_1 \dot{x}(t_1)dt_1.$$

Hence we can now evaluate the mean-square value of the phase $\langle \Delta\Phi^2 \rangle(t)$ as

$$\langle \Delta\Phi^2 \rangle = 2\gamma^2 G^2 \int_0^t \int_0^{t_1} t_1 t_2 \langle \dot{x}(t_1)\dot{x}(t_2)\rangle dt_1 dt_2$$

$$= \frac{\gamma^2 G^2 kT}{3\beta^4 m}\left[6 + t^2\beta^2(2t\beta - 3) - 6e^{-\beta t}(1 + t\beta)\right] \tag{3.4.22}$$

which reduces to the Carr–Purcell–Torrey result, Eq. (3.4.18), for long times $t\beta >> 1$. For short times, $t\beta << 1$, we have the purely kinematic result

$$\langle \Delta\Phi^2 \rangle \approx \frac{\gamma^2 G^2 kT t^4}{4m}. \tag{3.4.23}$$

Again $\Delta\Phi$ is a linear transformation of a Gaussian random variable, so that by the properties of characteristic functions

$$\langle e^{i\Delta\Phi} \rangle = e^{-\frac{1}{2}\langle \Delta\Phi^2 \rangle}. \tag{3.4.24}$$

Hence Eq. (3.4.22) yields the inertia corrected dephasing for a step gradient. In general, an infinity of fast relaxation modes will be generated, as a result of the double transcendental nature of Eq. (3.4.24), and one dominant mode, much

slower, which is that associated with the slow diffusive motion. An obvious generalization of the left hand side of Eq. (3.4.18), for arbitrary gradient shapes defined by Eq. (3.4.20), is

$$\left\langle \Delta\Phi^2 \right\rangle = 2\gamma^2 \int_0^t \int_0^{t_1} \left\langle \dot{x}(t_1)\dot{x}(t_2) \right\rangle R(t_1)R(t_2)dt_1 dt_2 . \tag{3.4.25}$$

Hence, in order to calculate the dephasing for a Gaussian process, all that is required is knowledge of the velocity ACF and the precise form of the field gradients. We remark that Eq. (3.4.25) was previously derived by Stepišnik and Callaghan [27] in connection with measurement of flow by NMR spectroscopy and long-time tails of the molecular velocity correlation function in a confined fluid. In Chapter 12, Section 12.8, the above calculations are extended to a more general model, namely the fractional Brownian motion of a free particle coupled to a fractal heat bath, using a fractional generalization of the Langevin equation.

3.5. Brownian motion of a harmonic oscillator

The equation of motion of a Brownian harmonic oscillator driven by a white noise force $F(t)$ is [3, 5]

$$m\ddot{x}(t) + \zeta\dot{x}(t) + m\omega_0^2 x(t) = F(t). \tag{3.5.1}$$

We now demonstrate how the *correlation matrix*, which contains two auto- and two cross-correlation functions, namely,

$$\begin{pmatrix} \left\langle x(t)x(t+\tau) \right\rangle & \left\langle x(t)\dot{x}(t+\tau) \right\rangle \\ \left\langle \dot{x}(t)x(t+\tau) \right\rangle & \left\langle \dot{x}(t)\dot{x}(t+\tau) \right\rangle \end{pmatrix}, \tag{3.5.2}$$

may also be calculated from the Wiener–Khinchin theorem. We first calculate the position ACF $\left\langle x(t)x(t+\tau) \right\rangle$. To this end, we rewrite the Langevin equation, Eq. (3.5.1), as

$$\ddot{x}(t) + \beta\dot{x}(t) + \omega_0^2 x(t) = \frac{F(t)}{m}. \tag{3.5.3}$$

We have, as in Section 3.3,

$$\tilde{x}(\omega) = \frac{\tilde{F}(\omega)}{m(\omega_0^2 + i\omega\beta - \omega^2)},$$

and the spectral density $\Phi_x(\omega)$ of the displacement is

$$\Phi_x(\omega) = \frac{\Phi_F(\omega)}{m^2\left[(\omega_0^2 - \omega^2)^2 + \omega^2\beta^2\right]}. \tag{3.5.4}$$

Since the spectral density of the noise is $\Phi_F(\omega) = 2\beta mkT$, we have by the Wiener–Khinchin theorem

$$\langle x(t)x(t+\tau)\rangle = \frac{\beta kT}{\pi m}\int_{-\infty}^{\infty}\frac{e^{-i\omega\tau}\,d\omega}{(\omega_0^2-\omega^2)^2+\omega^2\beta^2}. \tag{3.5.5}$$

The imaginary part of this integral vanishes, because it gives rise to an odd function in the integrand. For $\omega_0^2 > \beta^2/4$ and $\tau \geq 0$, we have [3]

$$\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\cos\omega\tau\, d\omega}{(\omega_0^2-\omega^2)^2+\omega^2\beta^2} = \frac{e^{-\beta\tau/2}}{\beta\omega_0^2}\left(\cos\omega_1\tau + \frac{\beta}{2\omega_1}\sin\omega_1\tau\right), \tag{3.5.6}$$

where the damped natural frequency ω_1 is defined as

$$\omega_1^2 = \omega_0^2 - \frac{\beta^2}{4}.$$

Hence the position ACF is given by

$$\langle x(t)x(t+\tau)\rangle = \frac{kT}{m\omega_0^2}e^{-\frac{\beta\tau}{2}}\left(\cos\omega_1\tau + \frac{\beta}{2\omega_1}\sin\omega_1\tau\right). \tag{3.5.7}$$

We may now use this result to calculate the remaining elements of the correlation matrix by differentiation. We have

$$\langle x(t)\dot{x}(t+\tau)\rangle = \left\langle x(t)\frac{d}{d\tau}x(t+\tau)\right\rangle = \frac{d}{d\tau}\langle x(t)x(t+\tau)\rangle, \tag{3.5.8}$$

so that with Eq. (3.5.7)

$$\langle x(t)\dot{x}(t+\tau)\rangle = -\frac{kT}{m\omega_1}e^{-\beta\tau/2}\sin\omega_1\tau. \tag{3.5.9}$$

In order to evaluate the two remaining correlation functions, we note that, *by stationarity* shifting the time axis from t to $t-\tau$,

$$\left\langle x(t+\tau)\frac{d}{dt}x(t)\right\rangle = -\frac{d}{d\tau}\langle x(t)x(t+\tau)\rangle = \frac{kT}{m\omega_1}e^{-\beta\tau/2}\sin\omega_1\tau. \tag{3.5.10}$$

The velocity ACF may likewise be evaluated. We have, by stationarity,

$$\langle\dot{x}(t)\dot{x}(t+\tau)\rangle = -\frac{d}{d\tau}\langle x(t)\dot{x}(t+\tau)\rangle = -\frac{d^2}{d\tau^2}\langle x(t)x(t+\tau)\rangle, \tag{3.5.11}$$

whence

$$\langle\dot{x}(t)\dot{x}(t+\tau)\rangle = \frac{kT}{m}e^{-\beta\tau/2}\left(\cos\omega_1\tau - \frac{\beta}{2\omega_1}\sin\omega_1\tau\right). \tag{3.5.12}$$

The correlation matrix of the harmonic oscillator is thus

$$\frac{kT}{m}e^{-\beta\tau/2}\begin{pmatrix}\dfrac{1}{\omega_0^2}\left(\cos\omega_1\tau+\dfrac{\beta}{2\omega_1}\sin\omega_1\tau\right) & -\dfrac{1}{\omega_1}\sin\omega_1\tau \\ \dfrac{1}{\omega_1}\sin\omega_1\tau & \cos\omega_1\tau-\dfrac{\beta}{2\omega_1}\sin\omega\tau\end{pmatrix}. \tag{3.5.13}$$

Clearly, the under-damped process has significant memory of previous positions (cf. Fig. 1.3.1.1). Thus, $x(t)$ is regarded as [3] the projection of the two-dimensional Markov process $\{x(t),\dot{x}(t)\}$.

3.6. Rotational Brownian motion of a fixed-axis rotator

In his first model of the phenomenon of dielectric relaxation, given in 1913, Debye [12] considered a system of molecules each carrying a permanent dipole $\boldsymbol{\mu}$, with every molecule free to rotate about a fixed axis (see Chapter 2, Section 2.6). Supposing that an external spatially uniform small d.c. electric field $\mathbf{E}$ ($\xi=\mu E/(kT)<<1$) had been applied to the system at $t=-\infty$, and at time $t=0$ the field has been switched off, the equation of motion of the fixed-axis rotator is

$$\varsigma\dot{\theta}(t)+\mu E\sin\theta(t)=\lambda(t),\ \ t\le 0,\ \text{and}\ \varsigma\dot{\theta}(t)=\lambda(t),\ \ t>0, \tag{3.6.1}$$

where $\theta(t)$ is the angle between the dipole $\boldsymbol{\mu}$ and the direction the field $\mathbf{E}$, and $\lambda(t)$ is a white-noise driving torque. One can then show that the PDF $f(\theta,t)$ of the dipole moment orientations satisfies the Smoluchowski equation

$$\tau_{\mathrm{D}}\frac{\partial f}{\partial t}=\frac{\partial^2 f}{\partial\theta^2},\qquad t>0, \tag{3.6.2}$$

where $\tau_{\mathrm{D}}=\varsigma/(kT)$ is the Debye relaxation time for rotation about a fixed axis. Equation (3.6.2) together with the initial condition

$$f(\theta,0)=\frac{1}{2\pi}\left(1+\frac{\mu E}{kT}\cos\theta+\cdots\right) \tag{3.6.3}$$

then yields in the linear response approximation the well-known result [12] for the mean dipole moment

$$\mu\langle\cos\theta\rangle=\frac{\mu^2 E}{2kT}e^{-t/\tau_{\mathrm{D}}}. \tag{3.6.4}$$

Inertial effects are included by simply restoring the inertial term $I\ddot{\theta}$ in Eq. (3.6.1) above. Thus, that equation becomes

$$I\ddot{\theta}(t)+\varsigma\dot{\theta}(t)+\mu E\sin\theta(t)=\lambda(t) \tag{3.6.5}$$

for $t<0$, and

$$I\ddot{\theta}(t)+\varsigma\dot{\theta}(t)=\lambda(t) \tag{3.6.6}$$

for $t>0$. Equation (3.6.6) is a Langevin equation of the same form as that governing translational Brownian motion; see Eq. (3.2.3). Consequently, all the results we have previously obtained for the translational case can be applied to rotational Brownian motion. In particular, the mean-square angular displacement $\langle(\Delta\theta)^2\rangle$ is given by

$$\langle(\Delta\theta)^2\rangle=\frac{2kT}{I\beta^2}\left(\beta t-1+e^{-\beta t}\right), \tag{3.6.7}$$

where $\beta=\varsigma/I$ is the rotational damping coefficient. We note that, just as in all the other models treated in this Chapter, Eq. (3.6.6) comprises a linear stochastic differential equation with constant coefficients. This is of central importance to what follows, where a theorem about characteristic functions of Gaussian random variables [28] is used to calculate the dipole moment ACF.

Theorem about Gaussian random variables

The theorem is that, if X is a random variable with a Gaussian distribution, then [28]

$$\left\langle e^{iX}\right\rangle=e^{i\langle X\rangle-\left(\langle X^2\rangle-\langle X\rangle^2\right)/2} \tag{3.6.8}$$

(cf. Eq. (3.4.24); see also Chapter 1, Section 1.6.3). Consider now the ACF $\langle\cos\theta(t_1)\cos\theta(t_2)\rangle=\langle\cos\theta(t_1)\cos[\theta(t_1)+\Delta\theta]\rangle$, where $\Delta\theta=\theta(t_2)-\theta(t_1)$. This becomes, on expanding the terms within the angular brackets,

$$\begin{aligned}\left\langle\cos\theta(t_1)\cos\theta(t_2)\right\rangle&=\frac{1}{2}\left\{\left\langle\cos\Delta\theta\right\rangle+\left\langle\cos\left[\Delta\theta+2\theta(t_1)\right]\right\rangle\right\}\\&=\frac{1}{2}\mathrm{Re}\left[\left\langle e^{i\Delta\theta}\right\rangle+\left\langle e^{i\Delta\theta+2\theta(t_1)}\right\rangle\right],\end{aligned} \tag{3.6.9}$$

where Re denotes "real part of." Now, if $\theta(t_1)$ and $\theta(t_2)$ are *Gaussian* random variables, any linear combination of them (e.g., $\Delta\theta$) is also a Gaussian random variable. Hence

$$\begin{aligned}\left\langle\cos\theta\left(t_1\right)\cos\theta\left(t_2\right)\right\rangle=\frac{1}{2}\mathrm{Re}\Bigg(&e^{i\langle\Delta\theta\rangle-\frac{1}{2}\left[\langle(\Delta\theta)^2\rangle-\langle\Delta\theta\rangle^2\right]}\\&+e^{i\langle\Delta\theta+2\theta(t_1)\rangle-\frac{1}{2}\left[\left\langle\left[\Delta\theta+2\theta(t_1)\right]^2\right\rangle-\left\langle\left[\Delta\theta+2\theta(t_1)\right]\right\rangle^2\right]}\Bigg)\end{aligned} \tag{3.6.10}$$

Now, if the process we are considering is stationary, only those terms in Eq. (3.6.10) which are functions of the *time difference* $|t_2 - t_1|$ will survive, so that Eq. (3.6.10) will take on the simple form

$$\left\langle \cos\theta(t_1)\cos\theta(t_2)\right\rangle = (1/2)e^{-\left[\left\langle(\Delta\theta)^2\right\rangle - \left\langle\Delta\theta\right\rangle^2\right]/2}\,\mathrm{Re}\left\{e^{i\left\langle\Delta\theta\right\rangle}\right\}. \tag{3.6.11}$$

Further, if θ is a *centered* Gaussian random variable (i.e., $\langle\theta\rangle = 0$), then Eq. (3.6.11) reduces to

$$\left\langle \cos\theta(t_1)\cos\theta(t_2)\right\rangle = (1/2)e^{-\left\langle(\Delta\theta)^2\right\rangle/2}. \tag{3.6.12}$$

Thus knowledge of $\langle(\Delta\theta)\rangle^2$ is now sufficient to allow us to calculate averages. We have given the theorem for $n = 1$. For any integer value of n it is simply

$$\left\langle \cos n\theta(t_1)\cos n\theta(t_2)\right\rangle = (1/2)e^{-n^2\left\langle(\Delta\theta)^2\right\rangle/2}. \tag{3.6.13}$$

We reiterate that this equation is true only for *centered Gaussian* random variables. Thus the theorem will only hold good for those systems where θ satisfies a linear differential equation of motion.

Application to dielectric relaxation

We may have, from Eq. (3.6.7) and (3.6.12), the ACF $C(t)$:

$$C(t) = \left\langle \cos\theta(0)\cos\theta(t)\right\rangle \Big/ \left\langle \cos^2\theta(0)\right\rangle = e^{-\frac{kT}{I\beta^2}\left(\beta t - 1 + e^{-\beta t}\right)}. \tag{3.6.14}$$

The complex polarizability α is written down using the linear response formula, Chapter 2, Eq. (2.8.10). It is (with $i\omega = s$)

$$\frac{\alpha(s)}{\alpha'(0)} = 1 - s\int_0^\infty e^{-st}C(t)dt. \tag{3.6.15}$$

Hence [7]

$$\frac{\alpha(s)}{\alpha'(0)} = 1 - \frac{s}{s+\gamma\beta}\left[1 + \frac{\gamma}{(s/\beta)+\gamma+1} + \frac{\gamma^2}{[(s/\beta)+\gamma+1][(s/\beta)+\gamma+2]} + \cdots\right]$$

$$= 1 - \frac{s\tau_D}{1+s\tau_D} M\left[1, 1+\gamma(1+s\tau_D), \gamma\right], \tag{3.6.16}$$

where $\gamma = kT/(I\beta^2)$ is Sack's inertial parameter [57], $\tau_D = 1/(\beta\gamma)$, and $M(a,b,z)$ is the confluent hypergeometric (Kummer) function defined [29] as

$$M(a,b,z) = 1 + \frac{a}{b}z + \frac{a(a+1)}{b(b+1)}\frac{z^2}{2!} + \frac{a(a+1)(a+2)}{b(b+1)(b+2)}\frac{z^3}{3!} + \cdots. \tag{3.6.17}$$

This result shows that the effect of including the inertia of the dipole is to produce a *denumerable* set of relaxation mechanisms. The series in Eq. (3.6.16) may be rewritten as the continued fraction [7, 8]

$$\frac{\alpha(s)}{\alpha'(0)} = 1 - \cfrac{s/\beta}{s/\beta + \cfrac{\gamma}{1 + s/\beta + \cfrac{2\gamma}{2 + s/\beta + \cfrac{3\gamma}{3 + s/\beta + \cdots}}}}. \tag{3.6.18}$$

The first convergent of Eq. (3.6.18) yields the Debye relaxation formula

$$\frac{\alpha(s)}{\alpha'(0)} = \frac{1}{1 + s\tau_D}. \tag{3.6.19}$$

The second convergent of Eq. (3.6.18) yields the Rocard equation [30]

$$\frac{\alpha(s)}{\alpha'(0)} = \frac{\gamma\beta^2}{(s+\gamma\beta)(s+\beta)} \cong \frac{1}{1 + s\tau_D + s^2\tau_D/\beta}. \tag{3.6.20}$$

This provides [7] a good approximation to the relaxation behavior, provided that $\gamma \leq 0.05$. Equations (3.6.16) and (3.6.20) have been exhaustively discussed in Chapter 2 of *Molecular Dynamics* [10]. It is evident that the simple Debye model, including an inertial correction, is not sufficient to explain the experimental evidence. The inertial correction embodied in Eq. (3.6.20) does, however, remove the unacceptable plateau in the high-frequency absorption profile (see Section 1.15.1). The same holds true for all the three-dimensional versions of the Debye model, including inertial effects. These are the sphere, prolate and oblate spheroid, and general ellipsoid. The far-infrared absorption and the microwave absorption linked to it cannot be satisfactorily explained by the Debye theory *with inertial corrections only.*

As a prelude to the itinerant oscillator model of Chapter 11, which is an attempt to address the Poley absorption theoretically, we now treat the torsional oscillator model, originally discussed by Calderwood *et al.* [9].

3.7. Torsional oscillator model: example of the use of the Wiener integral

The simplest model that takes any account of the effect of the neighbors of a molecule on its relaxation behavior is where we regard the molecule as a torsional oscillator. Thus, we suppose that at a time t after the switching off of a field which had been steady up to $t = 0$, the equation of motion of the dipole is

$$\ddot{\theta}(t) + \beta\dot{\theta}(t) + \omega_0^2\theta(t) = \dot{W}(t), \tag{3.7.1}$$

where $W(t)$ is the Wiener process (the symbol W being used for ease of comparison with the original literature), $\omega_0^2 = \kappa / I$, $\beta = \varsigma / I$, and I is the moment of inertia. We use the Wiener process here in order to illustrate how this process, and the Wiener integral, may be used in the computation of averages. We have

$$\langle W(t) \rangle = 0, \quad \langle W(t_1) W(t_2) \rangle = c^2 \min(t_1, t_2), \quad W(t_2) - W(t_1) = \xi(t_2 - t_1).$$

If Δ and Δ' denote the time differences $t_i - t_j$ and $t_i' - t_j'$, respectively, then (see Chapter 1, Section 1.8.1) $\langle \xi(\Delta) \rangle = 0$, $\langle \xi(\Delta) \xi(\Delta') \rangle = c^2 \, | \Delta \cap \Delta' |$. The restoring torque $\kappa \theta(t)$ is used to crudely represent the effect of interaction due to the neighbors of the molecule. In reality, this restoring torque is not at all linear, because the torque on a dipole $\boldsymbol{\mu}$ placed in a field $\mathbf{E}$ is $\mathbf{T} = \boldsymbol{\mu} \times \mathbf{E}$, so that $|\mathbf{T}| = |\boldsymbol{\mu}||\mathbf{E}| \sin\theta$. Hence, Eq. (3.7.1) should only hold for small θ. The case of unrestricted θ is considered in detail in Chapter 10. We now proceed as in the free-particle problem, and write Eq. (3.7.1) in matrix form

$$\dot{\mathbf{X}}(t) = \mathbf{A}\mathbf{X}(t) + \mathbf{B}U(t),$$

$$\mathbf{X}(t) = \begin{bmatrix} \theta(t) \\ \dot{\theta}(t) \end{bmatrix}, \quad \mathbf{A} = \begin{bmatrix} 0 & 1 \\ -\omega_0^2 & -\beta \end{bmatrix}, \quad \mathbf{B} = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \quad U = \dot{W}. \tag{3.7.2}$$

The solution of Eq. (3.7.2) may be calculated just as for the free particle. We have

$$\begin{bmatrix} \theta(t) \\ \dot{\theta}(t) \end{bmatrix} = \begin{bmatrix} e_0(t)\left[c_0(t) + \beta s_0(t)/\beta_1\right] & -2e_0(t)s_0(t)/\beta_1 \\ -\omega_0^2 e_0(t)s_0(t)/(2\beta_1) & e_0(t)\left[c_0(t) - \beta s_0(t)/\beta_1\right] \end{bmatrix} \begin{bmatrix} \theta \\ \dot{\theta}_0 \end{bmatrix}$$

$$+ \int_0^t \begin{bmatrix} e_\tau(t)\left[c_\tau(t) + \beta s_\tau(t)/\beta_1\right] & -2e_\tau(t)s_\tau(t)/\beta_1 \\ -\omega_0^2 e_\tau(t)s_\tau(t)/(2\beta_1) & e_\tau(t)\left[c_\tau(t) - \beta s_\tau(t)/\beta_1\right] \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \xi(d\tau), \tag{3.7.3}$$

where we have abbreviated

$$e_\tau(t) = e^{-\beta(t-\tau)/2}, \quad s_\tau(t) = \sinh\left[\beta_1(t-\tau)/2\right], \quad c_\tau(t) = \cosh\left[\beta_1(t-\tau)/2\right],$$

so that $\tau = 0$ on the first line in Eq. (3.7.3). We use the stationary solution of Eq. (3.7.3), rather than averaging over the initial conditions again, as an example of an alternative method of calculation of the desired averages. The stationary solution is found by simply extending the lower limit of integration to $-\infty$ and setting the complementary part of the solution equal to zero in Eq. (3.7.3). The matrix elements which are useful to us are θ and $\dot{\theta}$. We have

$$\theta(t) = \frac{2}{\beta_1} \int_{-\infty}^{t} e^{-\beta(t-\tau)/2} \sinh\left[\beta_1(t-\tau)/2\right] \xi(d\tau)$$

and thus

$$\dot{\theta}(t) = \int_{-\infty}^{t} e^{-\beta(t-\tau)/2} \left(\cosh\left[\beta_1(t-\tau)/2\right] - (\beta/\beta_1)\sinh\left[\beta_1(t-\tau)/2\right]\right)\xi(d\tau),$$

where $\beta_1^2 = \beta^2 - 4\omega_0^2$. The formulas appropriate for the periodic (β_1 is imaginary) and the critically damped ($\beta_1 = 0$) cases can be written down by replacing $\beta_1^{-1}\sinh(\beta_1 t/2)$ and $\cosh(\beta_1 t/2)$, respectively, by $(2\omega_1)^{-1}\sin\omega_1 t$ and $\cos\omega_1 t$, in the periodic case, and by 1 and $t/2$ in the critically damped case.

We now define a function

$$g_t(\tau) = \begin{cases} (2/\beta_1)e^{-\beta(t-\tau)/2}\sinh\left[\beta_1(t-\tau)/2\right], & \tau \le t, \\ 0, & \tau > t. \end{cases}$$

Thus by the properties of the Wiener integral,

$$\left\langle \theta(t_1)\theta(t_2)\right\rangle = c^2\int_{-\infty}^{\infty} g_{t_1}(\tau)g_{t_2}(\tau)d\tau$$

$$= \frac{4c^2}{\beta_1^2}\int_{-\infty}^{\min(t_1,t_2)} e^{-\frac{\beta}{2}(t_1-\tau)}\sinh\left[\frac{\beta_1}{2}(t_1-\tau)\right]e^{-\frac{\beta}{2}(t_2-\tau)}\sinh\left[\frac{\beta_1}{2}(t_2-\tau)\right]d\tau$$

$$= \frac{c^2}{2\beta\omega_0^2}\left(\cosh\left[\frac{\beta_1}{2}(t_2-t_1)\right] + \frac{\beta}{\beta_1}\sinh\left(\frac{\beta_1}{2}|t_2-t_1|\right)\right)e^{-\frac{\beta}{2}|t_2-t_1|}.$$

Similarly, one may deduce that

$$\left\langle \dot{\theta}(t_1)\dot{\theta}(t_2)\right\rangle = \frac{c^2}{2\beta}\left(\cosh\left[\beta_1(t_2-t_1)/2\right] - \frac{\beta}{\beta_1}\sinh\left[\beta_1|t_2-t_1|/2\right]\right)e^{-\beta|t_2-t_1|/2}$$

and that $\left\langle\theta(t_1)\right\rangle = \left\langle\theta(t_2)\right\rangle = 0$. Thus, for equal times, $t_1 = t_2 = t$ say, we have $\left\langle\theta^2(t)\right\rangle = c^2/(2\beta\omega_0^2)$ and $\left\langle\dot{\theta}^2(t)\right\rangle = c^2/(2\beta)$. If we assume the Maxwellian distribution for the angular velocity $\dot{\theta}(t)$, we must have $I\left\langle\dot{\theta}^2(t)\right\rangle/2 = kT/2$ and thus $c^2/(2\beta) = kT/I$. From this, with $t_1 = 0$, $t_2 = t$, we have

$$\left\langle\theta(0)\theta(t)\right\rangle = \frac{kT}{I\omega_0^2}\left[\cosh(\beta_1 t/2) + \frac{\beta}{\beta_1}\sinh(\beta_1 t/2)\right]e^{-\beta t/2}$$

and $\langle\theta^2(0)\rangle = \langle\theta^2(t)\rangle = kT/(I\omega_0^2)$. Substituting from all these equations into Eq. (3.6.10), we find that [9]

$$\left\langle\cos\theta(0)\cos\theta(t)\right\rangle = e^{-\gamma}\cosh\left\{\gamma e^{-\beta t/2}\left[\cosh(\beta_1 t/2) + (\beta/\beta_1)\sinh(\beta_1 t/2)\right]\right\},$$

where, in this instance, $\gamma = kT/(I\omega_0^2)$. Note that Eq. (3.6.10) must be used rather than Eq. (3.6.13), because the second term on the right of Eq. (3.6.10) does not now vanish, as a result of the influence of the restoring torque.

Likewise, one may show that $\langle \cos\theta(0)\rangle^2 = e^{-\gamma}$ and thus the after-effect function $b(t) = [\mu^2/(kT)][\langle \cos\theta(0)\cos\theta(t)\rangle - \langle \cos\theta(0)\rangle^2]$ is

$$b(t) = \frac{\mu^2}{kT} e^{-\gamma} \left\{ \cosh\left(\gamma e^{-\beta t/2} \left[\cosh(\beta_1 t/2) + (\beta/\beta_1)\sinh(\beta_1 t/2) \right] \right) - 1 \right\}. \quad (3.7.4)$$

It is instructive to make some comments on this equation. First we consider the limiting value of $b(t)$ when ω_0 is allowed to tend to zero. We find, by L'Hôpital's rule, that

$$\lim_{\omega_0 \to 0} b(t) = \frac{\mu^2}{2kT} e^{-\frac{kT}{I\beta^2}\left(\beta t - 1 + e^{-\beta t}\right)}, \quad (3.7.5)$$

in agreement with the result for the free rotator. Returning now to Eq. (3.7.4), we consider the behavior of $b(t)$ for large and small values of time t. For very short times ($t \ll \beta^{-1}$), we find that

$$b(t) = \frac{\mu^2 e^{-\gamma}}{kT} \left[\cosh\gamma\left(1 - \omega_0^2 t^2\right) - 1 \right]. \quad (3.7.6)$$

Thus, for short times, $b(t)$ is *independent of the friction coefficient* β. On the other hand, as t tends to infinity, we find that $\lim_{t\to\infty} b(t) = 0$, a condition which $b(t)$ must, by definition, satisfy. We remark [1] that in the over-damped case, the displacement is again effectively a Markov process.

We have, by expanding Eq. (3.7.4) as a Taylor series in powers of γ, the following expression for the after-effect function $b(t)$:

$$b(t) = \frac{\mu^2}{kT} e^{-\gamma} \sum_{n=1}^{\infty} \frac{\gamma^{2n} e^{-n\beta t}}{(2n)!} \left[\cosh(\beta_1 t/2) + (\beta/\beta_1)\sinh(\beta_1 t/2) \right]^{2n}, \quad (3.7.7)$$

which, on introduction of the angle ϕ, where

$$\sinh\phi = \frac{\beta_1}{2\omega_0} \quad \text{and} \quad \cosh\phi = \frac{\beta}{2\omega_0},$$

may be written as

$$b(t) = \frac{\mu^2}{kT} e^{-\gamma} \sum_{n=1}^{\infty} \frac{\gamma^{2n}}{(2n)!} e^{-n\beta t} \left(2\omega_0/\beta_1\right)^{2n} \sinh^{2n}\left(\beta_1 t/2 + \phi\right).$$

From the binomial theorem, we have

$$b(t) = \frac{\mu^2 e^{-\gamma}}{kT} \sum_{n=1}^{\infty} \left\{ \frac{\gamma^{2n}}{(2n)!} \left(\frac{\omega_0}{\beta_1}\right)^{2n} \left[\sum_{m=0}^{2n} (-1)^m \binom{2n}{m} e^{2(n-m)\phi} e^{-[m\beta_1 + n(\beta - \beta_1)]t} \right] \right\}. \quad (3.7.8)$$

We now recall that the complex polarizability $\alpha(\omega)$ is defined by Eq. (2.8.9) of Chapter 2. From this, with Eq. (3.7.8), we have

$$\alpha(\omega) = \mu^2 \frac{e^{-\gamma}}{kT} \sum_{n=1}^{\infty} \frac{\gamma^{2n}}{(2n)!} \left(\frac{\omega_0}{\beta_1}\right)^{2n} \left[\sum_{m=0}^{2n} (-1)^m \binom{2n}{m} \frac{e^{2(n-m)\phi}}{1+i\omega\tau_{m,n}}\right]. \tag{3.7.9}$$

Here $\tau_{m,n}^{-1} = m\beta_1 + n(\beta - \beta_1)$. The factor in square brackets in Eq. (3.7.9) represents the partial-fraction expansion of the Fourier transform of

$$e^{-n\beta t} \sinh^{2n}(\beta_1 t/2 + \phi).$$

One may calculate successive terms in Eq. (3.7.9) by expanding the expression in square brackets in that equation for $n = 1, 2, 3, \ldots$. Thus for $n = 1$, the value of this expression is

$$\frac{2\beta_1^2(2\beta + i\omega)}{(\beta + i\omega)[(\beta + i\omega)^2 - \beta_1^2]}, \tag{3.7.10}$$

while for $n = 2$ we must add the term

$$4\frac{\beta_1^4}{\omega_0^2} \left\{ \frac{(2\beta + i\omega)^3 + 3\beta(2\beta + i\omega)^2 + 2(5\omega_0^2 + \beta^2)(2\beta + i\omega) + 12\omega_0^2\beta}{(2\beta + i\omega)[(2\beta + i\omega)^2 - \beta_1^2][(2\beta + i\omega)^2 - 4\beta_1^2]} \right\}.$$

Clearly, the polarizability in the under-damped case $\omega_0^2 > \beta^2/4$ consists of a discrete set of resonant absorptions [31]. This is of importance in connection with the itinerant oscillator model, which has been extensively used to discuss the far-infrared (Poley) absorption [10, 31]; we describe this in Chapter 11 (see also Chapter 10, Section 10.4.3).

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