ular Dynamics and Monte Carlo simulations. However, in addition to the static equilibrium properties, we can also measure dynamic equilibrium properties in a Molecular Dynamics simulation. At first sight, a dynamic equilibrium property appears to be a contradiction: in equilibrium all properties are independent of time, hence any time dependence in the macroscopic properties of a system would seem to be related to non-equilibrium behavior. However, as explained in section 2.5.2 on Linear Response Theory, the time-dependent behavior of a system that is only weakly perturbed is completely described by the time-correlation function of fluctuations in the system at equilibrium.

Before discussing the relation between time-correlation functions and transport coefficients, we first describe another widely used method to study transport properties using equilibrium simulations, using the coefficient of self-diffusion as an example.

5.2.1 Diffusion

Diffusion is the process whereby an initially nonuniform concentration profile (e.g., an ink drop in water) is smoothed in the absence of flow (no stirring). Diffusion is caused by the molecular motion of the particles in the fluid. The macroscopic law that describes diffusion is known as Fick's law, which states that the flux $\mathbf{j}$ of the diffusing species is proportional to the negative gradient in the concentration of that species:

$$\mathbf{j} = -D\nabla c, \tag{5.2.1}$$

where D, the constant of proportionality, is referred to as the *diffusion coefficient*.[7] In what follows, we shall be discussing a particularly simple form of diffusion, namely, the case where the molecules of the diffusing species are identical to the other molecules, but for a label that does not affect the interaction of the labeled molecules with the others. For instance, this label could be a particular polarization of the nuclear spin of the diffusing species (see e.g., [149]) or a modified isotopic composition. Diffusion of a labeled molecule among other identical molecules is called *self-diffusion*.[8]

We can use Fick's law to compute the time-dependence of the concentration profile $c(\mathbf{r}, t)$ of the tagged species, under the assumption that, at time $t = 0$, the tagged species was concentrated at the origin of our coordinate frame. To compute the time evolution of the concentration profile, we combine Fick's law with

---

[7] In Appendix D we discuss diffusion in the context of non-equilibrium thermodynamics, where the primary driving force is the gradient of the chemical potential, rather than the concentration gradient.

[8] Eq. (5.2.1) is a simplification of the basic diffusion equation relating the particle flux to the gradient of the chemical potential. The full expression can be found in ref. [57]. However, for self-diffusion, Eq. (5.2.1) is not an approximation.

an equation that expresses conservation of the total amount of labeled material:

$$\frac{\partial c(\mathbf{r},t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r},t) = 0. \tag{5.2.2}$$

Combining Eq. (5.2.2) with Eq. (5.2.1), we obtain

$$\frac{\partial c(\mathbf{r},t)}{\partial t} - D\nabla^2 c(\mathbf{r},t) = 0. \tag{5.2.3}$$

We can solve Eq. (5.2.3) with the boundary condition

$$c(\mathbf{r},0) = \delta(\mathbf{r}) \tag{5.2.4}$$

($\delta(\mathbf{r})$ is the d-dimensional Dirac delta function) to yield

$$c(r,t) = \frac{1}{(4\pi Dt)^{d/2}} \exp\left(-\frac{r^2}{4Dt}\right), \tag{5.2.5}$$

where r is the scalar distance from the origin. As before, d denotes the dimensionality of the system. For what follows we do not need $c(r,t)$ itself, but only the time dependence of its second moment:

$$\left\langle r^2(t) \right\rangle \equiv \int d\mathbf{r}\, c(r,t) r^2, \tag{5.2.6}$$

where we have used the fact that we have imposed

$$\int d\mathbf{r}\, c(r,t) = 1. \tag{5.2.7}$$

We can obtain an expression for the time evolution of $\langle r^2(t) \rangle$ by multiplying Eq. (5.2.3) by r^2 and integrating over all space. We then obtain:

$$\frac{\partial}{\partial t} \int d\mathbf{r}\, r^2 c(r,t) = D \int d\mathbf{r}\, r^2 \nabla^2 c(r,t). \tag{5.2.8}$$

The left-hand side of this equation is simply equal to

$$\frac{\partial \left\langle r^2(t) \right\rangle}{\partial t}. \tag{5.2.9}$$

Applying partial integration to the right-hand side, we obtain

$$\begin{aligned}\frac{\partial \left\langle r^2(t) \right\rangle}{\partial t} &= D \int d\mathbf{r}\, r^2 \nabla^2 c(r,t) \\ &= D \int d\mathbf{r}\, \nabla \cdot (r^2 \nabla c(r,t)) - D \int d\mathbf{r}\, \nabla r^2 \cdot \nabla c(r,t)\end{aligned}$$

$$
\begin{aligned}
&= D\int \mathrm{d}\mathbf{S}\,(r^2\nabla c(r,t)) - 2D\int \mathrm{d}\mathbf{r}\,\mathbf{r}\cdot\nabla c(r,t) \\
&= 0 - 2D\int \mathrm{d}\mathbf{r}\,(\nabla\cdot\mathbf{r}c(r,t)) + 2D\int \mathrm{d}\mathbf{r}\,(\nabla\cdot\mathbf{r})c(r,t) \\
&= 0 + 2dD\int \mathrm{d}\mathbf{r}\,c(r,t) \\
&= 2dD. \qquad (5.2.10)
\end{aligned}
$$

Eq. (5.2.10) relates the (self)diffusion coefficient D to the width of the concentration profile. Eq. (5.2.10) was derived by Einstein and is therefore called an *Einstein relation*. The important feature of Eq. (5.2.10) is that it relates a macroscopic transport coefficient (D), to a microscopic observable ($\langle r^2(t)\rangle$), which is the mean-squared distance over which the labeled molecules have moved in a time interval t. Eq. (5.2.10) suggests how to measure D in a computer simulation. For every particle i, we measure the distance traveled in time t, $\Delta\mathbf{r}_i(t)$, and we plot the mean square of these distances as a function of the time t:

$$
\left\langle \Delta r(t)^2\right\rangle = \frac{1}{N}\sum_{i=1}^{N}\Delta\mathbf{r}_i(t)^2. \qquad (5.2.11)
$$

An example of such a plot is shown in Fig. 5.9. We should be specific about what we mean with the displacement of a particle in a system with periodic boundary conditions. The displacement that we are interested in, is the time integral of the velocity of the tagged particle:

$$
\Delta\mathbf{r}(t) = \int_0^t \mathrm{d}t'\,\mathbf{v}(t'). \qquad (5.2.12)
$$

Eq. (5.2.12) allows us to express the diffusion coefficient in terms of the particle velocities. We start with the relation

$$
2D = \lim_{t\to\infty}\frac{\partial\left\langle x^2(t)\right\rangle}{\partial t}, \qquad (5.2.13)
$$

where, for convenience, we consider only one Cartesian component of the mean-squared displacement. Expressing $x(t)$ as the time integral of the x-component of the tagged-particle velocity, we obtain

$$
\begin{aligned}
\left\langle x^2(t)\right\rangle &= \left\langle\left(\int_0^t \mathrm{d}t'\,v_x(t')\right)^2\right\rangle \\
&= \int_0^t\int_0^t \mathrm{d}t'\mathrm{d}t''\left\langle v_x(t')v_x(t'')\right\rangle \\
&= 2\int_0^t\int_0^{t'} \mathrm{d}t'\mathrm{d}t''\left\langle v_x(t')v_x(t'')\right\rangle. \qquad (5.2.14)
\end{aligned}
$$

The quantity $\left\langle v_x(t')v_x(t'')\right\rangle$ is the velocity autocorrelation function of the tagged particle (see section 2.5.2, Eq. (2.5.9)). It measures the correlation between the velocity of a particle at times t' and t''. As time correlation functions in equilibrium only depend on the difference of t' and t'', we can write

$$\left\langle v_x(t')v_x(t'')\right\rangle = \left\langle v_x(t'-t'')v_x(0)\right\rangle . \tag{5.2.15}$$

Inserting Eq. (5.2.14) in Eq. (5.2.13), we obtain

$$\begin{aligned} 2D &= \lim_{t\to\infty} 2\int_0^t \mathrm{d}t'' \left\langle v_x(t-t'')v_x(0)\right\rangle \\ D &= \int_0^\infty \mathrm{d}\tau \ \langle v_x(\tau)v_x(0)\rangle . \end{aligned} \tag{5.2.16}$$

In the last line of Eq. (5.2.16) we introduced the coordinate $\tau \equiv t - t''$. Eq. (5.2.16) shows that we can relate the diffusion coefficient D to the integral of the velocity auto-correlation function. Eq. (5.2.16) is an example of a *Green-Kubo relation* (see section 2.5.2).

One note of caution: the calculation of the diffusion coefficient is subject to large and slowly decaying finite-size effects. Due to the hydrodynamic interactions between a particle and its periodic images, the diffusion coefficient approaches the infinite-system limit as $1/N^{1/3}$ [150–152] in 3d. In 2d, the diffusion coefficient diverges.[9]

Illustration 3 (Diffusion coefficients). There are different ways to measure diffusion coefficients experimentally. An interesting example is the diffusion coefficient of gases adsorbed in a porous material (e.g., a zeolite or metal-organic framework). These materials are used to separate gases or as membranes. For these applications, it is important to have a molecular understanding of the diffusion of these gases in the pores.

With pulse-field-gradient NMR, one can measure the self-diffusion coefficient, D^s [153]. However, in practical applications of these materials, we are more interested in the transport or Fick diffusion coefficient D^t. This diffusion coefficient is often estimated from the rate at which the weight of material increases upon adsorption. These two diffusion coefficients are not the same, so in comparing molecular simulation results with experimental data, it is important to be aware of these differences.

The transport or Fick diffusion coefficient D^t, is obtained by measuring the flux, J caused by a gradient in the concentration:

$$J(c) \equiv -D^t(c)\nabla c. \tag{5.2.17}$$

---

[9] The fact that the integral in Eq. (5.2.16) may diverge does not mean that particles diffuse infinitely fast, just that $\left\langle x^2(t)\right\rangle$ increases faster than linear with t.