Lecture 1
Statistical Physics IV

References:
"Stochastic Methods"
C. Gardiner Chapter 1

Brownian Motion: Einstein derivation

- Botanist R. Brown 1827 ⇒ study of pollen grains and observation of random motion. Explanation was given by Einstein in 1905 and Smoluchowski

1 Dimensional Einsten treatment. Δ: stepsize of particle in fluid

Number of particles making a step $\Delta \ldots \Delta + d\Delta$

$$\boxed{dn = n \cdot \Phi(\Delta) \cdot d\Delta}$$

$\uparrow$ total number of partcles

$\Phi(\Delta)$: probability to make a step of size Δ.

where $\int_{-\infty}^{\infty} \Phi(\Delta) = 1$ (normalization) such that $\int_{-\infty}^{\infty} dn = n$

First consider a symmetric random walk. $\Phi(+\Delta) = \Phi(-\Delta)$

Let $f(x,t)$ be the particles per unit volume at location x and time t.

CHAPMAN KOLMOGOROV EQS. (MARKOV PROCESS)

Einsten 1905

$$(*) \quad \boxed{\underbrace{f(x,t+\tau)\,dx}_{\text{particles passing through } (x..x+dx) \text{ at } (t+\tau) \text{ time}} = dx \cdot \int_{-\infty}^{\infty} \Phi(\Delta) \cdot d\Delta \cdot \underbrace{f(x+\Delta,t)}_{\text{paticles at position } x+\Delta \text{ at time } t.}}$$

Taylor expand in x, τ : $f(x+\Delta,t) = f(x,t) + \Delta \cdot \frac{\partial f(x,t)}{\partial x} + \frac{\Delta^2}{2!}\frac{\partial^2 f(x,t)}{\partial x^2}$

$$\Leftrightarrow \quad f(x,t) + \frac{\partial f}{\partial \tau}\cdot \tau = f \cdot \underbrace{\int_{-\infty}^{\infty} \Phi(\Delta) \cdot d\Delta}_{\text{unity}} + \underbrace{\frac{\partial f}{\partial x}\int_{-\infty}^{\infty} \Delta \Phi(\Delta)\, d\Delta}_{=0 \text{ for a symmetric random walk}} + \frac{\partial^2 f}{\partial x^2}\int_{-\infty}^{\infty} \frac{\Delta^2}{2!}\Phi(\Delta)\, d\Delta$$

$$\Leftrightarrow \quad \frac{\partial f}{\partial \tau}\cdot \tau = \frac{\partial^2 f}{\partial x^2}\int_{-\infty}^{\infty} \frac{\Delta^2}{2}\Phi(\Delta)\, d\Delta$$

calling $\frac{1}{\tau}\int_{-\infty}^{\infty} \frac{\Delta^2}{2}\Phi(\Delta)\,d\Delta \equiv D$ leads to $\boxed{\frac{\partial f}{\partial t} = D \cdot \frac{\partial^2 f}{\partial x^2}}$ Diffusion equation (i.e a Fokker Planck eqs).

Mathematically:

$$\boxed{f(x,t) = \frac{n}{\sqrt{4\pi D t}}\, e^{-x^2/4Dt}}$$

Einstein found that $D = \frac{k_B T}{m \cdot \gamma}$ (later) properties $\quad p(x,t) = f(x,t)/n \quad$ probability density

$$\begin{cases} p(x,t) > 0 & \text{always positive obviously} \\ \int_{-\infty}^{\infty} p(x,t)\,dx = 1 & \text{normalization} \\ \lim_{t\to 0} p(x,t) = \delta(x) & \text{initial condition} \end{cases}$$

Displacement around x : $\quad \langle x^2 \rangle = \int_{-\infty}^{\infty} f(x,t)\, x^2\, dx$

$$\boxed{\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 \frac{1}{\sqrt{4\pi D t}} e^{-x^2/4Dt} = 2Dt}$$

Comment: The expansion marked with "*" is called Kramers Moyal Expansion.

Interpretation: the probability to find a particle at time $(t+\tau)$ is given by the sum of all probabilities that takes the particle to x from $x+\Delta$ multiplied by the probability of the particle to be at $(X+\Delta)$ at time t.

2nd approach:

LANGEVIN TREATMENT. Langevin considered the microscopic equation of motion which Einstein avoided.

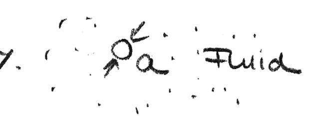
Statistical mechanics requires: $\langle \frac{1}{2} m v_x^2 \rangle = \frac{k_B T}{2}$ (i.e $\langle \frac{1}{2} m \vec{v}^2 \rangle = 3\frac{k_B T}{2}$ in 3-dimensions.)

Particle in a fluid experiences a drag force:

$$F = -6\pi \cdot \eta\, a \frac{dx}{dt} \propto v \quad \eta\text{: viscosity} \qquad a\text{: particle radius.}$$

$$\boxed{m \frac{d^2x}{dt^2} = -6\pi\eta a \frac{dx}{dt} + F(t)}$$

$v \equiv \frac{dx}{dt}$ velocity.



$F(t)$: is a fluctuating force causing the random motion ("LANGEVIN FORCE")

multiply eqs by $x(t)$:

Thus:
$$\frac{m}{2}\frac{d^2(x^2)}{dt} - mv^2 = -3\pi\eta a \frac{dx^2}{dt} + F(t)\cdot x$$

Next average the r.h.s and l.h.s

$$\frac{m}{2}\frac{d^2}{dt^2}\langle x^2 \rangle - \underbrace{m\langle v^2 \rangle}_{k_B T} = -3\eta a \frac{d}{dt}\langle x^2 \rangle + \langle F(t)\, x(t) \rangle$$

Key insight. $\langle F(t).x(t) \rangle = 0$ since the random force is NOT correlated with the position of the particle. Important: the same is NOT true for $\langle F(t)\, v(t) \rangle$.

$$\Leftrightarrow \quad \frac{d}{dt}\langle x^2\rangle = \frac{k_BT}{3\pi\eta a} + C\exp\left(-\frac{6\pi\eta a}{m}t\right)$$

constant $C \in \mathbb{R}$
this is homogeneous solution

of the equation: $$\frac{m}{2}\frac{d^2}{dt^2}\langle x^2\rangle + 3\eta\pi a\frac{d}{dt}\langle x^2\rangle = k_BT$$

Thus for $t \to \infty$:

$$\boxed{\langle x^2\rangle - \langle x_0^2\rangle = \left(\frac{k_BT}{3\eta a\pi}\right)t}$$

we recover the diffusive behavior i.e $\langle x^2\rangle \propto t$ where the diffusion constant is given by

$$\boxed{D = \frac{k_BT}{6\pi\eta a}}$$

Independently derived by Langevin (similar to Einstein)

3rd Derivation

Method to derive $P(x,t)$ by a Master Equation (finite difference method)

$P(n\cdot\Delta,\ k\cdot T)$ must fullfill a difference equation (1D-chain)

$$\boxed{P(n\cdot\Delta,\ [k+1]\cdot T) = p\cdot P([n-1]\Delta,\ kT) + q\cdot P([n+1]\cdot\Delta,\ kT)}$$

Probability to observe
particle at $x = n\cdot\Delta$ at time $t = kT$

This can be rewritten as:

$$P(n\Delta, (k+1)T) - P(n\Delta, kT) = \frac{1}{2}\left(P((n+1)\Delta, kT) - 2P(n\Delta, kT) + P((n-1)\Delta, kT)\right)$$

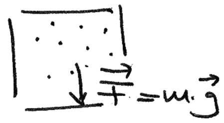
$$\Leftrightarrow \frac{P(x, t+T) - P(x,t)}{T} = \underbrace{\frac{\Delta^2}{T}}_{\hat{=} D} \; \frac{P(x+\Delta, t) - 2P(x,t) + P(x-\Delta, t)}{\Delta^2} \Bigg|_{\substack{t = kT \\ x = n\Delta}}$$

consider limit as $T \to 0$ and $\Delta \to 0$

$$\boxed{\frac{\partial P(x,t)}{\partial t} = \underbrace{\frac{\Delta^2}{T}}_{\hat{=} D} \frac{\partial^2 P(x,t)}{\partial x^2}}$$ Diffusion Equation.

returning to the Einstein treatment and the diffusion coefficient D:

Derivation of D: consider particles in a gravitational field $\vec{g}$



$n(x,t) = N\cdot p(x,t)$

$\frac{\partial}{\partial t} n(x,t) = D\cdot\frac{\partial^2}{\partial x^2} n(x,t)$ call $\boxed{j_D(x,t) \equiv -D\frac{\partial}{\partial x} n(x,t)}$ FICKS LAW

the particle current

diffusive current due to concentration gradient

continuity equation: $\boxed{\frac{\partial}{\partial t} n(x,t) = -\frac{\partial}{\partial x} j_D(x,t)}$

Equation of motion $m\frac{d}{dt}v(t) = -m\cdot g \underbrace{- m\gamma\cdot v(t)}_{\text{drag (damping force)}}$

stationary case $\frac{d}{dt}\langle v\rangle = 0 \Rightarrow v = -\frac{g}{\gamma}$

Define the current $j_{grav} = n(x,t)\cdot v(t) = -\frac{g}{\gamma}\cdot n(x,t)$

Statistical mechanics predicts: $n(x) = n(x_0)\cdot e^{-V(x-x_0)/k_BT} = n(x_0)e^{-\frac{mg(x-x_0)}{k_BT}}$

(V = Potential)

results in diffusive current: $j_D(x) = -D\cdot\frac{\partial}{\partial x} n(x) = D\cdot\frac{mg}{k_BT} n(x)$

total current $J_{tot} = 0 = j_{grav} + j_D = -\frac{g}{\gamma} n(x) + \frac{D\, mg\, n(x)}{k_BT} = 0$

$\Leftrightarrow \boxed{D = k_BT/m\gamma}$ independent of $\vec{g}$ (example of fluct.diss. theorem)

Lecture 1

How to describe Brownian motion in a force field with the master equation approach? assume now: $p \neq q$

$p = \frac{1}{2} + \alpha\Delta \qquad q = \frac{1}{2} - \alpha\Delta$ Same approach as outlined before:

$$P(n\Delta,(k+1)T) - \underline{P(n\Delta,kT)} = \frac{1}{2}\left[P((n+1)\Delta,kT) - 2\underline{P(n\Delta,kT)} + P((n-1)\Delta,kT\right]$$
$$- \alpha\Delta\left(P((n+1)\Delta,kT) - P((n-1)\Delta,kT)\right)$$

[...] limit of $x = n\Delta$ and $T \to 0$ $\Delta \to 0$:

$$\boxed{\frac{\partial}{\partial t}P(x,t) = -4\alpha D\frac{\partial}{\partial x}P(x,t) + D\frac{\partial^2}{\partial x^2}P(x,t)}$$ SMOLUCHOWSKI EQUATION

$$D \equiv \frac{\Delta^2}{2T}$$

Next, assume that the Brownian Motion is spatially varying ie $\alpha = \alpha(n\cdot\Delta)$. e.g BM in a gravitational field.

$$P(n\Delta,(k+1)T) = p((n-1)\Delta)\cdot P((n-1)\Delta,kT) + q((n+1)\Delta)P((n+1)\Delta,kT)$$

with:

$$P(n\Delta,(k+1)T) - P(n\Delta,kT) = \frac{1}{2}P((n+1)\Delta,kT) - 2P(n\Delta,kT) + P((n+1)\Delta,kT)$$
$$- \Delta\left[\alpha((n+1)\Delta))P((n+1)\Delta,kT) - \alpha((n-1)\Delta)P((n-1)\Delta,kT)\right]$$

yields in the above limit:

$$\boxed{\frac{\partial}{\partial t}P(x,t) = -4D\frac{\partial}{\partial x}\left(\alpha(x)P(x,t)\right) + D\frac{\partial^2}{\partial x^2}P(x,t)}$$

For dimensional reasons $4D\alpha(x) = \frac{F(x)}{m\gamma}$

$$\boxed{\frac{\partial}{\partial t}P(x,t) = -\frac{1}{m\gamma}\frac{\partial}{\partial x}\left(F(x)P(x,t)\right) + D\cdot\frac{\partial^2}{\partial x^2}P(x,t)}$$ SMOLUCHOWSKI EQUATION

Application: e.g particle escape problems.

Example : gravitational field $F = -mg$ or harmonic potential $F = -kx$

Solutions are of form: $P(x,t) = \frac{1}{\sqrt{2\pi\sigma(t)}}e^{-(x-a(t))^2/2\sigma(t)}$

Theory of Langevin : Theory of Microscopic Evolution
Einstein : Theory of Probability

Langevin:

$$\frac{d\langle v(t)\rangle}{dt} = -\gamma \langle v(t)\rangle \quad \text{Average}$$

Langevin Force

Actual Eqn: $\frac{dv}{dt} = -\gamma \cdot v(t) + \tilde{F}(t)$

1st Hypothesis $\langle f(t)\rangle = \frac{1}{N}\sum_i f_i(t) = 0$

$$\langle v(t)\rangle = e^{-\gamma t}(\bar{v}(0)) \qquad x(t) = \int_0^T \langle v(t)\rangle dt = v_0\left[\frac{1-e^{-\gamma t}}{\gamma}\right] \quad \text{mean position}$$

2nd Hypothesis of Langevin

Since $F_L(t)$ varies on the timescale of microscopic collisions the correlation time is very short t_c ; much shorter than the relaxation time γ^{-1} $\boxed{t_c \ll \gamma^{-1}}$

This implies that:

$$\boxed{\langle f(t_1) f(t_2)\rangle = c\,\delta(t_1-t_2)} \quad c \in \mathbb{R} \quad \text{correlation Function for Langevin Force}$$

Velocity Fluctuations

$$v(t) = v_0 e^{-\gamma t} + \frac{1}{m}\int_0^t ds\, e^{-\gamma(t-s)} F_L(s)$$

Hence

$$\langle v(t_1) v(t_2)\rangle = \frac{1}{m^2}\int_0^{t_1}\int_0^{t_2} ds_1 ds_2\, e^{-\gamma(t_1-s_1)} e^{-\gamma(t_2-s_2)} \underbrace{\langle F(s_1)F(s_2)\rangle}_{c\,\delta(s_1-s_2)} + v_0^2 e^{-\gamma(t_1+t_2)}$$

Hence:

$$\int_0^{t_1} ds_1 \int_0^{t_2} ds_2\, e^{\gamma(s_1+s_2)}\delta(s_1-s_2)$$

$$= \int_0^{\infty}\int_0^{\infty} ds_1\, e^{\gamma(s_1+s_2)}\,\Theta(t_1-s_1)\Theta(t_2-s_2)\,\delta(s_1-s_2)$$

$$= \int_0^{\infty} e^{2\gamma s_1}\,\Theta(t_1-s_1)\Theta(t_2-s_1)$$

$$= \int_0^{\min(t_1,t_2)} e^{2\gamma s_1} = \frac{1}{2\gamma}\left(e^{2\gamma\min(t_1,t_2)} - 1\right)$$

Hence $t_1+t_2 - 2\min(t_1,t_2) = |t_1-t_2|$

$$\langle v(t_1) v(t_2)\rangle = \frac{c}{2\gamma m^2}\left(e^{-\gamma|t_1-t_2|} - e^{-\gamma|t_1+t_2|}\right) + v_0^2 e^{-\gamma(t_1+t_2)}$$

$$\boxed{\langle v^2(t)\rangle = \frac{c}{2\gamma m^2}\left(1-e^{-2\gamma t}\right) + v_0^2 e^{-\gamma t}} \xrightarrow{t\to\infty} v^2(t) = \frac{c}{2\gamma m^2} \overset{!}{=} \frac{k_B T}{m}$$

Thus

$$\lim_{t\to\infty} \frac{1}{2} m \langle v^2(t) \rangle = \frac{1}{2} k_B T$$

$$\Leftarrow \lim_{t\to\infty} \frac{1}{2} m \langle v^2(t) \rangle^2 = \frac{C}{2\gamma m^2}$$

combining yields:

$$C = 2m\gamma k_B T$$

Hence

$$\boxed{\langle F_L(t) F_L(t') \rangle = 2m\gamma k_B T \, \delta(t-t')}$$

Correlation function & damping rate

Wrong in the quantum world! As $\langle F_L(t) F_L(t') \rangle \Rightarrow 0$ as $T \to 0$