Nonequilibrium statistical mechanics - I

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1 Relation between Boltzmann and Thermodynamic entropy

The definitions of the Boltzmann and theromodynamic entropies [1] are as follows:

$$S_B \equiv k_B \ln \Omega_E \qquad \text{(Boltzmann Entropy)} \tag{1.1}$$

$$S_T \equiv \int \frac{dQ}{T} \qquad \text{(Thermodynamic Entropy)} \tag{1.2}$$

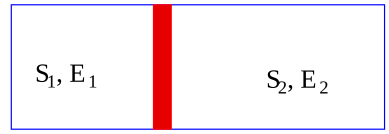
Here, Ω_E is the total number of states available for a given energy E, which in other words is the "surface area" of the available phase space. Since from the above definitions it is not apparent whether they represent the same or different quantities, we will see that they are actually equivalent.

First, consider the energy conservation relation for a system undergoing a qausi-static process:

$$dE = TdS - PdV. \tag{1.3}$$

Here, TdS is the heat *absorbed* by the system, and $-PdV$ is the work done *on* the system. This gives

$$\frac{\partial S}{\partial E} = \frac{1}{T}. \tag{1.4}$$



This is definitely a constant at thermal equilibrium. Consider two boxes joined by an immovable diathermal wall and at thermal equilibrium with each other.

Now, the total entropy of the composite system is

$$S_{tot} = S_1(E_1) + S_2(E_2) = S_1(E_1) + S_2(E - E_1). \tag{1.5}$$

Since E_1 and E_2 will reach a value that maximizes the total entropy at equilibrium, the value of E_1 must be given by

$$\frac{\partial S_1(E_1)}{\partial E_1} + \frac{\partial S_2(E - E_1)}{\partial E_1} = 0 \quad \Rightarrow \quad \frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} = \frac{1}{T}, \tag{1.6}$$

as expected (we have used $\partial/\partial E_1 = -\partial/\partial E_2$). Now comes microscopics. Since $S_1 + S_2$ reaches a constant value at equilibrium, we must find what microscopic but extensive quantity reaches a constant value at thermal equilibrium. We find that the the total number of microscopic states reaches a constant value at equilibrium and is given by

$$\Omega(E) = \Omega_1(E_1)\Omega_2(E_2). \tag{1.7}$$

However, the total number of states is a product of the individual number of states, instead of being an additive quantity like the entropy. This immediately tells us that the logarithm of the above quantity is additive and must be proportional to the entropy:

$$S(E) \propto \ln \Omega(E). \tag{1.8}$$

The proportionality constant that gives the correct value for entropy whose derivative with respect to energy gives the inverse temperature is given by k_B, which is the Boltzmann constant.

2 Entropy in other ensembles

As we have seen, entropy in microcanonical ensemble is given by $S = k_B \ln \Omega$. What about, say, the canonical ensemble? We will prove that it is given by

$$S = -\sum_i P_i \ln P_i, \tag{2.1}$$

where P_i is the probability of the i^{th} microstate. To derive this, let us consider the full composite supersystem consisting of the system of interest and the heat bath. This supersystem now follows the microcanonical ensemble. Let us consider N such elements in the ensemble, and among these, let the system of interest be in the i^{th} microstate in n_i elements. Then number of possible microstates (consistent with the *total* energy of the supersystem) of all the systems in the ensemble will be given by (completely ignoring the bath *micro*states):

$$\Omega_N(E) = \frac{N!}{n_1! n_2! \cdots n_k!}$$
$$\Rightarrow S_N(E)/k_B = \ln \Omega_N(E) = \ln(N!) - \sum_{i=1}^{k} \ln(n_i!)$$

$$\approx N\ln N - N - \sum_{i=1}^{k}(n_i \ln n_i - n_i)$$
$$= N\ln N - \sum_{i=1}^{k}(n_i \ln n_i)$$
$$= \sum_{i=1}^{k}(n_i \ln N - n_i \ln n_i) = -\sum_{i=1}^{k} n_i \ln\frac{n_i}{N}$$
$$\Rightarrow S(E)/k_B \equiv S_N(E)/N = -\sum_{i=1}^{k}\frac{n_i}{N}\ln\frac{n_i}{N} = -\sum_i P_i \ln P_i. \quad (2.2)$$

In the last step, the system entropy is defined as the mean over the total entropy of the full ensemble.

3 Density of states

Let us consider a dilute gas in a d-dimensional system with N particles. The phase space of this system will be a $2Nd$-dimensional one, described by $(q_1, q_2, \cdots, q_n, p_1, p_2, \cdots, p_n)$, where $n = Nd$. We can define a function $\Phi(E)$ which will give the number of energy states below some given energy E. For knowing this, we need to calculate the volume of the n-dimensional hypersphere in momentum space.

3.1 Volume of an n-dimensional hypersphere

To find the volume of the n-dimensional hypersphere [3], we first consider the integral

$$I = \int_{-\infty}^{\infty} d\rho_1 \cdots d\rho_n \; e^{-(\rho_1^2+\cdots+\rho_n^2)} = (\sqrt{\pi})^n. \quad (3.1)$$

Next, we write the same integral in polar coordinates:

$$I = \int_0^{\infty} e^{-\rho^2}\rho^{n-1} d\rho \; d\Omega_n = \frac{1}{2}\int dt \; t^{\frac{d}{2}-1} e^{-t}\int d\Omega_n = \frac{1}{2}\Gamma(n/2)\int d\Omega_n, \quad (3.2)$$

where Ω_n is the surface element of a unit sphere. Comparing (3.1) and (3.2), we get the surface area of the unit sphere as

$$\boxed{\int d\Omega_n = \frac{2\pi^{n/2}}{\Gamma(n/2)}.} \quad (3.3)$$

The volume will be given by:

$$\begin{aligned} V_n(r) &= \int_0^r d\rho \; \rho^{n-1}\int d\Omega_n = \frac{2\pi^{n/2}}{\Gamma(n/2)}\int_0^r d\rho \; \rho^{n-1} \\ &= \; = \frac{2\pi^{n/2}}{\Gamma(n/2)}\cdot\frac{r^n}{n} = \frac{r^n\pi^{n/2}}{\frac{n}{2}\Gamma(n/2)} = \frac{r^n\pi^{n/2}}{\Gamma(1+\frac{n}{2})}, \end{aligned} \quad (3.4)$$

which is the desired expression for the volume of an n-dimensional hypersphere.

3.2 Finding density of states

For doing this, we first define a function $\Phi(E)$ as follows:

$$\Phi(E) \equiv \text{Number of energy states with energy} \leq E \text{ for } N \text{ particles in } d \text{ spatial dimensions.} \quad (3.5)$$

What we need is to count the number of momentum states within a hypersphere of radius $k \equiv \sqrt{2mE}/\hbar$. Let the phase space coordinates be $(q_1, q_2, \cdots, q_n, p_1, p_2, \cdots, p_n)$ We consider the container to be a cubical box of dimension L, so that $\Delta k = 2\pi/L$, k being the magnitude of the wave vector.

$$\begin{aligned} \Phi(E) &= \frac{1}{N!}\frac{V_n(k)}{(2\pi/L)^n} = \frac{L^{Nd}}{(2\pi)^n N!}\cdot\frac{\pi^{n/2}}{\Gamma(1+\frac{n}{2})}\left(\frac{\sqrt{2mE}}{\hbar}\right)^n \\ &= \frac{V^N}{(2\pi\hbar)^n N!}\frac{(2\pi m E)^{n/2}}{\Gamma(1+\frac{n}{2})} = \frac{V^N}{h^n N!}\frac{(2\pi m E)^{n/2}}{\Gamma(1+\frac{n}{2})}, \end{aligned} \tag{3.6}$$

N being the number of particles given by $N = n/d$, and the factor $N!$ comes because of the indistinguishability of the particles. Last but certainly not the least, the density of the states $g(E, V)$ is obtained from $\Phi(E)$ by simply differentiating it w.r.t. E:

$$\boxed{g(E,V) \equiv \frac{\partial \Phi(E)}{\partial E} = \frac{V^N}{h^n N!}\frac{(2\pi m)^{n/2}}{\Gamma(n/2)}\cdot E^{n/2-1},} \tag{3.7}$$

where we have used $\Gamma(1+\frac{n}{2}) = \frac{n}{2}\Gamma(n/2)$.

4 Free energy minimization principle

4.1 Free energy

The following are the various free energies connected through the Legendre transformation:

$$F = E - TS \qquad \text{(Helmholtz free energy)} \tag{4.1}$$

$$G = E - TS + PV \qquad \text{(Gibbs free energy)} \tag{4.2}$$

$$H = E + PV \qquad \text{(Enthalpy)} \tag{4.3}$$

The Euler equation states[1],

$$E = TS - PV + \mu N, \tag{4.4}$$

where μ is the chemical potential. Thus, we have

$$G = E - TS + PV = \mu N. \tag{4.5}$$

4.2 Minimization of energy

The first law states,

$$dE = -\delta Q + \delta W = -\delta Q - PdV. \tag{4.6}$$

If system entropy is held fixed, then second law gives $dQ \geq 0 \quad \Rightarrow \quad -dQ \leq 0$. If the volume is also kept fixed, then the above equation gives

$$dE \leq 0. \tag{4.7}$$

Thus for an isentropic and isochoric process ($dS = 0,\ dV = 0$), the internal energy of the system is minimized at equilibrium.

[1] $E = E(S, V, N) \equiv E(\{y_i\})$. Extensivity implies $E(\alpha\{y_i\}) = \alpha E(\{y_i\})$. Therefore,

$$\frac{\partial E(\alpha\{y_i\})}{\partial \alpha} = E(\{y_i\}) = \sum_i \frac{\partial E(\alpha y_i)}{\partial(\alpha y_i)}\frac{\partial(\alpha y_i)}{\partial \alpha} = \sum_i y_i \frac{\partial E(\alpha y_i)}{\partial(\alpha y_i)}.$$

Putting $\alpha = 1$, we get $E(\{y_i\}) = \sum_i y_i \frac{\partial E(\{y_i\})}{\partial y_i}$, which is the Euler equation.

4.3 Minimization of Helmhotz free energy

We have,

$$\begin{aligned} dF = d(E - TS) &= -\delta Q + \delta W - TdS - SdT \\ &\leq \delta W - SdT. \end{aligned} \tag{4.8}$$

Here we have used the second law, $dS + \delta Q/T \geq 0$. Thus, for an isothermal and isochoric process ($dT = 0,\ dV = 0$), we get

$$dF \leq 0, \tag{4.9}$$

which implies that F is minimized at equilibrium.

4.4 Minimization of Gibbs free energy

$$\begin{aligned} dG = d(E - TS + PV) &= -\delta Q + \delta W - TdS - SdT + PdV + VdP \\ &\leq \delta W - SdT + PdV + VdP = -SdT + VdP, \end{aligned} \tag{4.10}$$

since $\delta W = -PdV$ and $\delta Q + TdS \geq 0$. Thus, for an isothermal and isobaric process ($dT = 0,\ dP = 0$), we have

$$dG \leq 0. \tag{4.11}$$

5 The Liouville's theorem and its implications

5.1 Derivation of Liouville's theorem

The continuity equation for phase space density $\rho(\mathbf{q}, \mathbf{p}, t) \equiv \rho(q_1, \cdots, q_n, p_1, \cdots, p_n)$ during Hamiltonian evolution is given by

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \mathbf{q}} \cdot (\rho \dot{\mathbf{q}}) + \frac{\partial}{\partial \mathbf{p}} \cdot (\rho \dot{\mathbf{p}}) = 0. \tag{5.1}$$

This implies

$$\begin{aligned} & \frac{\partial \rho}{\partial t} + \sum_{k=1}^{n} \left[\frac{\partial}{\partial q_k} (\rho \dot{q}_k) + \frac{\partial}{\partial p_k} (\rho \dot{p}_k) \right] = 0 \\ \Rightarrow \quad & \frac{\partial \rho}{\partial t} + \sum_{k} \left[\frac{\partial \rho}{\partial q_k} \dot{q}_k + \rho \frac{\partial \dot{q}_k}{\partial q_k} + \frac{\partial \rho}{\partial p_k} \dot{p}_k + \rho \frac{\partial \dot{p}_k}{\partial p_k} \right] = 0 \\ \Rightarrow \quad & \frac{\partial \rho}{\partial t} + \sum_{k} \left[\frac{\partial \rho}{\partial q_k} \dot{q}_k + \rho \frac{\partial^2 H}{\partial q_k \partial p_k} + \frac{\partial \rho}{\partial p_k} \dot{p}_k - \rho \frac{\partial^2 H}{\partial p_k \partial q_k} \right] = 0 \\ \Rightarrow \quad & \frac{\partial \rho}{\partial t} + \sum_{k} \left[\frac{\partial \rho}{\partial q_k} \dot{q}_k + \frac{\partial \rho}{\partial p_k} \dot{p}_k \right] = \frac{d\rho}{dt} = 0, \end{aligned} \tag{5.2}$$

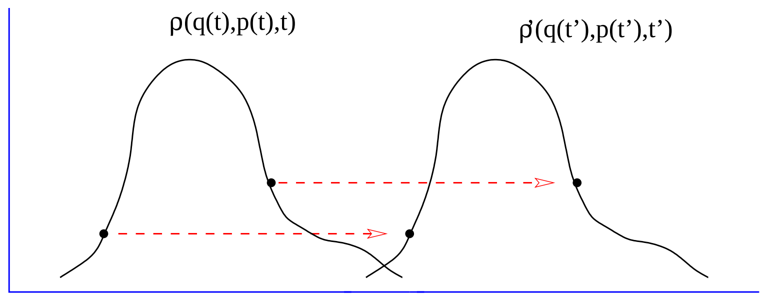
which is the celebrated Liouville's theorem on phase space density:

$$\boxed{\frac{d\rho}{dt} = 0.} \tag{5.3}$$

This implies

$$\rho(\mathbf{q}(t), \mathbf{p}(t), t) = \rho'(\mathbf{q}(t'), \mathbf{p}(t'), t'). \tag{5.4}$$

In other words, the functional form of the density of phase points (systems) in the phase space around a given point remains constant in time, *provided the observer moves with the point*. However, if the observer is fixed at one point, he will find the functional form changing, because its *partial* derivative w.r.t time is non-zero: $\frac{\partial \rho}{\partial t} \neq 0$(note that with respect to the fixed coordinate in the figure below, the mean of the density function has changed):



5.2 Implications of the Liouville's theorem

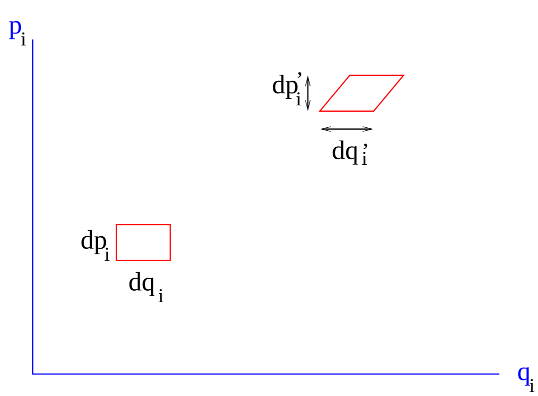
1. **Constancy of occupancy in any given volume element:** Let us consider an infinitesimally small volume about a given phase space point $(\mathbf{q}(t), \mathbf{p}(t))$. This, say, evolves to a new volume element around $(\mathbf{q}(t'), \mathbf{p}(t'))$. Claim is, no representative point can cross the bundary of this volume element. Why? Let us consider a point which attempts to do so. When it touches the border, it is coincident with some representative point at the border. Thus, due to the uniqueness of a deterministic trajectory, those two coincident points must follow a coincident trajectory theafter so that the point is never allowed to cross the boundary. The same argument says that even an external point cannot enter the volume element. This means that the number of phase points δN within a volume element $\delta\Gamma$ always remains the same.

2. **Constancy of phase space measure:** Since $\rho \equiv \frac{d\Gamma}{dN}$=const, we can write

$$\frac{d\Gamma(t_1)}{dN(t_1)} = \frac{d\Gamma(t_2)}{dN(t_2)} \tag{5.5}$$

We already know, by token of the above argument, that $dN(t_1) = dN(t_2)$. Therefore, the above equation also says that $d\Gamma(t_1) = d\Gamma(t_2)$. Thus, phase space measure remains constant with time.

3. **Alternative way to derive the above result:**



We suppose that the phase space volume element $dq_i dp_i$ goes to $dq'_i dp'_i$ in time dt, as shown in the adjacent figure (this are the i^{th} generelized coordinates and momenta of the system). Then we can write,

$$\begin{aligned} q'_i &= q_i + \dot{q}_i dt + O(dt^2); \\ p'_i &= p_i + \dot{p}_i dt + O(dt^2). \end{aligned} \tag{5.6}$$

$$\begin{aligned} \therefore\ dq'_i &= dq_i + \frac{\partial \dot{q}_i}{\partial q_i} dq_i dt + O(dt^2); \\ dp'_i &= dp_i + \frac{\partial \dot{p}_i}{\partial p_i} dp_i dt + O(dt^2). \end{aligned} \tag{5.7}$$

Multiplying the above two relations, we obtain

$$dq_i' dp_i' = dq_i dp_i \left[1 + \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) dt + O(dt^2)\right]. \tag{5.8}$$

Using Hamilton's equations of motion, we find that the term within parantheses () on the RHS desappears. In the limit $dt \to 0$, we then have

$$dq_i' dp_i' = dq_i dp_i. \qquad \text{QED} \tag{5.9}$$

4. **Constancy of Gibbs entropy:**

   The Gibbs' entropy is defined as

$$S \equiv -\int \rho(q,p) \ln \rho(q,p), \tag{5.10}$$

   where (q,p) denots all the coordinates and momenta of the system. Differentiating with respect to time, using the continuity equation with $\mathbf{v} \equiv (\dot{q}, \dot{p})$ we have

$$\begin{aligned} \frac{dS}{dt} &= -\int dqdp \ \frac{\partial}{\partial t}(\rho \ln \rho) = -\int dqdp \ (1 + \ln \rho)\frac{\partial \rho}{\partial t} \\ &= -\int dqdp \ \ln \rho \ \frac{\partial \rho}{\partial t} = +\int dqdp \ \ln \rho \ \boldsymbol{\nabla} \cdot (\rho \mathbf{v}) \\ &= -\int dqdp \ \rho \mathbf{v} \cdot \boldsymbol{\nabla} \ln \rho = -\int dqdp \ \mathbf{v} \cdot \boldsymbol{\nabla} \rho \\ &= -\int dqdp \ \left(\frac{\partial \rho}{\partial q}\dot{q} + \frac{\partial \rho}{\partial p}\dot{p}\right) = -\int dqdp \ \dot{\rho} = 0, \end{aligned} \tag{5.11}$$

   using Liouville's equation. In the second line, we have used $\int dt \partial\rho/\partial t = 0$, from normalization condition. While going from second to the third line, we have used integration by parts. Thus, $S \equiv -\int \rho(q,p) \ln \rho(q,p)$ remains constant under Hamiltonian evolution.

5.3 Derivation of Quantum Liouville equation:

The density matrix is defined as

$$\rho(t) \equiv \sum_i p_i |\psi_i(t)\rangle\langle\psi_i(t)|. \tag{5.12}$$

in terms of the state vectors.

$$\begin{aligned} \therefore i\hbar \frac{\partial \rho(t)}{\partial t} &= i\hbar \sum_i p_i \left[\frac{\partial |\psi_i(t)\rangle}{\partial t}\langle\psi_i(t)| + |\psi_i(t)\rangle \frac{\partial \langle\psi_i(t)|}{\partial t}\right] \\ &= \sum_i p_i \left[H|\psi_i(t)\rangle\langle\psi_i(t)| - |\psi_i(t)\rangle\langle\psi_i(t)|H\right] = -[\rho, H] \\ \Rightarrow \ & \boxed{\frac{\partial \rho(t)}{\partial t} = \frac{i}{\hbar}[\rho, H].} \end{aligned} \tag{5.13}$$

It is important to note that this is in the **Schrödinger picture** and not in the Heisenberg picture, where a minus sign will appear on the RHS.

Constancy of von Neumann entropy: The von Neumann entropy is defined through

$$S \equiv -\text{Tr } (\rho \ln \rho). \tag{5.14}$$

Then,

$$\begin{aligned} \frac{dS}{dt} &= -\text{Tr } \left\{ (1 + \ln \rho) \frac{\partial \rho}{\partial t} \right\} = -\text{Tr } \left\{ \ln \rho \frac{\partial \rho}{\partial t} \right\} \\ &= -\frac{i}{\hbar} \text{Tr } ([\rho, H] \ln \rho) = -\frac{i}{\hbar} \text{Tr } (\rho H \ln \rho - H \rho \ln \rho) \\ &= -\frac{i}{\hbar} \text{Tr } (\ln \rho \; \rho H - \rho \ln \rho \; H) = -\frac{i}{\hbar} \text{Tr } ([\ln \rho, \rho] H) = 0, \end{aligned} \tag{5.15}$$

where while going from second to the third line we have used the cyclic property of trace. Thus, $S \equiv -\text{Tr } (\rho \ln \rho)$ remains constant in unitary evolution.

6 Overdamped equation of motion

Let the underdamped equation be

$$m\ddot{x} + \gamma \dot{x} + Kx = F(x, t). \tag{6.1}$$

We consider the homogeneous equation:

$$m\ddot{x} + \gamma \dot{x} + Kx = 0. \tag{6.2}$$

Putting $x = e^{-t/\tau}$ into the homogeneous equation, one gets

$$\frac{m}{\tau^2} - \frac{\gamma}{\tau} + K = 0 \qquad \Rightarrow \qquad K\tau^2 - \gamma\tau + m = 0. \tag{6.3}$$

$$\therefore \tau_{s,f} = \frac{\gamma \pm \sqrt{\gamma^2 - 4Km}}{2K}, \tag{6.4}$$

where s and f stand for slow and fast relaxation time scales, resepctively, assuming that $\gamma^2 > 4Km$, so that oscillations are absent (i.e., both τ_s and τ_f are real). The *overdamped* limit of the dynamis will be the one in which the fast time scale is assumed to be zero, so that we are left only with one time scale, namely τ_s. From eqn. (6.4), we note that $\tau_f \to 0$ is possible only if $\gamma^2 \gg 4Km$. In this limit, we have $\tau_s = \frac{\gamma}{K}$. This is equivalent to the time-scale obtained from the *first order* DE

$$\boxed{\gamma \dot{x} + Kx = 0.} \tag{6.5}$$

This equation is equivalent to the one obtained from (6.2) by simply setting $m = 0$.

If we had, instead of (6.2), the stochastic term $\xi(t)$, i.e.,

$$m\ddot{x} + \gamma \dot{x} + Kx = g\xi(t), \tag{6.6}$$

where mean of the stochastic force is zero and g is the noise strength ($g = \sqrt{2\gamma k_B T}$), then it is the *average* position $\langle x \rangle$ that follows the same equation as (6.2):

$$m\langle \ddot{x} \rangle + \gamma \langle \dot{x} \rangle + K\langle x \rangle = 0. \tag{6.7}$$

Thus once again the overdamped limit is taken by letting $m = 0$.

However, if the noise strength g is a function of position as well, $g \equiv g(x)$, then this cannot be done, because the RHS no longer vanishes but gives instead $\langle g(x)\xi(t) \rangle$ which is non-zero.

6.1 State-dependent diffusion

This happens quite often in physical systems. Examples are:
(i) Particle in suspension near a wall.
(ii) Mutual diffusion of two particles in a suspension.
(iii) Particle diffusing in a reversible chemical polymer gel.
(iv) Dynamics of fluid membranes.

To resolve this issue, we consider [4] the general form of the overdamped equation:

$$\dot{x} = \underbrace{-\Gamma(x)\frac{\partial V(x)}{\partial x} + f_1(x)}_{f(x)} + g(x)\xi(t) = f(x) + g(x)\xi(t), \tag{6.8}$$

where $\Gamma(x) = 1/\gamma(x)$ and $g^2(x) = 2\Gamma(x)k_BT$. The extra term $f_1(x)$ has been added to the ordinary overdamped Langevin equation. Had $\xi(t)$ been continuous, we would have obtained on integrating between t and $t + \Delta t$

$$\begin{aligned} x(t+\Delta t) - x(t) \quad &\equiv \quad \Delta x(t+\Delta t) = \int_t^{t+\Delta t} ds\{f[x(s)] + g[x(s)]\xi(s)\} \\ &= \quad f[x(t_1)]\Delta t + g[x(t_1)]\int_t^{t+\Delta t}\xi(s)ds \\ \Rightarrow \Delta x(t+\Delta t) \quad &\xrightarrow{\Delta t\to 0} \quad f[x(t)]\Delta t + g[x(t)]\int_t^{t+\Delta t}\xi(s)ds. \end{aligned} \tag{6.9}$$

Here, $t_1 \in [t, t+\Delta t]$. The second line follows from the mean value theorem for definite integrals, *provided* $\xi(t)$ is continuous. Since it is not, we define

$$I(t,\Delta t) \equiv \int_0^{t+\Delta t} g[x(s)]\xi(s)ds = g[(1-\alpha)x(t) + \alpha x(t+\Delta t)]\int_0^{t+\Delta t}\xi(s)ds, \tag{6.10}$$

where $\alpha \in [0,1]$. One can rewrite

$$(1-\alpha)x(t) + \alpha x(t+\Delta t) = \alpha\{x(t+\Delta t) - x(t)\} + x(t) = x(t) + \alpha\Delta x(t+\Delta x). \tag{6.11}$$

Thus, (6.9) will be written as (as $\Delta t \to 0$), setting $x(t) = x_0$,

$$\Delta x = f[x_0 + \alpha\Delta x]\Delta t + g[x_0 + \alpha\Delta x]\int_t^{t+\Delta t}\xi(s)ds. \tag{6.12}$$

Expanding up to first order in Δt, we get

$$\begin{aligned} \Delta x \quad &= \quad f(x_0)\Delta t + \{g(x_0) + \alpha\Delta x\ g'(x_0)\}\int_t^{t+\Delta t}\xi(s)ds \\ &= \quad f(x_0)\Delta t + g(x_0)\int_t^{t+\Delta t}\xi(s)ds \\ &\quad\ +\alpha g'(x_0)\left[f(x_0)\Delta t + \{g(x_0) + \alpha\Delta x\ g'(x_0)\}\int_t^{t+\Delta t}\xi(s')ds'\right]\int_t^{t+\Delta t}\xi(s)ds \\ \Rightarrow \langle\Delta x\rangle \quad &= \quad f(x_0)\Delta t + \alpha g(x_0)g'(x_0)\underbrace{\int_t^{t+\Delta t} ds\int_t^{t+\Delta t} ds'\underbrace{\langle\xi(s)\xi(s')\rangle}_{\delta(s-s')}}_{\Delta t} \ + \ O(\Delta x\Delta t) \end{aligned}$$

$$= \quad f(x_0)\Delta t + \alpha g(x_0) g'(x_0)\Delta t.$$

Thus, we have,

$$\boxed{\langle \Delta x\rangle = f(x_0)\Delta t + \alpha g(x_0) g'(x_0)\Delta t.} \tag{6.13}$$

From (6.12) we also get

$$\begin{aligned}
(\Delta x)^2 &= \left[f(x_0)\Delta t + \{g(x_0) + \alpha\Delta x\ g'(x_0)\}\int_t^{t+\Delta t} \xi(s)ds \right]^2 \\
&= \left[g^2(x_0) + 2\alpha\Delta x g(x_0) g'(x_0)\right] \int_t^{t+\Delta t} ds \int_t^{t+\Delta t} ds' \langle \xi(s)\xi(s')\rangle \\
&= \left[g^2(x_0) + 2\alpha\Delta x g(x_0) g'(x_0)\right] \Delta t \\
&= g^2(x_0)\Delta t + O(\Delta x\Delta t).
\end{aligned} \tag{6.14}$$

$$\therefore \boxed{\langle (\Delta x)^2\rangle = g^2(x_0)\Delta t.} \tag{6.15}$$

Derivation of the Fokker-Planck equation : Let us now derive the FPE corresponding to the above Langevin equation. We will derive a more general FPE in section 13. We start with the Chapman-Kolmogorov equation (CKE)for Markov processes, which will be derived in detail in section 17.9. However, the equation looks intuitively obvious, so it will not be very necessary for the reader to go back to its derivation before reading this section. The CKE is given by

$$P(x, t+\Delta t) = \int dx_0\ P(x, t+\Delta t|x_0, t)\ P(x_0, t). \tag{6.16}$$

It simply says that the a particle can reach x at time $t + \Delta t$ from any other point x_0 where it was present at time t. Also, we have from the basic definition of probability,

$$P(x, t+\Delta t|x_0, t) = \langle \delta[x - x(t+\Delta t)]\rangle_{x_0, t}. \tag{6.17}$$

Now, we taylor expand the RHS of (6.17) around x_0:

$$\begin{aligned}
P(x, t+\Delta t|x_0, t) &= P(x_0 + \Delta x, t+\Delta t|x_0, t) \\
&= \delta(x - x_0) - \langle \Delta x\rangle \frac{\partial}{\partial x}\delta(x - x_0) + \frac{1}{2}\langle (\Delta x)^2\rangle \frac{\partial^2}{\partial x^2}\delta(x - x_0) + \cdots .
\end{aligned} \tag{6.18}$$

From (17.9) we then get

$$\begin{aligned}
P(x, t+\Delta t) &= \int dx_0 \left[\delta(x - x_0) - \langle\Delta x\rangle \left\{\frac{\partial}{\partial x}\delta(x - x_0)\right\} + \frac{1}{2}\langle(\Delta x)^2\rangle \left\{\frac{\partial^2}{\partial x^2}\delta(x - x_0)\right\} + \cdots \right] P(x_0, t) \\
&= P(x, t) - \int dx_0 \langle\Delta x\rangle \left\{\frac{\partial}{\partial x}\delta(x - x_0)\right\} P(x_0, t) + \frac{1}{2}\int dx_0 \langle(\Delta x)^2\rangle \left\{\frac{\partial^2}{\partial x^2}\delta(x - x_0)\right\} P(x_0, t) \\
&= P(x, t) - \int dx_0\ [f(x_0)\Delta t + \alpha g(x_0) g'(x_0)\Delta t] \left\{\frac{\partial}{\partial x}\delta(x - x_0)\right\} P(x_0, t) \\
&\quad + \int dx_0\ [g^2(x_0)\Delta t]\frac{1}{2}\left\{\frac{\partial^2}{\partial x^2}\delta(x - x_0)\right\} P(x_0, t) \\
&= P(x, t) - \frac{\partial}{\partial x}\int dx_0\ [f(x_0)\Delta t + \alpha g(x_0) g'(x_0)\Delta t]\delta(x - x_0) P(x_0, t) \\
&\quad + \frac{1}{2}\frac{\partial^2}{\partial x^2}\int dx_0\ [g^2(x_0)\Delta t]\delta(x - x_0) P(x_0, t)
\end{aligned}$$

(6.19)

From the definition

$$\frac{\partial P(x,t)}{\partial t} = \frac{P(x,t+\Delta t) - P(x,t)}{\Delta t},$$

we get the FPE

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left\{[f(x) + \alpha g(x) g'(x)] P(x,t)\right\} + \frac{1}{2}\frac{\partial^2}{\partial x^2}\{g^2(x) P(x,t)\}. \tag{6.20}$$

Plugging in the expression for $f(x)$, we get

$$\boxed{\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left\{\left[\Gamma(x)V'(x) - f_1(x) + (1-\alpha) g(x) g'(x) + \frac{1}{2} g^2(x)\frac{\partial}{\partial x}\right] P(x,t)\right\}} \tag{6.21}$$

Now, for a system at equilibrium, we must have

$$P(x,t) \sim e^{-\beta H}. \tag{6.22}$$

Now, from (15.3), we have

$$\begin{aligned}
& \frac{\partial}{\partial x}\left\{\left[\Gamma(x)V'(x) - f_1(x) + (1-\alpha) g(x) g'(x) + \frac{1}{2} g^2(x)\frac{\partial}{\partial x}\right] P(x,t)\right\} = 0 \\
\Rightarrow\quad & \left[\Gamma(x)V'(x) - f_1(x) + (1-\alpha) g(x) g'(x) + \frac{1}{2} g^2(x)\frac{\partial}{\partial x}\right] P(x,t) = C \\
\Rightarrow\quad & \frac{1}{2} g^2(x) \frac{\partial P(x,t)}{\partial x} + [\Gamma(x)V'(x) - f_1(x) + (1-\alpha) g(x) g'(x)] P(x,t) = C \\
\Rightarrow\quad & \frac{\partial P(x,t)}{\partial x} + \underbrace{\frac{2}{g^2(x)}[\Gamma(x)V'(x) - f_1(x) + (1-\alpha) g(x) g'(x)]}_{\lambda(x)} P(x,t) = \frac{2C}{g^2(x)}
\end{aligned} \tag{6.23}$$

We note that the integrating factor will be $\exp\left[\int \lambda(x) dx\right]$. To meet the criterion $P(x) \sim e^{-\beta V(x)}$, we must have

$$\int \lambda(x) dx \quad = \quad \beta V(x) \quad \Rightarrow \quad \lambda(x) = \beta V'(x). \tag{6.24}$$

Thus we must have

$$g^2(x) \quad = \quad 2 k_B T \Gamma(x). \tag{6.25a}$$

$$f_1(x) \quad = \quad (1-\alpha) g(x) g'(x) = (1-\alpha) k_B T \Gamma'(x). \tag{6.25b}$$

We return to our original Langevin equation:

$$\dot{x} = -\Gamma(x)\frac{\partial V(x)}{\partial x} + f_1(x) + g(x)\xi(t). \tag{6.26}$$

Using (6.25) and substituting $\gamma(x) = \frac{1}{\Gamma(x)}$, along with the relation $\Gamma'(x) = -\frac{\gamma'(x)}{\gamma^2(x)}$ we arrive at our modified LE:

$$\boxed{\gamma(x)\dot{x} = -V'(x) - (1-\alpha) k_B T \frac{\gamma'(x)}{\gamma(x)} + \sqrt{2 k_B T \gamma(x)}\; \xi(t).} \tag{6.27}$$

7 The linear response theory

Let us consider the system Hamiltonian to be of the form

$$H(t) = H_0 + H'(t). \tag{7.1}$$

Here, H_0 is the Hamiltonian for the unperturbed system, while $H'(t)$ is the perturbation term, which is assumed to be small compared to H_0. we assume that the perturbation term is coupled to the external drive $f(\mathbf{x}, t)$ through

$$H'(t) = -\int d^3x A(\mathbf{x}) f(\mathbf{x}, t). \tag{7.2}$$

We have the *von Neumann* equation of motion for the density matrix $\rho(t) \equiv \sum_i p_i |\psi_i(t)\rangle\langle\psi_i(t)|$, given by[2]

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar}[H, \rho(t)]. \tag{7.3}$$

Here, the density operator $\rho(t)$ **is in the Schrödinger picture** and not in Heisenberg picture. We rewrite the above as [5]

$$\frac{\partial \rho(t)}{\partial t} = -i\mathcal{L}\rho(t), \tag{7.4}$$

where

$$\mathcal{L} \circ \equiv \frac{1}{\hbar}[H, \circ]. \tag{7.5}$$

We divide the above operator as follows:

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}', \tag{7.6}$$

with

$$\mathcal{L}_0 \circ \equiv \frac{1}{\hbar}[H_0, \circ]; \qquad \mathcal{L}' \circ \equiv \frac{1}{\hbar}[H', \circ]. \tag{7.7}$$

We also assume the total density matrix $\rho(t)$ to be related to the unperturbed density matrix ρ_0 as

$$\rho(t) = \rho_0 + \Delta\rho(t). \tag{7.8}$$

Thus, from (7.4) we get

$$\begin{aligned} \frac{\partial}{\partial t}(\rho_0 + \Delta\rho(t)) &= -i(\mathcal{L}_0 + \mathcal{L}')(\rho_0 + \Delta\rho(t)) \\ \frac{\partial \Delta\rho(t)}{\partial t} &= -i\mathcal{L}_0 \Delta\rho(t) - i\mathcal{L}'\rho_0, \end{aligned} \tag{7.9}$$

where we have used the fact that ρ_0 has no explicit time dependence and it commutes with H_0, and we have neglected the term $\mathcal{L}'\Delta\rho(t) \sim O(H'^2)$. Its formal solution can be written down as

$$\boxed{\Delta\rho(t) = -i\int_{-\infty}^{t} dt' e^{-i(t-t')\mathcal{L}_0}\mathcal{L}'(t')\rho_0.} \tag{7.10}$$

Let $B(t)$ be some dynamical variable in the *Heisenberg representation*:

$$B(t) = e^{iH_0 t/\hbar} B e^{-iH_0 t/\hbar} = e^{it\mathcal{L}_0} B. \tag{7.11}$$

[2] $i\hbar\frac{\partial\rho(t)}{\partial t} = i\hbar\sum_i p_i \left[\frac{\partial|\psi_i(t)\rangle}{\partial t}\langle\psi_i(t)| + |\psi_i(t)\rangle\frac{\partial\langle\psi_i(t)|}{\partial t}\right] = \sum_i p_i \left[H|\psi_i(t)\rangle\langle\psi_i(t)| - |\psi_i(t)\rangle\langle\psi_i(t)|H\right]$, from which the von Neumann equation follows.

See footnote for details.[3] Now, we have, for any two operators C and D, using cyclic property of trace,

$$\begin{aligned} &\text{Tr } \{\mathcal{L}_0 CD\} = \text{Tr } \{[H_0, C]D\} = \text{Tr } \{H_0 CD - CH_0 D\} = -\text{Tr } \{CH_0 D - CDH_0\} \\ \Rightarrow &\text{Tr } \{\mathcal{L}_0 CD\} = -\text{Tr } \{C\mathcal{L}_0 D\}. \end{aligned} \tag{7.14}$$

Similarly, it can be easily seen that (consider taking the $\mathcal{L}_0$ operator inside twice)

$$\text{Tr } \{\mathcal{L}_0^2 CD\} = +\text{Tr } \{C\mathcal{L}_0^2 D\}. \tag{7.15}$$

Using the fact that the terms odd and even in $\mathcal{L}$ pick up a minus and a plus sign when taken to the middle, we get

$$\begin{aligned} \text{Tr } \{e^{-it\mathcal{L}_0} CD\} &= \text{Tr } \left\{CD - it\mathcal{L}_0 CD - \frac{t^2}{2}\mathcal{L}_0^2 CD + \cdots\right\} \\ &= \text{Tr } \left\{CD + itC\mathcal{L}_0 D - \frac{t^2}{2}C\mathcal{L}_0^2 D + \cdots\right\} = \text{Tr } \{Ce^{+it\mathcal{L}_0} D\}. \end{aligned} \tag{7.16}$$

Now, the ensemble average of any dynamical variable B is defined as (we will assume $\langle B\rangle_0 \equiv \text{Tr } [\rho_0 B] = 0$)

$$\begin{aligned} \langle B(\mathbf{x}, t)\rangle &= \text{Tr } [\rho(t)B(\mathbf{x})] = \text{Tr } [(\rho_0 + \Delta\rho(t))B(\mathbf{x})] \\ &= \text{Tr } [\Delta\rho(t)B(\mathbf{x})] = -i\int_{-\infty}^{t} dt'\text{Tr } \left\{e^{-i(t-t')\mathcal{L}_0}\mathcal{L}'(t')\rho_0 B(\mathbf{x})\right\} \\ &= -\frac{i}{\hbar}\int_{-\infty}^{t} dt'\text{Tr } \left\{e^{-i(t-t')\mathcal{L}_0}[H'(t'), \rho_0]B(\mathbf{x})\right\} \\ &= \frac{i}{\hbar}\int d^3x' \int_{-\infty}^{t} dt' f(\mathbf{x}', t')\text{Tr } \left\{e^{-i(t-t')\mathcal{L}_0}[A(\mathbf{x}'), \rho_0]B(\mathbf{x})\right\}. \\ &= -\frac{i}{\hbar}\int d^3x' \int_{-\infty}^{t} dt' f(\mathbf{x}', t')\text{Tr } \left\{[A(\mathbf{x}'), \rho_0]e^{i(t-t')\mathcal{L}_0}B(\mathbf{x})\right\} \\ &= -\frac{i}{\hbar}\int d^3x' \int_{-\infty}^{t} dt' f(\mathbf{x}', t')\text{Tr } \{A(\mathbf{x}')\rho_0 B(\mathbf{x}, t-t') - \rho_0 A(\mathbf{x}')B(\mathbf{x}, t-t')\} \\ &= -\frac{i}{\hbar}\int d^3x' \int_{-\infty}^{t} dt' f(\mathbf{x}', t')\text{Tr } \{\rho_0 B(\mathbf{x}, t-t')A(\mathbf{x}') - \rho_0 A(\mathbf{x}')B(\mathbf{x}, t-t')\} \\ &= -\frac{i}{\hbar}\int d^3x' \int_{-\infty}^{t} dt' f(\mathbf{x}', t')\langle[B(\mathbf{x}, t-t'), A(\mathbf{x}')]\rangle_0 \end{aligned}$$

$$\Rightarrow \boxed{\langle B(\mathbf{x}, t)\rangle = -\frac{i}{\hbar}\int d^3x' \int_{-\infty}^{t} dt' f(\mathbf{x}', t')\langle[B(\mathbf{x}-\mathbf{x}', t-t'), A(0)]\rangle_0,} \tag{7.17}$$

[3] Proof:

$$\begin{aligned} e^{it\mathcal{L}_0}B &= \left(1 + it\mathcal{L}_0 - \frac{t^2}{2}\mathcal{L}_0^2\cdots\right)B = B + \frac{it}{\hbar}[H_0, B] - \frac{t^2}{2\hbar^2}[H_0, [H_0, B]]\cdots \\ &= B + it(H_0 B - BH_0) - \frac{t^2}{2\hbar^2}(H_0^2 B - 2H_0 BH_0 + BH_0^2)\cdots, \end{aligned} \tag{7.12}$$

while

$$\begin{aligned} e^{iH_0 t/\hbar}Be^{-iH_0 t/\hbar} &= \left(1 + \frac{it}{\hbar}H_0 - \frac{t^2}{2\hbar^2}H_0^2\cdots\right)B\left(1 - \frac{it}{\hbar}H_0 - \frac{t^2}{2\hbar^2}H_0^2\cdots\right) \\ &= B + \frac{it}{\hbar}(H_0 B - BH_0) - \frac{t^2}{2}(H_0^2 B - 2H_0 BH_0 - BH_0^2)\cdots = e^{it\mathcal{L}_0}B \qquad \text{QED.} \end{aligned} \tag{7.13}$$

where in the fifth line we have used (7.11) and last line we have assumed spatial homogeneity of the system. Since $\langle B(\mathbf{x},t)\rangle$ can depend only on $t' < t$, the RHS must vanish if $t < t'$. For this we rewrite the above relation as

$$\langle B(\mathbf{x},t)\rangle = -\frac{i}{\hbar}\int d^3x' \int_{-\infty}^{t} dt' f(\mathbf{x}',t')\chi_{BA}(\mathbf{x}-\mathbf{x}',t-t'), \tag{7.18}$$

where the *causal function* is defined through

$$\chi_{BA}(\mathbf{x},t) = \langle [B(\mathbf{x},t), A(0)]\rangle_0, \tag{7.19}$$

which is zero if $t < 0$.

7.1 The Kubo identity

The *Heisenberg* equation of motion for any dynamical variable $A(t)$ is given by

$$\frac{dA(t)}{dt} = \frac{i}{\hbar}[H_0, A(t)], \tag{7.20}$$

where

$$A(t) = e^{iHt/\hbar} A e^{-iHt/\hbar}. \tag{7.21}$$

Since

$$\begin{aligned}[][\rho_0, A(t)] &= \frac{1}{Z}\left[e^{-\beta H_0}A(t) - A(t)e^{-\beta H_0}\right] = \frac{e^{-\beta H_0}}{Z}\left[A(t) - e^{\beta H_0}A(t)e^{-\beta H_0}\right] \\ &= \rho_0\left[A(t) - e^{\beta H_0}A(t)e^{-\beta H_0}\right]. \end{aligned} \tag{7.22}$$

Let

$$\phi(\lambda) \equiv A(t) - e^{\lambda H_0}A(t)e^{-\lambda H_0}. \tag{7.23}$$

$$\begin{aligned} \therefore \phi(\beta) &= \int_0^\beta d\lambda \frac{\partial \phi(\lambda)}{\partial \lambda} = -\int_0^\beta d\lambda \frac{\partial}{\partial\lambda}\left[e^{\lambda H_0}A(t)e^{-\lambda H_0}\right] \\ &= -\int_0^\beta d\lambda\; e^{\lambda H_0}[H_0, A(t)]e^{-\lambda H_0}. \end{aligned} \tag{7.24}$$

Then, from (7.22), we have, using (15.21),

$$\begin{aligned}[][\rho_0, A(t)] &= \rho_0\phi(\beta) = -\rho_0\int_0^\beta d\lambda\; e^{\lambda H_0}[H_0, A(t)]e^{-\lambda H_0} \\ &= i\hbar\rho_0 \int_0^\beta d\lambda\; e^{\lambda H_0}\dot{A}(t)e^{-\lambda H_0} \\ &\Rightarrow \boxed{[\rho_0, A(t)] = i\hbar\rho_0\int_0^\beta d\lambda\; \dot{A}(t-i\hbar\lambda).} \end{aligned} \tag{7.25}$$

Eq. (7.25) is known as the Kubo identity.

8 The generalized susceptibility

The derivation follows almost entirely the treatment of [8]. The equation of motion of a damped oscillator is given by

$$\dot{q} = \frac{p}{m} \tag{8.1a}$$

$$\dot{p} = -m\omega_0^2 q - \frac{\gamma p}{m} + \xi(t). \tag{8.1b}$$

Here, the symbols have their usual meanings, and ω_0 is the *natural* frequency of the oscillator, in *absence* of friction, $\xi(t)$ is the stochastic force term. We rewrite (8.1) as

$$m\ddot{q} + \gamma\dot{q} + m\omega_0^2 q = \xi(t). \tag{8.2}$$

Substituting $q(t)$ in terms of its Fourier transform,

$$q(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega q_\omega e^{-i\omega t}, \tag{8.3}$$

we get

$$(-m\omega^2 - i\omega\gamma + m\omega_0^2)q_\omega = \xi_\omega. \tag{8.4}$$

We consider a perturbation $V(t)$ to the Hamiltonian,

$$H(t) = H_0 + V(t). \tag{8.5}$$

We assume the form of perturbation to be

$$V(t) = -xf(t). \tag{8.6}$$

One can write the following linear response relation between the perturbing force and the response:

$$\boxed{\langle x(\tau)\rangle = \int_{-\infty}^{\tau} \chi(\tau - t) f(t) dt = \int_0^{\infty} \chi(t) f(\tau - t) dt}\,. \tag{8.7}$$

Since the response at time τ depends only on earlier times ($\tau - t < \tau$), the above definition of the function $\chi(t)$ respects causality. Translating the above equation entirely to the Fourier space, we write

$$\begin{aligned}
\frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \langle x_\omega\rangle e^{-i\omega\tau} &= \frac{1}{(2\pi)^2}\int_0^{\infty} dt \int_{-\infty}^{\infty} d\omega \chi_\omega e^{-i\omega t} \int_{-\infty}^{\infty} d\omega' f_{\omega'} e^{-i\omega'(\tau - t)} \\
&= \frac{1}{(2\pi)^2}\int_0^{\infty} dt\ e^{-i(\omega-\omega')t} \int_{-\infty}^{\infty} d\omega\ \chi_\omega \int_{-\infty}^{\infty} d\omega'\ f_{\omega'} e^{-i\omega'\tau} \\
&= \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\ \chi_\omega f_\omega e^{-i\omega\tau} \\
\Rightarrow & \boxed{\langle x_\omega\rangle = \chi(\omega) f_\omega}\,.
\end{aligned} \tag{8.8}$$

The last line follows from the fact that the integrals on LHS and RHS are equal for *any* value of τ. We call $\chi(\omega)$ the *generalized suceptibility*. In general, it is a complex quantity:

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega). \tag{8.9}$$

Since $\chi(\omega) = \int_0^\infty dt\ \chi(t)e^{i\omega t}$, we deduce that ($\chi(t)$ being real)

$$\chi^*(\omega) = \chi(-\omega); \qquad \chi'(-\omega) = \chi'(\omega); \qquad \chi''(-\omega) = -\chi''(\omega). \tag{8.10}$$

Let the external force be monochromatic (for simplicity):

$$f(t) \equiv \mathrm{Re}\left[f_0 e^{-i\omega t}\right] = \frac{1}{2}\left[f_0 e^{-i\omega t} + f_0^* e^{i\omega t}\right]. \tag{8.11}$$

$$\therefore \langle x(t)\rangle = \mathrm{Re}\left[\chi(\omega) f_0 e^{-i\omega t}\right] = \frac{1}{2}\left[\chi(\omega) f_0 e^{-i\omega t} + \chi(-\omega) f_0^* e^{i\omega t}\right]. \tag{8.12}$$

Since

$$\frac{dE}{dt} = -\langle x\rangle \frac{df}{dt}, \tag{8.13}$$

we get from (8.11) and (8.12):

$$\begin{aligned}\frac{dE}{dt} &= -\frac{1}{2}\left[\chi(\omega)f_0e^{-i\omega t} + \chi(-\omega)f_0^*e^{i\omega t}\right] \times \left[-i\omega f_0e^{-i\omega t} + i\omega f_0^*e^{i\omega t}\right] \\ &= \frac{i\omega}{4}\left[\chi(\omega)f_0^2e^{-2i\omega t} - \chi(\omega)|f_0|^2 + \chi(-\omega)|f_0|^2 - \chi(-\omega)f_0^{*2}e^{2i\omega t}\right].\end{aligned} \tag{8.14}$$

Now, averaging over time (time period of external drive is τ_ω), we get the *mean dissipated heat* as

$$\begin{aligned}Q &\equiv \frac{1}{\tau_\omega}\int_0^{\tau_\omega} dt\frac{dE}{dt} = -\frac{i\omega}{4\tau_\omega}|f_0|^2\int_0^{\tau_\omega} dt[\chi(\omega) - \chi(-\omega)] \\ &= -\frac{i\omega}{4\tau_\omega}\,2i\chi''(\omega)\tau_\omega \Rightarrow \boxed{Q = \frac{1}{2}\omega\chi''(\omega)|f_0|^2}.\end{aligned} \tag{8.15}$$

Thus, the *imaginary* part of susceptibility determines dissipation. Since dissipation is always positive, we deduce that

$$\chi''(\omega) \geq 0 \quad \text{(always)}. \tag{8.16}$$

Returning to the frequency space, we write

$$\omega = \omega' + i\omega''. \tag{8.17}$$

Now we consider

$$\chi(\omega) = \int_0^\infty \chi(t)e^{i(\omega'+i\omega'')t} = \int_0^\infty \chi(t)e^{i\omega' t}e^{-\omega'' t}. \tag{8.18}$$

Thus, $\chi(\omega)$ is analytic in the upper half of ω-plane, including on the real axis. Evidently we have

$$\chi(-\omega^*) = \int_0^\infty \chi(t)e^{-i(\omega'-i\omega'')t}dt = \int_0^\infty \chi(t)e^{-i\omega' t}e^{-\omega'' t}dt = \chi^*(\omega). \tag{8.19}$$

Thus, $\chi(\omega)$ takes real values when

$$\chi(\omega) = \chi^*(\omega) \quad \Rightarrow \quad \int_0^\infty \chi(t)e^{i\omega' t}e^{-\omega'' t}dt = \int_0^\infty \chi(t)e^{-i\omega' t}e^{-\omega'' t}dt. \tag{8.20}$$

This can happen only on the $\omega' = 0$ axis, i.e., on the $\mathrm{Im}(\omega)$ axis. Then we have

$$\chi(i\omega'') = \chi^*(i\omega'') = \int_0^\infty \chi(t)e^{-\omega'' t}dt. \tag{8.21}$$

This function decreases *monotonically* from $\chi(i0) = \int_0^\infty \chi(t)dt \equiv \chi_0$ to $\equiv \chi(i\infty) = 0$ on the $\mathrm{Im}(\omega)$ axis, as ω'' increases from 0 to ∞.

To get a relation between $\chi'(\omega)$ and $\chi''(\omega)$, we consider the integral

$$I = \oint_C \frac{\chi(\omega)\, d\omega}{\omega - \omega_0}, \tag{8.22}$$

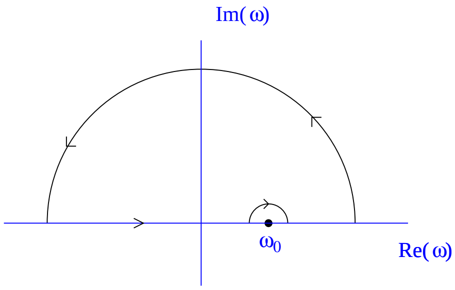
where ω_0 is a point on the $\mathrm{Re}(\omega)$ axis.

Thus, equating the real and imaginary parts, we get

$$\chi'(\omega) = \frac{1}{\pi}P\int_{-\infty}^\infty \frac{\chi''(\zeta)}{\zeta - \omega}d\zeta; \tag{8.25}$$

$$\chi''(\omega) = -\frac{1}{\pi}P\int_{-\infty}^\infty \frac{\chi'(\zeta)}{\zeta - \omega}d\zeta, \tag{8.26}$$

which are the well-known Kramers-Kronig relations for the generalized susceptibility.



We use the contour see (see adjacent diagram) to perform the integral. By the rules of contour integral, we have

$$P\int_{-\infty}^{\infty}\frac{\chi(\omega)\,d\omega}{\omega-\omega_0}=i\pi\chi(\omega_0), \tag{8.23}$$

where P denotes principal value of the integral. Or, replacing $\omega_0 \to \omega$ and $\omega \to \zeta$,

$$i\pi[\chi'(\omega)+i\chi''(\omega)]=P\int_{-\infty}^{\infty}\frac{\chi'(\zeta)+i\chi''(\zeta)}{\zeta-\omega}d\zeta. \tag{8.24}$$

9 The quantum fluctuation-dissipation theorem

We will see in this section how the equilibrium fluctuations of an observable is related to energy dissipation in the quantum case. The *spectral resolution* of an observable $A(t)$ is defined as [8]

$$\tilde{A}(\omega)\equiv\int_{-\infty}^{\infty}dtA(t)e^{i\omega t}. \tag{9.1}$$

The correlation function is defined as

$$\phi(t,t')\equiv\langle A(t)A(t')\rangle=\frac{1}{(2\pi)^2}\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\langle\tilde{A}(\omega)\tilde{A}(\omega')\rangle e^{-i(\omega t+\omega' t')}. \tag{9.2}$$

We know that the correlation function at equilibrium is a function of only the time difference $|t-t'|$, we must have

$$\langle\tilde{A}(\omega)\tilde{A}(\omega')\rangle=2\pi S(\omega)\delta(\omega+\omega'), \tag{9.3}$$

where $S(\omega)$ is a quantity known as the spectral density. We can then write,

$$\phi(t-t')=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega S(\omega)e^{-i\omega(t-t')}\quad\Rightarrow\quad\phi(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega S(\omega)e^{-i\omega t}. \tag{9.4}$$

Therefore the spectral density is simply the Fourier transform of the correlation function. Now, in quantum case, the equation (9.11) must be modified to

$$C_(\omega,\omega')\equiv\frac{1}{2}\langle\tilde{A}(\omega)\tilde{A}(\omega')+\tilde{A}(\omega')\tilde{A}(\omega)\rangle=2\pi S(\omega)\delta(\omega+\omega'). \tag{9.5}$$

But we have, if the system is initially in the state $|n\rangle$

$$\begin{aligned}C_n(\omega,\omega')&=\frac{1}{2}\langle n|\tilde{A}(\omega)\tilde{A}(\omega')+\tilde{A}(\omega')\tilde{A}(\omega)|n\rangle\\&=\frac{1}{2}\sum_m(\langle n|\tilde{A}(\omega)|m\rangle\langle m|\tilde{A}(\omega')|n\rangle+\langle n|\tilde{A}(\omega')|m\rangle\langle m|\tilde{A}(\omega)|n\rangle)\\&=\frac{1}{2}\sum_m[\tilde{A}_{mn}(\omega)\tilde{A}_{nm}(\omega')+\tilde{A}_{mn}(\omega')\tilde{A}_{nm}(\omega)].\end{aligned} \tag{9.6}$$

Now, we have

$$\begin{aligned}A_{nm}(t)&=\langle n|A(t)|m\rangle=\langle n(t)|A|m(t)\rangle\\&=\langle n|e^{iE_nt/\hbar}Ae^{-iE_mt/\hbar}|m\rangle\equiv A_{nm}e^{i\omega_{nm}t},\end{aligned} \tag{9.7}$$

where $\omega_{nm}=(E_n-E_m)/\hbar$.

$$\tilde{A}_{nm}(\omega) = \int_{-\infty}^{\infty} A_{nm} e^{i(\omega_{nm}+\omega)t} = 2\pi A_{nm}\delta(\omega_{nm}+\omega). \tag{9.8}$$

$$\begin{aligned}
\therefore C_n(\omega,\omega') &= 2\pi^2 \sum_m [A_{mn}A_{nm}\delta(\omega_{mn}+\omega)\delta(\omega_{nm}+\omega') + A_{mn}A_{nm}\delta(\omega_{mn}+\omega')\delta(\omega_{nm}+\omega)] \\
&= 2\pi^2 \sum_m |A_{nm}|^2[\delta(\omega_{mn}+\omega)\delta(\omega_{nm}+\omega') + \delta(\omega_{mn}+\omega')\delta(\omega_{nm}+\omega)] \\
&= 2\pi^2 \sum_m |A_{nm}|^2\delta(\omega+\omega')[\delta(\omega_{mn}+\omega) + \delta(\omega_{nm}+\omega)].
\end{aligned} \tag{9.9}$$

In the last step, we have used the fact that (since $\omega_{mn} = -\omega_{nm}$, see (**??**))

$$\begin{aligned}
\delta(\omega_{mn}+\omega)\delta(\omega_{nm}+\omega') = \delta(\omega_{mn}+\omega)\delta(-\omega_{mn}+\omega') = \delta(\omega_{mn}+\omega)\delta(\omega+\omega'). \\
\delta(\omega_{mn}+\omega')\delta(\omega_{nm}+\omega) = \delta(-\omega_{nm}+\omega')\delta(\omega_{nm}+\omega) = \delta(\omega+\omega')\delta(\omega_{nm}+\omega).
\end{aligned} \tag{9.10}$$

Now, using (9.5), we get

$$\begin{aligned}
C_n(\omega,\omega') = 2\pi S(\omega)\delta(\omega+\omega') &= 2\pi^2 \sum_m |A_{nm}|^2\delta(\omega+\omega')[\delta(\omega_{mn}+\omega) + \delta(\omega_{nm}+\omega)] \\
\Rightarrow S_n(\omega) &= \pi \sum_m |A_{nm}|^2[\delta(\omega_{mn}+\omega) + \delta(\omega_{nm}+\omega)].
\end{aligned} \tag{9.11}$$

We now subject the system to a monochromatic periodic perturbation:

$$V(t) = -\frac{1}{2}(f_0 e^{-i\omega t} + f_0^* e^{i\omega t})x. \tag{9.12}$$

The *Fermi Golden Rule* then provides us with the transition rate from $n \to m$ as

$$w(m|n) = \frac{\pi|f_0|^2}{2\hbar^2}|A_{mn}|^2[\delta(\omega+\omega_{mn}) + \delta(\omega+\omega_{nm})]. \tag{9.13}$$

The mean energy absorbed per unit time will be

$$\begin{aligned}
Q = \sum_m w(m|n)\hbar\omega_{mn} &= \frac{\pi|f_0|^2}{2\hbar}\sum_m |A_{mn}|^2[\delta(\omega+\omega_{mn}) + \delta(\omega+\omega_{nm})]\omega_{mn} \\
&= \frac{\pi|f_0|^2}{2\hbar}\omega\sum_m |A_{mn}|^2[\delta(\omega+\omega_{nm}) - \delta(\omega+\omega_{mn})].
\end{aligned} \tag{9.14}$$

But we have already seen (see (8.15))

$$Q = \frac{1}{2}\omega\chi''(\omega)|f_0|^2. \tag{9.15}$$

Equating the above two equations, we then get

$$\chi_n''(\omega) = \frac{\pi}{\hbar}\sum_m |A_{nm}|^2[\delta(\omega+\omega_{nm}) - \delta(\omega+\omega_{mn})]. \tag{9.16}$$

Next, we average $S(\omega)$ (eq. (9.11)) over the initial Gibbs distribution, $p_n = e^{-\beta E_n}/Z$:

$$S(\omega) = \sum_n p_n S_n(\omega) = \pi \sum_{mn} p_n |A_{nm}|^2[\delta(\omega_{mn}+\omega) + \delta(\omega_{nm}+\omega)]$$

$$
\begin{aligned}
&= \pi \sum_{mn} p_n |A_{nm}|^2 \delta(\omega + \omega_{nm}) + \pi \sum_{nm} p_m |A_{mn}|^2 \delta(\omega + \omega_{nm}) \\
&= \pi \sum_{mn} (p_n + p_m) |A_{nm}|^2 \delta(\omega + \omega_{nm}) \\
&= \pi \sum_{mn} p_n \left(1 + e^{\beta\hbar\omega_{nm}}\right) |A_{nm}|^2 \delta(\omega + \omega_{nm}) \\
\Rightarrow S(\omega) &= \pi \left(1 + e^{-\beta\hbar\omega}\right) \sum_{mn} |A_{nm}|^2 \delta(\omega + \omega_{nm}).
\end{aligned} \tag{9.17}
$$

Similarly, from (9.16) we have,

$$
\begin{aligned}
\chi''(\omega) &= \frac{\pi}{\hbar} \sum_{mn} |A_{nm}|^2 [\delta(\omega + \omega_{nm}) - \delta(\omega + \omega_{mn})] \\
\Rightarrow \chi''(\omega) &= \frac{\pi}{\hbar} \left(1 - e^{-\beta\hbar\omega}\right) \sum_{mn} |A_{nm}|^2 \delta(\omega + \omega_{nm}).
\end{aligned} \tag{9.18}
$$

Thus, we finally obtain

$$
\boxed{S(\omega) = \hbar \, \frac{1 + e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \chi''(\omega) = \hbar \chi''(\omega) \coth(\beta\hbar\omega/2).} \tag{9.19}
$$

Since the correlation function $\phi(t)$ is the Fourier transform of the spectral density function (eq.(9.4)), we can write

$$
\phi(t) = \langle A(t)A(0) \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega S(\omega) e^{-i\omega t} = \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} d\omega \; e^{-i\omega t} \chi''(\omega) \coth(\beta\hbar\omega/2). \tag{9.20}
$$

As we have laready seen in the theory of linear response (putting $B = A$ in (7.17)),

$$
\langle A(t) \rangle = \int_0^{\infty} \chi(t - t') f(t') \quad \Rightarrow \quad \tilde{A}(\omega) = \tilde{\chi}(\omega) \tilde{f}(\omega). \tag{9.21}
$$

This gives,

$$
\langle \tilde{A}(\omega) \tilde{A}(\omega') \rangle = \tilde{\chi}(\omega) \tilde{\chi}(\omega') \langle \tilde{f}(\omega) \tilde{f}(\omega') \rangle = 2\pi S_A(\omega) \delta(\omega + \omega'), \tag{9.22}
$$

where we have made use of (9.11), and have explicitly written the subscript A for the spectral density corresponding to the variable A. We then similarly define the spectral density for f as:

$$
\langle \tilde{f}(\omega) \tilde{f}(\omega') \rangle = 2\pi S_f(\omega) \delta(\omega + \omega'). \tag{9.23}
$$

From (9.22) and (9.23), we have,

$$
\begin{aligned}
S_A(\omega) &= \tilde{\chi}(\omega) \tilde{\chi}(-\omega) S_f(\omega) = |\chi(\omega)|^2 S_f(\omega) \\
\Rightarrow & \boxed{S_f(\omega) == \frac{\hbar \chi''(\omega)}{|\chi(\omega)|^2} \coth(\beta\hbar\omega/2).}
\end{aligned} \tag{9.24}
$$

10 The Onsager Reciprocity Theorem

10.1 Affinities and fluxes

We consider a system that is sufficiently close to equilibrium, so that the *intensive* variables, namely the temperature, pressure, chemical potential, etc. are well-defined locally. We further assume that they are related to their conjugate *extensive* variables through the *equilibrium* equation of state. Thus the entropy density will be given by [7]

$$T ds = du - \sum_i X_i d\xi_i - \sum_j \mu_j dn_j. \tag{10.1}$$

Here, u is the energy density, X_i are the generalized forces and ξ_i are generalized displacements, μ_j are chemical potential of species j (note that the summation over i and j are different in general).

$$\therefore ds = \frac{1}{T}du - \frac{1}{T}\sum_i X_i d\xi_i - \frac{1}{T}\sum_j \mu_j dn_j \equiv \sum_k \phi_k d\rho_k, \tag{10.2}$$

where, in the above case, ϕ_k's (potentials) are equal to $1/T$, $-X_i/T$ and μ_j/T, while the ρ_k's can be read off from the equation above. The former are intensive and the latter are extensive variables.

Now suppose $\phi_k \equiv \phi_k(\mathbf{r})$. These will generate currents $\mathbf{j}_k$ that are related to the densities through the continuity equation (see appendix A for details):

$$\frac{\partial \rho_k}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{j}_k = 0. \tag{10.3}$$

Next, we define entropy current densities as

$$\mathbf{j}_s = \sum_k \phi_k \mathbf{j}_k. \tag{10.4}$$

The violation of conservation of entropy density is quantified by (see appendix A)

$$\frac{ds}{dt} = \frac{\partial s}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{j}_s \tag{10.5}$$

and eq.(10.2) says (since s depends explicitly on ρ_k's)

$$\frac{\partial s}{\partial t} = \sum_k \frac{\partial s}{\partial \rho_k}\frac{\partial \rho_k}{\partial t} = \sum_k \phi_k \frac{\partial \rho_k}{\partial t}. \tag{10.6}$$

Using eq.(10.4) and (10.6) in (10.5),

$$\frac{ds}{dt} = \sum_k \phi_k \frac{\partial \rho_k}{\partial t} + \sum_k \boldsymbol{\nabla} \cdot (\phi_k \mathbf{j}_k) = -\sum_k \phi_k \boldsymbol{\nabla} \cdot \mathbf{j}_k + \sum_k \boldsymbol{\nabla} \cdot (\phi_k \mathbf{j}_k)$$

so that

$$\boxed{\frac{ds}{dt} = \sum_k \boldsymbol{\nabla}\phi_k \cdot \mathbf{j}_k\ .} \tag{10.7}$$

In the above relation, the force fields $\boldsymbol{\nabla}\phi_k$ are called *affinities* and the current densities $\mathbf{j}_k$ are referred to as the *fluxes* [7, 9].

We next proceed to show that if the fluxes depende linearly on the forces,

$$\mathbf{j}_i = \sum_k L_{ik} \boldsymbol{\nabla}\phi_k, \tag{10.8}$$

then the coefficients of the forces are symmetric: $L_{ik} = L_{ki}$.

10.2 The Onsager Reciprocity

The relation (10.7) is very general. The linear approximation steps in at the level of eq.(10.8). Substituting (10.8) in (10.5), we get

$$\dot{s} = \sum_k \boldsymbol{\nabla}\phi_k \cdot \sum_l L_{kl} \boldsymbol{\nabla}\phi_l = \sum_{kl} L_{kl} \boldsymbol{\nabla}\phi_k \cdot \boldsymbol{\nabla}\phi_l. \tag{10.9}$$

Now, replacing $\boldsymbol{\nabla}\phi_k$ and $\boldsymbol{\nabla}\phi_l$ by their magnitudes F_k and F_l respectively, and absorbing the cosine term into the definition of L_{kl}, we obtain

$$\dot{s} = \sum_{kl} L_{kl} F_k F_l. \tag{10.10}$$

Thus we arrive at

$$\frac{\partial^2 \dot{s}}{\partial F_i \partial F_j} = L_{ij}. \tag{10.11}$$

Noting that the LHS is symmetric in the order of differentiation, we get

$$\boxed{L_{ij} = L_{ji},} \tag{10.12}$$

which is the Onsager's reciprocity theorem.

11 The Central Limit Theorem

Statement: *If Y be the mean of the variables $\{X_i\}$, each of which is statistically independent of the other, then as $N \to \infty$, the probability distribution of Y becomes a Gaussian, provided the moments of the variables do not diverge.* [10].

Derivation: Let the displacement in each step of a random walk be represented by x_i $(i = 1, \cdots, N)$, while the net displacement in N steps be denoted by Y:

$$y \equiv \sum_{i=1}^{N} x_i. \tag{11.1}$$

We define

$$\begin{aligned} P(y) &\equiv \text{Probability of finding } Y \in [y, y+dy] \\ \text{and } w_i(x_i) &\equiv \text{Probability of finding } X_i \in [x_i, x_i + dx_i] \end{aligned} \tag{11.2}$$

Therefore we can always write (since the steps are statistically independent)

$$P(y)dy = \int_{-\infty}^{\infty} dx_1 \cdots dx_N w_1(x_1) \cdots w_N(x_N) \tag{11.3}$$

subject to the condition

$$x_1 + \cdots + x_N \in [y, y+dy]. \tag{11.4}$$

To understand the reason for writing (11.3) will be evident if we consider the discrete limit: since $w(x_1)dx_1$ is the probability of finding particle 1 in $(x_1, x_1 + dx_1)$, etc., one can always find a combination $x_1, x_2, \cdots, x_N$ which will satisfy the condition that $y = \sum x_i \in [y, y+dy]$. Since the probabilities $w(x_1)dx_1$, etc. are independent, we will have the total joint probability as

$$P(y)dy \stackrel{?}{=} \prod_{i=1}^{N} w_i(x_i) dx_i. \tag{11.5}$$

However, the above product can always found for any set of values of $\{x_1, \cdots, x_N\}$ for which the above mentioned conditions is satisfied, so the total probability $P(y)dy$ will be summation of all these probabilities, and hence the presence of the integration over $(x_1, \cdots, x_N)$. Q.E.D.

Since evaluation of the integral in (11.3) is difficult, we incorporate the constraint (11.4) into (11.3) by means of a Dirac Delta function and thereafter integrate without any restriction:

$$\begin{aligned} P(y)dy &= \int dx_1 \cdots dx_N \left[\delta\left(y - \sum x_i\right) dy\right] w_1(x_1) \cdots w_N(x_N), \\ \Rightarrow P(y) &= \int dx_1 \cdots dx_N \delta\left(y - \sum x_i\right) w_1(x_1) \cdots w_N(x_N) \end{aligned} \tag{11.6}$$

The function $\delta(y - \sum x_i)dy$ is a function that takes the value unity (unlike just $\delta(y - \sum x_i)$ which assumes an infinite value) if the combination $\{x_1, \cdots, x_N\}$ is such that their summation equals y, and is zero elsewhere.

$$\delta\left(y - \sum x_i\right) dy = \begin{cases} 1 & \text{if } |y - \sum x_i| < \left|\frac{dy}{2}\right|, \\ 0 & \text{otherwise.} \end{cases} \tag{11.7}$$

Now, we know that

$$\delta\left(y - \sum x_i\right) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk \exp\left[-ik\left(y - \sum x_i\right)\right]. \tag{11.8}$$

Substituting (11.8) into (11.6), we obtain

$$\begin{aligned} P(y) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk\ dx_1 \cdots dx_N \exp\left[-ik\left(y - \sum x_i\right)\right] w_1(x_1) \cdots w_N(x_N) \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{-iky} Q_1 \cdots Q_N \end{aligned} \tag{11.9}$$

where

$$Q_i \equiv \int_{-\infty}^{\infty} w_i(x_i) e^{ikx_i} dx_i. \tag{11.10}$$

We need to find which approximations hold good in the limit as $N \to \infty$. Since Q fluctuates (about $x = 0$ axis) rapidly on account of the fluctuating term e^{ikx_i} as k is increased, Q decreases as k is increased, provided $w(x)$ is a slowly varying function of x:

$$\begin{aligned} \left|\frac{d}{dx}\left(we^{ikx}\right)\right| &\approx \left|w\frac{d}{dx}\left(e^{ikx}\right)\right| \gg \left|\frac{dw}{dx}\right| \\ \text{i.e.,} \qquad |wk| &\gg \left|\frac{dw}{dx}\right| \\ \text{or,} \quad \frac{1}{k}\left|\frac{dw}{dx}\right| &\ll |w|. \end{aligned} \tag{11.11}$$

Therefore, $Q_i \cdots Q_N$ (N large) becomes extremely small at large k because the positive and negative areas under the curve become almost equal in magnitude. Thus, we need to consider only small values of k, and hence we can use the standard trick of expanding the oscillating term into a Taylor's series:

$$Q_i(k) = \int dx_i w_i(x_i) e^{ikx_i}$$

$$
\begin{aligned}
&= \int w_i(x_i)\left[1 + ikx_i - \frac{k^2x_i^2}{2} + \cdots\right] \\
&= \int w_i(x_i)dx_i + ik\int x_i w_i(x_i) - \frac{k^2}{2}\int x_i^2 w_i(x_i)dx_i + \cdots \\
&= 1 + ik\langle x_i\rangle - \frac{k^2}{2}\langle x_i^2\rangle + \cdots \qquad (11.12)
\end{aligned}
$$

where $\langle x_i\rangle, \langle x_i^2\rangle$, etc. are the first, second, $\cdots$ moments of x.
Therefore, from (11.12) we have ($\ln Q_i(k)$ being a slowly varying function compared to $Q_i(k)$ itself):

$$
\ln Q_i(k) = \ln\left(1 + ik\langle x_i\rangle - \frac{k^2}{2}\langle x_i^2\rangle + \cdots\right) \qquad (11.13)
$$

Now, using

$$
\ln(1+p) = p - \frac{1}{2}p^2\cdots
$$

for $p \ll 1$,
we get

$$
\begin{aligned}
\ln Q(k) &= \left[\left(ik\langle x_i\rangle - \frac{k^2}{2}\langle x_i^2\rangle\right) - \frac{1}{2}\left(ik\langle x_i\rangle - \frac{k^2}{2}\langle x_i^2\rangle\right)^2 + \cdots\right] \\
&\approx_i \left[ik\langle x_i\rangle - \frac{k^2}{2}\langle x_i^2\rangle - \frac{k^2}{2}\langle x_i\rangle^2\right] \\
\Rightarrow Q(k) &= \exp\left[ik\langle x_i\rangle - \frac{1}{2}\sigma_i^2 k^2\right] \qquad (11.14)
\end{aligned}
$$

where σ_i is the variance of x_i.
Therefore we get

$$
\prod_i Q_i(k) = \prod_i \exp\left[i\langle x_i\rangle k - \frac{1}{2}\sigma_i^2 k^2\right]. \qquad (11.15)
$$

Now we get from eq. (11.9)

$$
\begin{aligned}
P(y) &= \frac{1}{2\pi}\int dk e^{-iky}\prod_i Q_i(k) \\
&= \frac{1}{2\pi}\int dk e^{-iky}\prod_i \exp\left[i\langle x_i\rangle k - \frac{1}{2}\sigma_i^2 k^2\right] \\
&= \frac{1}{2\pi}\int dk\ \exp\left[-\frac{k^2}{2}\left(\sum \sigma_i^2\right) + i\left(\sum_i \langle x_i\rangle - y\right)k\right]
\end{aligned}
$$

$$
\Rightarrow P(y) = \frac{1}{2\pi}\int dk e^{-ak^2+bk} \qquad (11.16)
$$

where

$$
a = \frac{1}{2}\sum \sigma_i^2, \qquad b = i\left(\sum\langle x_i\rangle - y\right). \qquad (11.17)
$$

$$
\begin{aligned}
\Rightarrow P(y) &= \frac{1}{2\pi}\int dk \exp\left[-a\left\{\left(k-\frac{b}{2a}\right)^2-\frac{b^2}{4a^2}\right\}\right] \\
&= \frac{1}{2\pi}e^{b^2/4a}\int dk \exp\left[-a\left(k-\frac{b}{2a}\right)^2\right] \\
&= \frac{e^{b^2/4a}}{2\pi}.\sqrt{\frac{\pi}{a}}. \qquad (11.18)
\end{aligned}
$$

Finally, on substituting the values of a and b from(11.17), we obtain

$$
P(y) = \frac{1}{2\pi}\left(\sqrt{\frac{2\pi}{\sum \sigma_i^2}}\right).\exp\left[-\frac{(y-\sum\langle x_i\rangle)^2}{2\sum\sigma_i^2}\right]
$$

$$
\Rightarrow \boxed{P(y) = \frac{1}{\sqrt{2\pi\sum\sigma_i^2}}\exp\left[-\frac{(y-\sum\langle x_i\rangle)^2}{2\sum\sigma_i^2}\right]} \qquad (11.19)
$$

$$
\text{Or, } \boxed{P(y) = \frac{1}{\sqrt{2\pi\sigma_y^2}}\exp\left[-\frac{(y-\langle y\rangle)^2}{2\sigma_y^2}\right]} \qquad (11.20)
$$

which is a Gaussian with mean and variance given by

$$
\begin{aligned}
\langle y\rangle &\equiv \sum\langle x_i\rangle \\
\sigma_y &\equiv \sqrt{\sum\sigma_i^2} \qquad (11.21)
\end{aligned}
$$

If instead of $Y = X_1 + X_2 + \cdots X_N$, we would have taken

$$
Y = \frac{X_1 + X_2 + \cdots X_N}{N}, \qquad (11.22)
$$

then we would have obtained (on replacing x by $\frac{x}{N}$),

$$
\begin{aligned}
\langle y\rangle &= \frac{\sum\langle x_i\rangle}{N}; \\
\sigma_y &= \frac{\sqrt{\sum\sigma_i^2}}{N}. \qquad (11.23)
\end{aligned}
$$

Now, suppose the functions w_1, w_2, etc. were all same (say w), i.e., the random variables that have been summed up were all sampled from the same distribution, then we have got, as can be seen from (11.23),

$$
\begin{aligned}
\langle y\rangle &= \langle x\rangle; \\
\sigma_y &= \frac{\sqrt{N\sigma^2}}{N} = \frac{\sigma}{\sqrt{N}}. \qquad (11.24)
\end{aligned}
$$

Equations (11.23) or (11.24) constitutes the Central Limit Theorem.

12 Basics of Langevin equation

The Langevin equation is the extension of Newton's equation of motion into the regime where thermal fluctuations are dominant and the motion is no longer deterministic. It is written as

$$m\dot{\mathbf{v}} = -\gamma \mathbf{v} - V'(\mathbf{x}, t) + \xi(t), \tag{12.1}$$

where $V'(\mathbf{x}, t)$ contains all the effects of the time-dependent perturbations that are conservative in nature (i.e. can be derived from a potential). In case non-conservative forces are present, we write it as an extra term $\mathbf{F}(\mathbf{t})$. However, for the time being we will not concern ourselves with these kinds of forces. $-\gamma\mathbf{v}$ is the damping or friction term. $\xi(t)$ is the stochastic term (noise), and in our case will be assumed to be Gaussian distributed and being delta-correlated:

$$\langle \xi(t) \rangle = 0; \qquad \langle \xi(t)\xi(t') \rangle = 2D\delta(t - t'). \tag{12.2}$$

The coefficient D is called the noise strength and is depends on the system parameters.

12.1 Finding noise strength

D can be derived from the solution of (12.2) in the simplest case: when the potential term is absent and the particle is a free one, moving in one dimension:

$$m\dot{v} = -\gamma v + \xi(t), \tag{12.3}$$

whose solution is

$$v(t) = v_0 e^{-\gamma t/m} + \frac{e^{-\gamma t/m}}{m} \int_0^t dt' \xi(t') e^{\gamma t'/m}. \tag{12.4}$$

$$\begin{aligned}
\therefore \langle v^2 \rangle &= \langle v_0^2 \rangle e^{-2\gamma t/m} + \frac{e^{-2\gamma t/m}}{m^2} \int_0^t dt' \int_0^t dt'' \langle \xi(t')\xi(t'') \rangle e^{-\gamma(t'+t'')/m} \\
&= \langle v_0^2 \rangle e^{-2\gamma t/m} + \frac{e^{-2\gamma t/m}}{m^2} 2D \int_0^t dt' \int_0^t dt'' \delta(t' - t'') e^{-\gamma(t'+t'')/m} \\
&= \langle v_0^2 \rangle e^{-2\gamma t/m} + \frac{e^{-2\gamma t/m}}{m^2} 2D \int_0^t dt' e^{2\gamma t'/m} \\
&= \langle v_0^2 \rangle e^{-2\gamma t/m} + \frac{e^{-2\gamma t/m} D}{m\gamma} (e^{2\gamma t/m} - 1) \\
&= \langle v_0^2 \rangle e^{-2\gamma t/m} + \frac{D}{m\gamma} (1 - e^{-2\gamma t/m}).
\end{aligned} \tag{12.5}$$

Now, as $t \to \infty$, the system relaxes to equilibrium in absence of any perturbation. Then, by equipartition theorem, we have,

$$\frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} k_B T. \tag{12.6}$$

Using this, we get from (eq:D) by putting $t \to \infty$,

$$\frac{k_B T}{m} = \frac{D}{m\gamma} \quad \Rightarrow \quad \boxed{D = \gamma k_B T}. \tag{12.7}$$

12.2 Finding variance in position

We note that, $x(t) = \int_0^t v(t')dt'$. Then we have,

$$
\begin{aligned}
x(t) &= \int_0^t dt' \left[v_0 e^{-\gamma t'/m} + \frac{e^{-\gamma t'/m}}{m} \int_0^{t'} dt'' \xi(t'') e^{\gamma t''/m} \right] \\
&= \frac{mv_0}{\gamma}(1 - e^{-\gamma t/m}) + \frac{1}{m} \int_0^t dt' e^{-\gamma t'/m} \int_0^{t'} dt'' \xi(t'') e^{\gamma t''/m} \\
&= \frac{mv_0}{\gamma}(1 - e^{-\gamma t/m}) + \frac{1}{m} \int_0^t dt'' \xi(t'') e^{\gamma t''/m} \int_{t''}^t dt' e^{-\gamma t'/m} \\
&= \frac{mv_0}{\gamma}(1 - e^{-\gamma t/m}) - \frac{1}{\gamma} \int_0^t dt'' \xi(t'') e^{\gamma t''/m} (e^{-\gamma t/m} - e^{-\gamma t''/m}) \\
&= \frac{mv_0}{\gamma}(1 - e^{-\gamma t/m}) + \frac{1}{\gamma} \int_0^t dt'' \xi(t'') - \frac{e^{-\gamma t/m}}{\gamma} \int_0^t dt'' \xi(t'') e^{\gamma t''/m}. \qquad (12.8)
\end{aligned}
$$

In the third line, the order of integration has been changed so that the integral of t' can be carried out explicitly. Then we get,

$$
\begin{aligned}
\langle x^2(t) \rangle &= \frac{m^2}{\gamma^2} \langle v_0^2 \rangle (1 - e^{-\gamma t/m})^2 + \frac{1}{\gamma^2} \int_0^t dt'' \int_0^t dt_2 \langle \xi(t'') \xi(t_2) \rangle - \frac{2e^{-\gamma t/m}}{\gamma^2} \int_0^t dt'' \int_0^t dt_2 \langle \xi(t'') \xi(t_2) \rangle e^{\gamma t''/m} \\
&\quad + \frac{e^{-2\gamma t/m}}{\gamma^2} \int_0^t dt'' \int_0^t dt_2 \langle \xi(t'') \xi(t_2) \rangle e^{\gamma (t'' + t_2)/m} \\
&= \frac{m^2}{\gamma^2} \langle v_0^2 \rangle (1 - e^{-\gamma t/m})^2 + \frac{2k_B T}{\gamma} \int_0^t dt'' - \frac{4k_B T}{\gamma} e^{-\gamma t/m} \int_0^t dt'' e^{\gamma t''/m} + \frac{2k_B T}{\gamma} e^{-2\gamma t/m} \int_0^t dt'' e^{2\gamma t''/m} \\
&= \frac{m^2}{\gamma^2} \langle v_0^2 \rangle (1 - 2e^{-\gamma t/m} + e^{-2\gamma t/m}) + \frac{2k_B T}{\gamma} t - \frac{4k_B T m}{\gamma^2} (1 - e^{-\gamma t/m}) + \frac{k_B T m}{\gamma^2} (1 - e^{-2\gamma t/m}). \qquad (12.9)
\end{aligned}
$$

For small times, $t \to 0$, we then have

$$
\begin{aligned}
\langle x^2(t) \rangle =& \frac{m^2}{\gamma^2} \langle v_0^2 \rangle \left[1 - 2 \left(1 - \frac{\gamma t}{m} + \frac{\gamma^2 t^2}{2m^2} \right) + \left(1 - \frac{2\gamma t}{m} + \frac{2\gamma^2 t^2}{m^2} \right) \right] \\
&+ \frac{2k_B T}{\gamma} t - \frac{4k_B T m}{\gamma^2} \left[1 - \left(1 - \frac{\gamma t}{m} + \frac{\gamma^2 t^2}{2m^2} \right) \right] + \frac{k_B T m}{\gamma^2} \left[1 - \left(1 - \frac{2\gamma t}{m} + \frac{2\gamma^2 t^2}{m^2} \right) \right] \\
=& \frac{m^2}{\gamma^2} \langle v_0^2 \rangle \left[\frac{\gamma^2 t^2}{m^2} \right] + \frac{2k_B T}{\gamma} t - \frac{4k_B T m}{\gamma^2} \left[\frac{\gamma t}{m} - \frac{\gamma^2 t^2}{2m^2} \right] + \frac{k_B T m}{\gamma^2} \left[\frac{2\gamma t}{m} - \frac{2\gamma^2 t^2}{m^2} \right] \\
=& \left[\langle v_0^2 \rangle + \frac{2k_B T}{m} - \frac{2k_B T}{m} \right] t^2 = \langle v_0^2 \rangle t^2. \qquad (12.10)
\end{aligned}
$$

In other words, the variance in position is proportional to t^2 for small times. However, at large times ($t \to \infty$), all exponential terms vanish, and the variance becomes

$$
\langle x^2(t) \rangle = \frac{m^2}{\gamma^2} \langle v_0^2 \rangle - \frac{3k_B T}{m^2} + \frac{2k_B T}{\gamma} t. \qquad (12.11)
$$

Thus, in the large time limit, we get back the linear dependence of position variance on time: $\langle x^2(t) \rangle \sim t$.

13 Derivation of the Fokker-Planck equation (FPE)

Let the generalized Langevin equation be [12]

$$\frac{d\mathbf{a}}{dt} = \mathbf{v}(\mathbf{a}) + \mathbf{F}(t). \tag{13.1}$$

here, $\mathbf{a}$, $\mathbf{v}(\mathbf{a})$ and $\mathbf{F}(t)$ are column vectors. The correlation is given by the usual delta function:

$$\langle \mathbf{F}(t)\mathbf{F}^{\dagger}(t')\rangle = 2\mathbf{B}\delta(t-t'). \tag{13.2}$$

where $\mathbf{B}$ is a square matrix, which is also symmetric owing to requirement same noise strength on interchange of t and t'. Next, we define $p(\mathbf{a},t)$ as the probability of obtaining the value $\mathbf{a}$ at time t. The normalization condition is given by

$$\int p(\mathbf{a},t)d\mathbf{a} = 1. \qquad \text{(for any } t\text{)} \tag{13.3}$$

As is obvious, we ought to have a continuity equation (which will eventually turn out to be the FPE) for this probability current:

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial \mathbf{a}} \cdot \left(\frac{\partial \mathbf{a}}{\partial t} p\right) = 0. \tag{13.4}$$

Using eq.(13.1) in eq.(13.4), we have

$$\frac{\partial p(\mathbf{a},t)}{\partial t} = -\frac{\partial}{\partial \mathbf{a}} \cdot [\mathbf{v}(\mathbf{a})p(\mathbf{a},t) + \mathbf{F}(t)p(\mathbf{a},t)]. \tag{13.5}$$

Let us define an operator L such that

$$L\Phi \equiv \frac{\partial}{\partial \mathbf{a}} \cdot (\mathbf{v}(\mathbf{a})\Phi). \tag{13.6}$$

Using this to write eq.(13.5), we get

$$\frac{\partial p}{\partial t} = -Lp - \frac{\partial}{\partial \mathbf{a}} \cdot (\mathbf{F}(t)p). \tag{13.7}$$

Writing above equation as

$$\frac{\partial p}{\partial t} + Lp = -\frac{\partial}{\partial \mathbf{a}}(\mathbf{F}(t)p),$$

we note that the integrating factor for the above first order DE is e^{tL}. Thus, multiplying both sides by this IF, we have

$$\frac{\partial}{\partial t}(pe^{tL}) = -e^{tL}\frac{\partial}{\partial \mathbf{a}} \cdot (\mathbf{F}(t)p) \tag{13.8}$$

so that finally we have

$$p(\mathbf{a},t) = e^{-tL}p(\mathbf{a},0) - \int_0^t dt' e^{(t'-t)L}\frac{\partial}{\partial \mathbf{a}} \cdot [\mathbf{F}(t')p(\mathbf{a},t')] \tag{13.9}$$

where $t' < t$ (always).

Now, substituting the expression for $p(\mathbf{a},t)$ from (13.9) into (13.7), we find

$$\begin{aligned} \frac{\partial p(\mathbf{a},t)}{\partial t} = & - \quad Lp(\mathbf{a},t) - \frac{\partial}{\partial \mathbf{a}} \cdot [\mathbf{F}(t)e^{-tL}p(\mathbf{a},0)] \\ & + \quad \frac{\partial}{\partial \mathbf{a}} \cdot \mathbf{F}(t)\int_0^t dt' e^{-(t-t')L}\frac{\partial}{\partial \mathbf{a}} \cdot [\mathbf{F}(t')p(\mathbf{a},t')] \end{aligned} \tag{13.10}$$

Next, we average over noise (i.e, we take the *ensemble average*), and immediately the second term vainshes owing to the relation $\langle \mathbf{F}(t)\rangle = 0$.

$$\begin{aligned}\frac{\partial \langle p(\mathbf{a},t)\rangle}{\partial t} &= -\frac{\partial}{\partial \mathbf{a}}[\mathbf{v}(\mathbf{a})p(\mathbf{a},t')] \\ &+ \frac{\partial}{\partial \mathbf{a}}.\int_0^t dt' \langle \mathbf{F}(t)\mathbf{F}^\dagger(t')\rangle e^{-(t-t')L}\frac{\partial}{\partial \mathbf{a}}\langle p(\mathbf{a},t')\rangle \end{aligned} \tag{13.11}$$

Note that since $p(\mathbf{a},t')$ contains implicit noise factors that are dependent on times *prior* to t', we can consider $p(\mathbf{a},t')$ and $\mathbf{F}(t')$ to be independent of each other and the noise averaging over their product equals the product of their noise averages.

Now, we have

$$\begin{aligned}\langle \mathbf{F}(t)\mathbf{F}^\dagger(t')\rangle &= 2\mathbf{B}\delta(t-t') \\ \Rightarrow \langle \mathbf{F}(t)\mathbf{F}^\dagger(t')\rangle_{t>t'} &= \mathbf{B}\delta(t-t'),\end{aligned} \tag{13.12}$$

so that finally we have (after the delta function restores $t' \to t$ and hence removes the exponential term):

$$\boxed{\frac{\partial \langle p(\mathbf{a},t)\rangle}{\partial t} = -\frac{\partial}{\partial \mathbf{a}}\cdot[\mathbf{v}(\mathbf{a})\langle p(\mathbf{a},t)\rangle] + \frac{\partial}{\partial \mathbf{a}}\cdot\mathbf{B}\cdot\frac{\partial}{\partial \mathbf{a}}\langle p(\mathbf{a},t)\rangle.} \tag{13.13}$$

Note: What is $\langle p(a,t)\rangle$? What does noise averaging of a distribution mean? Actually, when a Brownian particle is moving, an experimentalist cannot resolve the different molecular collisions ($\sim 10^{-13} sec$), because his resolution time is several orders of magnitude higher that that of mean free path of a particle. Thus, what is sees is an average effect of several millions of collisions, and the probability distribution that he is going to detect is $\langle p(a,t)\rangle$.

Eh.(13.13) is our much-coveted Fokker-Planck equation.

In the case of the underdamped Langevin equation,

$$\begin{aligned}\frac{dx}{dt} &= \frac{p}{m}, \\ \frac{dp}{dt} &= -V'(x) - \gamma\frac{p}{m} + \xi(t),\end{aligned} \tag{13.14}$$

we have

$$\begin{aligned}\mathbf{a} &= \begin{pmatrix} x \\ p \end{pmatrix}, \\ \mathbf{v}(\mathbf{a}) &= \begin{pmatrix} p/m \\ -V'(x) - \gamma p/m \end{pmatrix}, \\ \mathbf{F}(t) &= \begin{pmatrix} 0 \\ \xi(t), \end{pmatrix}, \\ \mathbf{B} &= \begin{pmatrix} 0 & 0 \\ 0 & \gamma k_B T \end{pmatrix}.\end{aligned} \tag{13.15}$$

so that the Fokker-Planck equation becomes

$$\frac{\partial P}{\partial t} = -\frac{p}{m}\frac{\partial}{\partial x}(pP) - \frac{\partial}{\partial p}[(-V'(x) - \gamma p/m)P] + \gamma k_B T\frac{\partial^2 P}{\partial p^2}. \tag{13.16}$$

The Smoluchowski equation The Fokker-Planck equation corresponding to the overdamped Langevin equation,

$$\frac{dx}{dt} = \frac{1}{\gamma}[-V'(x) + \xi(t)], \tag{13.17}$$

is known as the Smoluchowski equation.

In this case, our vectors and matrices in eq.(13.1) become

$$\mathbf{a} = x, \quad \mathbf{v}(\mathbf{a}) = -\frac{1}{\gamma}V'(x), \quad \mathbf{F}(t) = \frac{1}{\gamma}\xi(t), \quad \mathbf{B} = k_B T/\gamma. \tag{13.18}$$

(since $\langle F(t)F(t')\rangle = \frac{1}{\gamma^2}\langle \xi(t)\xi(t')\rangle = \frac{1}{\gamma^2}2k_BT$)

Substituting these expressions in eq.(13.13), we get

$$\begin{aligned} \frac{\partial p}{\partial t} &= -\frac{\partial}{\partial x}[-\frac{1}{\gamma}V'(x).p] + \frac{\partial}{\partial x}.2B.\frac{\partial}{\partial x}\frac{\partial p}{\partial x} \\ &= \frac{1}{\gamma}\frac{\partial}{\partial x}[V'(x)p] + \frac{k_BT}{\gamma}\frac{\partial^2 p}{\partial x^2}. \end{aligned} \tag{13.19}$$

where $p = p(x,t)$ in general. The above equation is the Smoluchowski equation.

14 Proof of second law using FPE

14.1 Overdamped dynamics

The FPE corresponding to overdamped Langevin equation, with $\gamma\dot{x} = F(x,t) + \xi(t)$ is

$$\boxed{\frac{\partial P(x,t)}{\partial t} = -\frac{\partial j(x,t)}{\partial x}} \tag{14.1}$$

where

$$j(x,t) \equiv \frac{FP}{\gamma} - \frac{T}{\gamma}\frac{\partial P}{\partial x}$$

(see eqn. (13.19)) (14.2)

$$\langle s\rangle = -\int_{-\infty}^{+\infty} P(x,t)\ln P(x,t)dx. \tag{14.3}$$

$$\begin{aligned} \Rightarrow \langle \dot{s}\rangle &= -\int \frac{\partial P}{\partial t}(\ln P + 1)dx \\ &= +\int \frac{\partial j}{\partial x}(\ln P + 1)dx \\ &= (\ln P + 1)(j)_{-\infty}^{+\infty} - \int j.\frac{\partial \ln P}{\partial x}dx \end{aligned} \tag{14.4}$$

The first term being zero ($j(x,t)$ vanishes at the boundaries), we have

$$\langle \dot{s}\rangle = -\int j.\frac{\partial \ln P}{\partial x}dx$$

$$= -\int \left(\frac{\partial \ln P}{\partial x} - \frac{F}{T}\right).j.dx - \underbrace{\int \frac{F.j}{T}dx}_{\langle \dot{s}_m \rangle} \tag{14.5}$$

$$\begin{aligned}
\Rightarrow \langle \dot{s} + \dot{s}_m \rangle &\equiv \langle \dot{s}_{tot} \rangle \\
&= -\int \left(\frac{\partial \ln P}{\partial x} - \frac{F}{T}\right).\left(\frac{FP}{\gamma} - \frac{T}{\gamma}\frac{\partial P}{\partial x}\right) \, dx \\
&= \frac{\gamma}{T}\int \left(\frac{F}{\gamma} - \frac{T}{\gamma}\frac{\partial \ln P}{\partial x}\right)\left(\frac{F}{\gamma} - \frac{T}{\gamma}\frac{\partial \ln P}{\partial x}\right) P \, dx \\
&= \frac{\gamma}{T}\int \left(\frac{F}{\gamma} - \frac{T}{\gamma}\frac{\partial \ln P}{\partial x}\right)^2 P dx \\
&= \frac{\gamma}{T}\int \frac{j^2}{P}dx \quad \geq 0.
\end{aligned} \tag{14.6}$$

where the second line follows from the definition (14.2)
Hence, finally we have

$$\boxed{\langle \dot{s}_{tot} \rangle \geq 0.} \tag{14.7}$$

which is the mesoscopic version of the second law.

Expression for $\langle \dot{s}_m \rangle$:
We have

$$\begin{aligned}
dQ &= -(-\gamma\dot{x} + \xi(t))dx = F(x,t)dx \\
\Rightarrow \dot{Q} &= F(x,t)\dot{x} \\
\Rightarrow \langle \dot{Q} \rangle &= \langle F(x,t)\dot{x} \rangle = \int dx \; P(x,t)\dot{x}F(x,t) = \int dx \; j(x,t)F(x,t). \qquad \text{QED}
\end{aligned} \tag{14.8}$$

14.2 Underdamped dynamics

The Langevin equation is

$$m\frac{dv}{dt} = F(x) - \gamma v + \xi(t); \qquad \frac{dx}{dt} = v \tag{14.9}$$

where $\langle \xi(t) \rangle)$; $\xi(t)\xi(t') = 2\gamma T$. The corresponding FPE is

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}(vP) - \frac{1}{m}\frac{\partial}{\partial v}\left[(F - \gamma v)P - \frac{\gamma}{m}T\frac{\partial P}{\partial v}\right]. \tag{14.10}$$

We can rewrite the above eqn as [15]

$$\frac{\partial P}{\partial t} = -K - \frac{\partial M}{\partial v}, \tag{14.11}$$

where

$$K \equiv \frac{F}{m}\frac{\partial P}{\partial v} + v\frac{\partial P}{\partial x}; \qquad M = -\frac{\gamma v}{m}P - \frac{\gamma T}{m^2}\frac{\partial P}{\partial v}. \tag{14.12}$$

The nonequilibrium entropy of the *system* is given by

$$S \equiv -\int P(x,v)\ln P(x,v)dxdv. \tag{14.13}$$

$$\begin{aligned}
\therefore \frac{dS}{dt} &= -\int (1+\ln P)\frac{\partial P}{\partial t}dxdv \\
&= -\int \ln P\frac{\partial P}{\partial t}dxdv \\
&= \int K\ln P dxdv + \int \frac{\partial M}{\partial v}\ln P dxdv.
\end{aligned} \tag{14.14}$$

The first integral becomes

$$\begin{aligned}
& \frac{1}{m}\int F\frac{\partial P}{\partial v}dx\ dv + \int v\frac{\partial P}{\partial x}\ln P dx\ dv \\
=& \frac{1}{m}\int \left[\frac{\partial}{\partial v}(FP\ln P) - P\frac{\partial}{\partial v}(F\ln P)\right]dxdv + \int \left[\frac{\partial}{\partial v}(Fv\ln P) - P\frac{\partial}{\partial v}(v\ln P)\right]dxdv \\
=& -\frac{1}{m}\int P\frac{\partial}{\partial v}(F\ln P)dxdv - \int P\frac{\partial}{\partial v}(v\ln P)dxdv \\
=& -\frac{1}{m}\int PF\frac{\partial \ln P}{\partial v}dxdv - \int Pv\frac{\partial \ln P}{\partial x}dxdv \\
=& -\frac{1}{m}\int F(x)dx\int \frac{\partial P}{\partial v}dv - \int vdv\int \frac{\partial P}{\partial x}dx = 0,
\end{aligned} \tag{14.15}$$

assuming that $P(x,v)$ vanishes at the boundaries of x or v. Thus, from (14.14),

$$\boxed{\frac{dS}{dt} = \int \frac{\partial M}{\partial v}\ln P\ dxdv.} \tag{14.16}$$

Integrating by parts, we can write the above integral as

$$\frac{dS}{dt} = -\int M\ \frac{\partial \ln P}{\partial v}dxdv.$$

But (14.12) allows us to write

$$\frac{M}{P} = -\frac{\gamma v}{m} - \frac{\gamma T}{m^2}\frac{\partial \ln P}{\partial v} \quad \Rightarrow \quad \frac{\partial \ln P}{\partial v} = -\frac{m^2}{\gamma T}\left(\frac{\gamma v}{m} + \frac{M}{P}\right) = -\frac{mv}{T} - \frac{m^2 M}{\gamma T P}. \tag{14.17}$$

$$\boxed{\frac{dS}{dt} = \frac{m}{T}\int vM\ dxdv + \frac{m^2}{\gamma T}\int \frac{M^2}{P}\ dxdv.} \tag{14.18}$$

Just as in the underdamped case, the second term is identified as the entropy production rate . To see why the first term on the RHS is the negatice of rate of medium entropy change, we explicitly write[4]

$$\begin{aligned}
\langle \dot{Q}|x,v,t\rangle &= -\frac{\partial E(x,v,t)}{\partial x}\langle \dot{x}|x,v,t\rangle - \frac{\partial E(x,v,t)}{\partial v}\langle \dot{v}|x,v,t\rangle \\
&= Fv - v\left(F - \gamma v - \frac{\gamma T}{m}\frac{\partial \ln P}{\partial v}\right) \\
&= v\left(\gamma v + \frac{\gamma T}{m}\frac{\partial \ln P}{\partial v}\right) = -mvM \\
\Rightarrow \langle \dot{s}_m|x,v,t\rangle &= -\frac{mv}{T}M.
\end{aligned} \tag{14.19}$$

[4]Here we will use the relation $\langle \dot{x}|x,v,t\rangle = \frac{J_x}{P} = v$, while $\langle \dot{v}|x,v,t\rangle = \frac{J_v}{P} = \frac{1}{P}\left[(F-\gamma v)P\frac{\gamma}{m}T\frac{\partial P}{\partial v}\right] = \left(F - \gamma v - \frac{\gamma T}{m}\frac{\partial \ln P}{\partial v}\right)$.

Here, we have used the notation $\langle \cdots | x, v, t\rangle$ for averaging over trajectories that pass through the point (x, v) at time t. Finally, averaging over the full phase space, we obtain

$$-\langle \dot{s}_m \rangle = \frac{m}{T}\int vM\ dxdv. \qquad \text{QED} \tag{14.20}$$

$$\boxed{\frac{d}{dt}\langle s_{tot}\rangle = \frac{m^2}{\gamma T}\int \frac{J^2}{P}\ dxdv \geq 0.} \tag{14.21}$$

15 Solution of Fokker-Planck equation for a linear harmonic potential

15.1 Ornstein Uhlenbeck Process

The Langevin equation is:

$$\frac{dx}{dt} = -V'(x) + \xi(t). \tag{15.1}$$

Here, we have $V(x) = \frac{1}{2}Kx^2$ for the linear harmonic potential. Therefore, our Langevin equation boils down to

$$\frac{dx}{dt} = -Kx + \xi(t). \tag{15.2}$$

The corresponding FPE is given by

$$\boxed{\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x}[-KxP(x,t)] + D\frac{\partial^2 P(x,t)}{\partial x^2}.} \tag{15.3}$$

The Fourier Transform [13] $P(\tilde{k}, t)$ of $P(x,t)$ is given by

$$P(x,t) \equiv \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx}\tilde{P}(k,t)dk \tag{15.4}$$

Substituting (15.4) into (15.3), we have

$$\begin{aligned}
\int e^{ikx}\frac{\partial \tilde{P}}{\partial t}dk &= K\frac{\partial}{\partial x}\left[x\int e^{ikx}\tilde{P}dk\right] + D\frac{\partial^2}{\partial x^2}\int e^{ikx}\tilde{P}dk \\
&= K\left[\int e^{ikx}\tilde{P}dk + x\int ik\int e^{ikx}\tilde{P}dk\right] + D\frac{\partial^2}{\partial x^2}\int e^{ikx}\tilde{P}dk \\
&= K\int(1+ikx)e^{ikx}\tilde{P}dk - D\int k^2 e^{ikx}\tilde{P}dk \\
&= K\int \frac{\partial}{\partial k}\left(ke^{ikx}\right)\tilde{P}dk - D\int k^2 e^{ikx}\tilde{P}dk
\end{aligned}$$

The first term is

$$k\left[\int \frac{\partial}{\partial k}\left(ke^{ikx}\tilde{P}\right)dk - \int ke^{ikx}\frac{\partial \tilde{P}}{\partial k}dk\right] = -K\int ke^{ikx}\frac{\partial \tilde{P}}{\partial k}dk$$

since the first term vanishes on account of $\tilde{P}$ vanishing at the boundaries.
Finally we have

$$\int e^{ikx}\frac{\partial \tilde{P}}{\partial k}dk = -K\int k\frac{\partial \tilde{P}}{\partial k}e^{ikx}dk - D\int k^2\tilde{P}e^{ikx}dk \tag{15.5}$$

Since the above equation holds for arbitrary x, we have

$$\boxed{\frac{\partial \tilde{P}}{\partial t} = -Kk\frac{\partial \tilde{P}}{\partial k} - Dk^2\tilde{P}} \tag{15.6}$$

which is a linear equation.
The initial condition for $P(x,t)$ is

$$P(x,t'|x',t') = \delta(x-x'). \tag{15.7}$$

$$\begin{aligned}\text{Therefore, } \tilde{P}(k,t|x',t') &= \int e^{-ikx}\delta(x-x')dx \\ \Rightarrow \tilde{P}(k,t|x',t') &= e^{-ikx'}.\end{aligned} \tag{15.8}$$

Equation (15.6) can be solved using the method of characteristics which I am going to detail below. The answer is

$$\boxed{\tilde{P}(k,t|x',t') = \exp\left[-ikx'e^{-K(t-t')} - \frac{Dk^2}{2K}\left(1-e^{-2K(t-t')}\right)\right].} \tag{15.9}$$

Finally, taking the inverse Fourier Transform, we arrive at (see (15.4)):

$$P(x,t) = \frac{1}{2\pi}\int dk \exp\left[ik\left(x - x'e^{-K(t-t')}\right) - \frac{Dk^2}{2K}\left(1-e^{-2K(t-t')}\right)\right]$$

We can write the above equation in the form

$$\Rightarrow P(x,t) = \exp(-ak^2 + bk) \tag{15.10}$$

where

$$\begin{aligned} a &= \frac{D}{2K}\left(1-e^{-2K(t-t')}\right) \\ b &= i\left(x - x'e^{-K(t-t')}\right). \end{aligned} \tag{15.11}$$

Therefore,

$$\begin{aligned} P(x,t) &= \frac{1}{2\pi}\int dk\ \exp\left(-a(k^2 - \frac{b}{a}k\right) \\ &= \frac{1}{2\pi}\int dk\ \exp\left[-a\left(k-\frac{b}{2a}\right)^2 - \frac{b^2}{4a^2}\right] \\ &= \frac{1}{2\pi}e^{b^2/4a}\int dk\ \exp\left[-a\left(k-\frac{b}{2a}\right)^2\right] \end{aligned} \tag{15.12}$$

This being a simple Gaussian integral can be easily evaluated.

Let $y = \sqrt{a}\left(k - \frac{b}{2a}\right)$, so that $dy = \sqrt{a}dk$. Substituting these in the above integral, we get

$$\begin{aligned} P(x,t) &= \frac{1}{2\pi} e^{b^2/4a} \int e^{-y^2} \frac{dy}{\sqrt{a}} \\ &= \frac{1}{2\sqrt{a\pi}} e^{b^2/4a} \end{aligned} \tag{15.13}$$

Now substituting for a and b from eq.(15.11) into the above expression for $P(x,t)$, we finally get

$$\boxed{P(x,t|x',t') = \left(\sqrt{\frac{K}{2\pi D\left(1 - e^{-2K(t-t')}\right)}}\right) \exp\left[-\frac{K\left(x - e^{-K(x-x')}x'\right)^2}{D\left(1 - e^{-2K(t-t')}\right)}\right].} \tag{15.14}$$

15.2 The Method of Characteristics

Our differential eqn is (15.6)

$$\frac{\partial \tilde{P}}{\partial t} = -Kk\frac{\partial \tilde{P}}{\partial k} - Dk^2\tilde{P}$$

Or,

$$\frac{\partial \tilde{P}}{\partial t} + Kk\frac{\partial \tilde{P}}{\partial k} = -Dk^2\tilde{P}. \tag{15.15}$$

with the boundary condition

$$\tilde{P}(k,t|x',t') = e^{-ikx'}. \tag{15.16}$$

Now, following the standard formula in partial differentiation, we can always write

$$\frac{\partial \tilde{P}}{\partial t}dt + \frac{\partial \tilde{P}}{\partial k}dk = d\tilde{P}. \tag{15.17}$$

Now, comparing (15.15) and (15.17) [14], we get

$$\frac{dt}{1} = \frac{dk}{Kk} = \frac{d\tilde{P}}{-Dk^2\tilde{P}}. \tag{15.18}$$

$$\text{So } k = C_k e^{Kt} \Rightarrow C_k = ke^{-Kt} \tag{15.19}$$

Again, from (15.18), we have

$$\begin{aligned} \frac{d\tilde{P}}{\tilde{P}} &= -\frac{D}{K}kdk \\ \Rightarrow \tilde{P} &= C_{\tilde{P}} e^{-Dk^2/2K} \\ \Rightarrow C_{\tilde{P}} &= \tilde{P}e^{Dk^2/2K}. \end{aligned} \tag{15.20}$$

Let

$$C_{\tilde{P}}(k,t,P) = \phi(C_k(k,t,P)) \tag{15.21}$$

Using (15.21) and (15.20), we get

$$\tilde{P} = e^{-Dk^2/2K}\phi\left(ke^{-Kt}\right) \tag{15.22}$$

Now, from (15.16),

$$e^{-ikx'} = e^{-Dk^2/2K}\phi\left(ke^{-Kt'}\right) \tag{15.23}$$

Putting $t' = 0$, one has

$$\phi(k) = \exp\left(-ikx' + \frac{Dk^2}{2K}\right). \tag{15.24}$$

Thus, we now have from eq. (15.22)

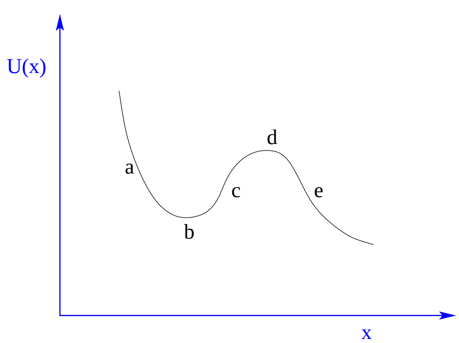
$$\begin{aligned} \tilde{P} &= e^{-Dk^2/2K}\exp\left[-i\left(ke^{-Kt}\right)x' + \frac{D}{2K}\left(k^2e^{-2Kt}\right)\right] \\ \tilde{P} &= \exp\left[-ikx'e^{-Kt} - \frac{Dk^2}{2K}\left(1 - e^{-2Kt}\right)\right] \end{aligned} \tag{15.25}$$

Since the origin of time can be shifted from $t = 0$ to $t = t'$, we get back (15.9):

$$\boxed{\tilde{P}(k,t|x',t') = \exp\left[-ikx'e^{-K(t-t')} - \frac{Dk^2}{2K}\left(1 - e^{-2K(t-t')}\right)\right].} \tag{15.26}$$

16 Expression for Kramer's rate

16.1 Overdamped case



We will keep the adjacent diagram as the reference figure [13]. We want to determine the rate with which, under the action of thermal noise, the particle will go from one well to the other well. It needs be mentioned that there is nothing quantum considered over here (for example, there is no concept of quantum tunneling), and the jumps are purely classical in nature. We will derive the rate expression in the overdamped regime, where the Langevin equation of motion reads

$$\gamma\dot{x} = -\frac{\partial U(x)}{\partial x} + \eta(t). \tag{16.1}$$

Here, $\eta(t)$ is the noise term (which is stochastic, being dependent only on t. The particle starts off its journey from the left well. We assume that the temperature T of the bath is very small compared to the barrier height $\Delta U \equiv U(d) - U(b)$, i.e., $k_BT \ll \Delta U$. In this case, the particle will stay for most of the time in the well, but due to rare large fluctuations will eventually cross the barrier. The corresponding Fokker-Planck equation is

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[\frac{1}{\gamma}U'(x)P(x,t) + DP'(x,t)\right], \tag{16.2}$$

where $2D = 2k_BT/\gamma$ is the strength of the Gaussian distributed delta-correlated (white) noise. Accordingly, the current is given by (by comparison with the equation of continuity):

$$J = -\left[\frac{1}{\gamma}U'(x)P(x,t) + DP'(x,t)\right]. \tag{16.3}$$

But, we can rewrite eq.(16.3) as

$$J = -De^{-U(x)/k_BT}\frac{\partial}{\partial x}\left(e^{U(x)/k_BT}P\right). \tag{16.4}$$

Thus, when $J = 0$, the term within parentheses must be a constant with respect to x, whence we have

$$\frac{\partial}{\partial x}\left(e^{\beta U(x)}P\right) = 0 \quad \Rightarrow \quad P(x) = e^{-\beta U(x)}P_0, \tag{16.5}$$

where P_0 has to be determined by imposing the normalization condition on $P(x)$. On the other, from the continuity equation,

$$\frac{\partial P}{\partial t} = -\frac{\partial J}{\partial x},$$

we find that J becomes independent of x if $\frac{\partial P}{\partial t} \to 0$.

Next, I write eq.(16.4)as

$$\begin{aligned}
\frac{\partial}{\partial x}\left(e^{\beta U(x)}P(x,t)\right) &= -\frac{J}{D}e^{\beta U(x)} \\
\Rightarrow \int_{x=b}^{x=e}\frac{\partial}{\partial x}\left(e^{\beta U(x)}P(x,t)\right)dx &= -\frac{J}{D}\int_{x=b}^{x=e}e^{\beta U(x)}dx \\
\text{(where } x = e \text{ is some } x \text{ beyond } x = b\text{)} & \\
\Rightarrow e^{\beta U(x)}P(x,t)\Big|_{x=b}^{x=e} &= -\frac{J}{D}\int_{x=b}^{x=e}e^{\beta U(x)}dx
\end{aligned}$$

$$\Rightarrow J = \frac{-D\left[e^{\beta U(e)}P(e,t) - e^{\beta U(b)}P(b,t)\right]}{\int_b^e e^{\beta U(x)}dx} \tag{16.6}$$

which, in the limit $P(e,t) \to 0$ (the point e being or the "abyss" being an absorbing boundary: a particle reaching this point is as good as disappears forever) gives

$$J = \frac{De^{\beta U(b)}P(b)}{\int_b^e e^{\beta U(x)}dx}. \tag{16.7}$$

This was all about finding the expression for current. But what about escape rate (r)? First, we define:

$$\begin{aligned}
r \equiv\ & \text{Conditional probability of escape per unit time,} \\
& \textit{given that} \text{ the particle is initially } \textit{inside} \text{ the well at } x = b.
\end{aligned} \tag{16.8}$$

Thus, if $p \equiv$ probability of the particle being in the well, then

$$J = pr \tag{16.9}$$

(Note the assumption that J is a constant).

To evaluate p, we first note that if the barrier is very high, then the following equilibrium distribution holds:

$$P(x) = P(b)e^{-\beta[U(x)-U(b)]}. \tag{16.10}$$

$$\Rightarrow p = \int_a^c P(x)dx = P(b)e^{\beta U(b)} \int_a^c dx\ e^{-\beta U(x)}.$$

thus we get

$$\begin{aligned} r &= \frac{J}{p} = \frac{De^{\beta U(b)}P(b)}{\int_b^e e^{\beta U(x)}dx} \cdot \frac{1}{P(b)e^{\beta U(b)} \int_a^c dx\ e^{-\beta U(x)}} \\ &= \frac{D}{\int_a^c dx\ e^{-\beta U(x)} \int_b^e dx'\ e^{\beta U(x')}}. \end{aligned} \tag{16.11}$$

In the denominator, the first integral receives the dominant contribution from $x = b$.

Therefore, one can expand the integrand about $x = b$ where $U(x)$ is smallest and $e^{-\beta U(x)}$ is largest. Similarly, one can expand the second integral in the denominator about $x = d$ where $U(x)$ is largest and $e^{\beta U(x)}$ is largest once again.

$$\begin{aligned} I_1 &= \int_a^c dx\ e^{-\beta U(x)} = \int_a^c dx\ e^{-\beta U(b)} \exp\left[-\frac{1}{2}\beta(x-b)^2 U''(b)\right] \\ &= \sqrt{\frac{2\pi}{\beta U''(b)}} \cdot e^{-\beta U(b)}; \end{aligned} \tag{16.12}$$

$$\begin{aligned} I_2 &= \int_b^e dx'\ e^{\beta U(x')} = \int_b^e dx'\ e^{\beta U(d)} \exp\left[\frac{1}{2}\beta(x'-d)^2 U''(d)\right] \\ &= \sqrt{\frac{2\pi}{\beta |U''(d)|}} \cdot e^{\beta U(d)} \end{aligned} \tag{16.13}$$

Therefore, from eq.(16.9), we have

$$r = \frac{J}{I_1 I_2} = \left(\frac{\gamma k_B T \sqrt{U''(b).|U''(d)|}}{2\pi k_B T}\right) e^{-\beta \Delta U}$$

$$\boxed{r = \frac{J}{I_1 I_2} = \left(\frac{\gamma \sqrt{U''(b).|U''(d)|}}{2\pi}\right) e^{-\beta \Delta U}.} \tag{16.14}$$

16.2 Underdamped case

I will follow the classic review of S. Chandrasekhar [16] in this subsection. We first af all shift the potential so that its left minimum appears on the origin.

The underdamped FPE is (see below)

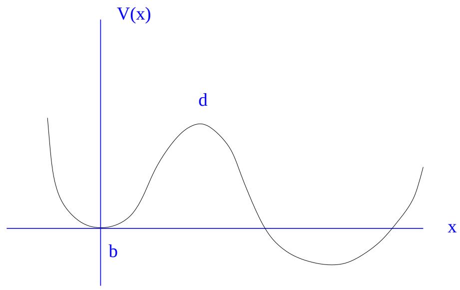
$$\frac{\partial P(x,v,t)}{\partial t} = -\frac{\partial}{\partial x}[vP] + \frac{1}{m}\frac{\partial}{\partial v}[\gamma v P + V'(x)P] + D\frac{\partial^2 P}{\partial v^2}. \tag{16.16}$$

It can be easily verified that the MB distribution *identically* satisfies the above FPE without the time-dependence (i.e., LHS=0):

$$P(x,v) = C\exp\left[-\beta\left\{\frac{1}{2}mv^2 + V(x)\right\}\right]. \tag{16.17}$$

Since we expect the distribution function near the minimum to be same as as (16.17) to a high degree of accuracy, we search for a solution of the form

$$P(x,v) = CF(x,v)\exp\left[-\beta\left\{\frac{1}{2}mv^2 + V(x)\right\}\right], \tag{16.18}$$



As before, we once again assume $\Delta V \gg k_B T$, so that the probability if crossing the barrier is small. The Langevin equation (one-dimensional) corresponding to the underdamped case is given by

$$m\frac{dv}{dt} = -\gamma v - V'(x) + \xi(t). \tag{16.15}$$

where we expect

$$\left.\begin{array}{ll} F(x,v) \approx 1, & x \to 0 \\ F(x,v) \approx 0, & x \gg x_d \end{array}\right\} \tag{16.19}$$

Near $x = x_d$, we have

$$V_d(x) = \Delta V + \frac{1}{2}V''(x_d)(x-x_d)^2 \equiv \Delta V - \frac{1}{2}m\omega_d^2 X^2, \tag{16.20}$$

where $\omega_d = -V''(x_d)/m$ and $X = x - x_d$. Then near the maximum the FPE becomes

$$\begin{aligned} 0 &= -v\frac{\partial P}{\partial X} + \frac{1}{m}\frac{\partial}{\partial v}[\gamma v P - m\omega_d^2 X P] + D\frac{\partial^2 P}{\partial v^2} \\ \Rightarrow \qquad v\frac{\partial P}{\partial X} + \omega_d^2 X\frac{\partial P}{\partial v} &= \frac{\gamma P}{m} + \frac{\gamma v}{m}\frac{\partial P}{\partial v} + D\frac{\partial^2 P}{\partial v^2}. \end{aligned} \tag{16.21}$$

Near $x = x_d$, we also have, using (16.18) and (16.20),

$$P_d(X,v) = Ce^{-\beta\Delta V}F(X,v)\exp\left[-\frac{\beta m}{2}\left(v^2 - \omega_d^2 X^2\right)\right]. \tag{16.22}$$

Substituting this in (16.21), we have

$$\begin{aligned} & v\frac{\partial}{\partial X}\left[F(X,v)e^{\beta m\omega_d^2 X^2/2}\right] + \left(\omega_d^2 X - \frac{\gamma v}{m}\right)\frac{\partial}{\partial v}\left[F(X,v)e^{-\beta m v^2/2}\right] \\ & \quad = \frac{\gamma}{m}F(X,v) + D\frac{\partial^2}{\partial v^2}\left[F(X,v)e^{-\beta m v^2/2}\right] \\ \Rightarrow \quad & v\frac{\partial F}{\partial X} + vF\beta m\omega_d^2 X + \omega_d^2 X\left[\frac{\partial F}{\partial v} - \beta m v F\right] - \frac{\gamma v}{m}\left[\frac{\partial F}{\partial v} - \beta m v F\right] \\ & \quad = \frac{\gamma}{m}F + \frac{\gamma}{\beta m^2}\left[\frac{\partial^2 F}{\partial v^2} - 2\beta m v\frac{\partial F}{\partial v} - \beta m F + \beta^2 m^2 v^2 F\right] \\ \Rightarrow \quad & \boxed{v\frac{\partial F}{\partial X} + \omega_d^2 X\frac{\partial F}{\partial v} = \frac{\gamma}{\beta m^2}\frac{\partial^2 F}{\partial v^2} - \frac{\gamma v}{m}\frac{\partial F}{\partial v}}. \end{aligned} \tag{16.23}$$

Here, the terms that cancel each other have been highlighted in the same colour. We find that although $F = const.$ satisfies the above equation identically, in our case the follwing boundary conditions must also be satisfied:

$$\left.\begin{array}{ll} F(X,v) \to 1, & \text{for} X \to -\infty \\ F(X,v) \to 0, & \text{for} X \to +\infty \end{array}\right\} \tag{16.24}$$

We now *assume* that following form for the solution:

$$F \equiv F(v - aX) \equiv F(\xi). \tag{16.25}$$

We then get the relations

$$\frac{\partial}{\partial X} = -a\frac{\partial}{\partial \xi}; \qquad \frac{\partial}{\partial v} = \frac{\partial}{\partial \xi}; \qquad \frac{\partial^2}{\partial v^2} = \frac{\partial^2}{\partial \xi^2}. \tag{16.26}$$

Then from (16.23) we have

$$\begin{aligned}
&\left[\frac{\gamma v}{m} - va + \omega_d^2 X\right]\frac{\partial F}{\partial \xi} = \frac{\gamma}{\beta m^2}\frac{\partial^2 F}{\partial \xi^2} \\
&\therefore \left[\left(\frac{\gamma}{m} - a\right)(\xi + aX) + \omega_d^2 X\right]\frac{\partial F}{\partial \xi} = \frac{\gamma}{\beta m^2}\frac{\partial^2 F}{\partial \xi^2} \\
&\Rightarrow \left[a\left\{\left(\frac{\gamma}{m} - a\right) + \omega_d^2\right\} X + \left(\frac{\gamma}{m} - a\right)\xi\right]\frac{\partial F}{\partial \xi} = \frac{\gamma}{\beta m^2}\frac{\partial^2 F}{\partial \xi^2}.
\end{aligned} \tag{16.27}$$

But, since $F = F(\xi)$, its double derivative cannot depend on X and ξ separately. This means that the coeffcient of X in the LHS must vanish:

$$a\left(\frac{\gamma}{m} - a\right) = -\omega_d^2. \tag{16.28}$$

Thus the FPE in terms of ξ becomes

$$\boxed{\left(\frac{\gamma}{m} - a\right)\xi\frac{\partial F}{\partial \xi} = \frac{\gamma}{\beta m^2}\frac{\partial^2 F}{\partial \xi^2}.} \tag{16.29}$$

Setting $y \equiv \frac{\partial F}{\partial \xi}$, the FPE becomes a first order DE:

$$\frac{1}{y}\frac{\partial y}{\partial \xi} = \frac{\beta m^2}{\gamma}\left(\frac{\gamma}{m} - a\right)\xi. \tag{16.30}$$

Its solution is

$$\begin{aligned}
&y(\xi) = y_0 \exp\left[\frac{\beta m^2}{2\gamma}\left(\frac{\gamma}{m} - a\right)\xi^2\right] \\
\Rightarrow\quad &\boxed{F(\xi) = F_0 \int_{-\infty}^{\xi} d\xi \exp\left[-\frac{\beta m^2}{2\gamma}\left(\frac{a-\gamma}{m}\right)\xi^2\right]},
\end{aligned} \tag{16.31}$$

where $F_0 = const$. From (16.28) we have

$$a^2 - a\gamma/m - \omega_d^2 = 0. \tag{16.32}$$

Therefore

$$a = \frac{\gamma}{2m} \pm \sqrt{\frac{\gamma^2}{4m^2} + \omega_d^2}\;. \tag{16.33}$$

We choose the positive root, which will lead us to the proper F that satisfies the required boundary conditions. Thus we have from (16.31),

$$\xi \to -\infty \quad \Rightarrow \quad F(\xi) \to 0.$$

On the other hand, if $\xi \to +\infty$, (recall that $\xi = v - aX = v - a[x - x_d]$)

$$F(\xi) = F_0 \int_{-\infty}^{\infty} d\xi \exp\left[-\left(a - \frac{\gamma}{m}\right)\frac{\beta m^2}{2\gamma}\xi^2\right]$$

$$= F_0\sqrt{\frac{2\pi\gamma}{\left(a-\frac{\gamma}{m}\right)\beta m^2}}\ . \tag{16.34}$$

Choosing

$$F_0 = \sqrt{\frac{\left(a-\frac{\gamma}{m}\right)\beta m^2}{2\pi\gamma}}, \tag{16.35}$$

we get $F(\xi) \to 1$ as $\xi \to \infty$. Thus,

$$\left.\begin{array}{lll} F \to 0 & \text{as} & \xi \to -\infty; \\ F \to 1 & \text{as} & \xi \to +\infty, \end{array}\right\} \tag{16.36}$$

which translate to

$$\left.\begin{array}{lll} F \to 0 & \text{as} & X \to +\infty; \\ F \to 1 & \text{as} & X \to -\infty. \end{array}\right\} \tag{16.37}$$

That's it! We then finally have,

$$\boxed{F(\xi) = \sqrt{\frac{\left(a-\frac{\gamma}{m}\right)\beta m^2}{2\pi\gamma}}\int_{-\infty}^{\xi} d\xi \exp\left[-\frac{\beta m^2}{2\gamma}\left(\frac{a-\gamma}{m}\right)\xi^2\right].} \tag{16.38}$$

Thus the *total* pdf becomes

$$\begin{aligned} P(x,v) &= CF(x,v)\exp\left[-\beta\left\{\frac{1}{2}mv^2 + V(x)\right\}\right] \\ \Rightarrow\quad P_d(x,v) &= C\sqrt{\frac{\left(a-\frac{\gamma}{m}\right)\beta m^2}{2\pi\gamma}}\ e^{-\beta\Delta V}\exp\left[-\beta\left\{\frac{1}{2}mv^2 - \frac{1}{2}m\omega_d^2(x-x_d)^2\right\}\right] \\ &\qquad\qquad \times\int_{-\infty}^{\xi}\exp\left[-\frac{\beta m^2}{2\gamma}\left(\frac{a-\gamma}{m}\right)\xi^2\right]. \end{aligned} \tag{16.39}$$

Near $x = x_b$,, we have

$$P_b(x,v) = C\exp\left[-\beta\left\{\frac{1}{2}mv^2 + \frac{1}{2}m\omega_b^2x^2\right\}\right]. \tag{16.40}$$

No. of particles near $x = x_b$ is given by (considering very small contribution from outside the region around $x = x_b$)

$$\begin{aligned} n_b &= C\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dv\exp\left[-\beta\left\{\frac{1}{2}mv^2 + \frac{1}{2}m\omega_b^2x^2\right\}\right] \\ &= C.\sqrt{\frac{2\pi}{\beta m}}\sqrt{\frac{2\pi}{\beta m\omega_b^2}} = C\frac{2\pi}{\beta\omega_b m}. \end{aligned} \tag{16.41}$$

The *diffusion current* across x_d is given by

$$J = \int_{-\infty}^{\infty}P_d(0,v)\ v\ dv. \tag{16.42}$$

Using (16.39), we have

$$\boxed{J = Ce^{-\beta\Delta V}\sqrt{\frac{\alpha}{\pi}}\int_{-\infty}^{\infty}e^{-\beta mv^2/2}v\ dv\int_{-\infty}^{v}e^{-\alpha\xi^2},} \tag{16.43}$$

where

$$\alpha \equiv \left(a-\frac{\gamma}{m}\right)\frac{\beta m^2}{2\gamma}. \tag{16.44}$$

We notice that in (16.43), the upper limit of the integral over ξ is *not* $+\infty$. This means that it is not a simple Gaussian integral. We employ the following trick of partial integration. We note that

$$\int_{-\infty}^{\infty} dv e^{-\beta m v^2/2} e^{-\alpha v^2}$$

$$= \left[e^{-\beta m v^2/2} \int_{-\infty}^{v} d\xi \; e^{-\alpha \xi^2} \right]_{v=-\infty}^{v=+\infty} \xrightarrow{} 0 \quad - \int_{-\infty}^{\infty} gv(-\beta m v) e^{-\beta m v^2/2} \int_{-\infty}^{v} d\xi \; e^{-\alpha \xi^2}$$

$$= \beta m \int_{-\infty}^{\infty} e^{-\beta m v^2/2} \int_{-\infty}^{v} d\xi \; e^{-\alpha \xi^2}.$$

$$\therefore \int_{-\infty}^{\infty} e^{-\beta m v^2/2} v \; dv \int_{-\infty}^{v} d\xi \; e^{-\alpha \xi^2} = \frac{1}{\beta m} \int_{-\infty}^{\infty} dv \; e^{-(\beta m/2 + \alpha) v^2} = \frac{1}{\beta m} \sqrt{\frac{\pi}{(\beta m/2) + \alpha}}. \tag{16.45}$$

But, from the definition (16.44), we get

$$\frac{\beta m}{2} + \alpha = \frac{\beta m}{2} + \left(a - \frac{\gamma}{m} \right) \frac{\beta m^2}{2\gamma} = \frac{a \beta m^2}{2\gamma}. \tag{16.46}$$

Thus from(16.45),

$$\boxed{\int_{-\infty}^{\infty} e^{-\beta m v^2/2} v \; dv \int_{-\infty}^{v} d\xi \; e^{-\alpha \xi^2} = \frac{1}{\beta m^2} \sqrt{\frac{2\pi\gamma}{a\beta}}.} \tag{16.47}$$

Using this in (16.43), we find

$$J = \frac{C e^{-\beta \Delta V}}{\beta m^2} \sqrt{\frac{\alpha}{\pi}} \sqrt{\frac{2\pi\gamma}{a\beta}} = \frac{C}{\beta m^2} \sqrt{\left(a - \frac{\gamma}{m} \right) \frac{\beta m^2}{2\pi\gamma} \frac{2\pi\gamma}{a\beta}}$$

$$= \frac{C e^{-\beta \Delta V}}{\beta m} \sqrt{\frac{a - \gamma/m}{a}} = \frac{C}{\beta m} \sqrt{\frac{\sqrt{\frac{\gamma^2}{4m^2} + \omega_d^2} - \frac{\gamma}{2m}}{\sqrt{\frac{\gamma^2}{4m^2} + \omega_d^2} + \frac{\gamma}{2m}}}$$

$$= \frac{C e^{-\beta \Delta V}}{\beta m} \sqrt{\frac{\left(\sqrt{\frac{\gamma^2}{4m^2} + \omega_d^2} - \frac{\gamma}{2m} \right)^2}{\omega_d^2}}$$

$$\Rightarrow \boxed{J = \frac{C}{\beta m \omega_d} \left(\sqrt{\frac{\gamma^2}{4m^2} + \omega_d^2} - \frac{\gamma}{2m} \right) e^{-\beta \Delta V}.} \tag{16.48}$$

But $r = J/n_b$ where $n_b = 2\pi C/(\beta \omega_b m)$ (see (16.41)). Thus,

$$\boxed{r = \frac{\omega_b}{2\pi\omega_d} \left(\sqrt{\frac{\gamma^2}{4m^2} + \omega_d^2} - \frac{\gamma}{2m} \right) e^{-\beta \Delta V}.} \tag{16.49}$$

17 The Chapman Kolmogorov Equation (CKE)

17.1 Important definitions

If $X(t)$ is a random function, and $x(t)$ be the values of the function at t. then [14]

$$P_1(x, t) \equiv \langle \delta(x - X(t)) \rangle. \tag{17.1}$$

$$\langle X(t)\rangle \equiv \int x P_1(x,t)dx = \lim_{N\to\infty} \frac{1}{N}\sum_{i=1}^{N} x_i(t) \tag{17.2}$$

where N is the number of realizations. The joint probability is defined by

$$P_2(x_2,t_2;x_1,t_1) \equiv \langle \delta(x_2 - X(t_2))\delta(x_1 - X(t_1))\rangle$$

(where the subscript of P gives the number of states whose joint probability is to be calculated) or, in a more compact notation,

$$P_2(2,1) = \langle \delta(x_2 - X(t_2))\delta(x_1, -X(t_1))\rangle \tag{17.3}$$

where we have replaced (x_i,t_i) by i.
The Bayes' Theorem gives

$$P_2(2,1) = P_{1|1}(2|1)P_1(1). \tag{17.4}$$

where the subscript $(1|1)$ of P means that it is the probability for going from 1 state to 1 state. We also have

$$\boxed{P_1(2) = \int P_2(2,1)dx_1 = \int P_{1|1}(2|1)P_1(1)} \tag{17.5}$$

A Markov process is defined as the one in which

$$\boxed{P_{1|n-1}(n|n-1,n-2,\cdots,1) = P_{1|1}(n|n-1)} \tag{17.6}$$

17.2 Derivation of the CKE

$$\begin{aligned} P_2(3,1) &= P_{1|1}(3|1)P_1(1) = \int dx_2 P_3(3,2,1) \\ &= \int dx_2 P_{1|2}(3|2,1)P_2(2,1) \\ &= \int dx_2 P_{1|2}(3|2,1)P_{1|1}(2|1)P_1(1) \end{aligned} \tag{17.7}$$

Dividing both sides by $P_1(1)$, we get

$$P_{1|1}(3|1) = \int dx_2 P_{1|2}(3|2,1)P_{1|1}(2|1) \tag{17.8}$$

$\therefore$ For a Markov process,

$$\boxed{P_{1|1}(3|1) = \int dx_2 P_{1|1}(3|2)P_{1|1}(2|1)} \tag{17.9}$$

which is the **Chapman-Kolmogorov Equation**.

18 The Master Equation

Assumptions [14]:

1. The random process is Markovian.
2. The process depends only on the time *difference* (say, τ)instead of on the absolute times.

On account of assumption 2, we can define

$$P_{1|1}(x_2, t_2|x_1, t_1) \equiv T_\tau(x_2|x_1), \tag{18.1}$$

with

$$\lim_{\tau\to 0} T_\tau(x_2|x_1) = \delta(x_2 - x_1).$$

Next, we expand $P_{1|1}(2|1)$ in terms of τ, we have

$$P_{1|1}(2|1) = \underbrace{[1 - a(x_1)\tau]}_{\text{strength of }\delta}.\delta(x_2 - x_1) + \tau.W(x_2|x_1) + O(\tau^2) \tag{18.2}$$

where the zeroth order term ensures that the strength of the δ-function is high *only* if τ is small.

The coefficient $W(x_2|x_1)$ is the *transition probability* per unit time for going from x_1 to x_2. The coefficient of $\delta(x_2 - x_1)$ is not unity, so that the normalization condition is satisfied. Otherwise integration w.r.t. x_2 will not give 1.

We have

$$\int P_{1|1}(2|1)dx_2 = 1. \tag{18.3}$$

$\therefore$ From equation 18.2, on integrating over x_2, we get

$$1 = 1 - a(x_1)\tau + \tau \int W(x_2|x_1)dx_2$$

which finally gives

$$\boxed{a(x_1) = \int W(x_2|x_1)dx_2.} \tag{18.4}$$

The strength of the δ-function in eq.18.2, i.e., $[1 - a(x_1)\tau]$ gives the probability that *no* transition has taken place from x_1 to x_2.

$$\begin{aligned}
P_{1|1}(2|0) &= \int dx_1 P_{1|1}(2|1)P_{1|1}(1|0) \\
&= \int dx_1 \left\{[1 - a(x_1)\tau].\delta(x_2 - x_1) + \tau.W(x_2|x_1)\right\} P_{1|1}(1|0) \\
&= \int dx_1 \left\{[1 - a(x_1)\tau].\delta(x_2 - x_1)P_{1|1}(1|0) + \tau.W(x_2|x_1)P_{1|1}(1|0)\right\} \\
&= [1 - a(x_2)\tau]P_{1|1}(x_2, t_1|0) + \tau \int dx_1 W(x_2|x_1)P_{1|1}(1|0) \qquad (18.5)
\end{aligned}$$

Now, putting $t_2 = t_1 + \tau$, one gets

$$P_{1|1}(x_2, t_1 + \tau|0) = P_{1|1}(x_2, t_1|0) + \tau \left[-a(x_2)P_{1|1}(x_2, t_1|0) + \int dx_1 W(x_2|x_1)P_{1|1}(1|0)\right]$$

$$\Rightarrow \frac{P_{1|1}(x_2, t_1+\tau|0) - P_{1|1}(x_2, t_1|0)}{\tau} = -a(x_2)P_{1|1}(x_2, t_1|0) + \int dx_1 W(x_2|x_1)P_{1|1}(1|0)$$

$$\Rightarrow \frac{\partial}{\partial t}P_{1|1}(x_2, t|0) = -\int dx_1 W(x_1|x_2)P_{1|1}(x_2, t_1|0) + \int dx_1 W(x_2|x_1)P_{1|1}(x_1, t_1|0)$$

Multiplying by $P_1(x_0, t_0)$ and integrating over x_0 on both sides, we get

$$\frac{\partial}{\partial t}P_1(x_2, t) = -\int dx_1 W(x_1|x_2)P_1(x_2, t_1) + \int dx_1 W(x_2|x_1)P_1(x_1, t_1).$$

Writing $x_1 \to x', x_2 \to x$ in above eqn, we have (writing second term first)

$$\boxed{\frac{\partial P(x,t)}{\partial t} = \int dx'[W(x|x')P(x',t) - W(x'|x)P(x,t)].} \tag{18.6}$$

which is commonly known as the **Master Equation**.

19 The Ornstein Uhlenbeck Process to solve general Langevin Equation

19.1 Searching for solution

The general Langevin equation is given by [13]

$$\dot{x}_i(t) + C_{ij}x_j(t) = \Gamma_i(t) \tag{19.1}$$

where Einstein's summation convention has been followed. C_{ij} is a square matrix, while $x_i(t)$ and $\Gamma_i(t)$ are column vectors in general.

The properties of the noise vector $\Gamma_i(t)$ are :

$$\begin{aligned} \langle \Gamma_i(t) \rangle &= 0; \\ \langle \Gamma_i(t)\Gamma_j(t') \rangle &= B_{ij}\delta(t-t'). \end{aligned} \tag{19.2}$$

Let $x_i(0) = x_{0i}$ be the initial conditions.

The homogeneous equation corresponding to (19.1) is given by

$$\dot{x}_i(t) + C_{ij}x_j(t) = 0. \tag{19.3}$$

If the Green's function corresponding to (19.3) is $G_{ij}(t)$, and if the corresponding solution be $x_i^h(t) = G_{ij}x_{0j}$, then the Green's function must follow the equation

$$\dot{G}_{ij}(t) + C_{ik}G_{kj}(t) = 0, \tag{19.4}$$

or, in compact notation,

$$\dot{\mathbf{G}}(t) + \mathbf{C}.\mathbf{G}(t) = 0.$$

[Verify that $\dot{x}_i^h(t) + C_{ij}x_j^h(t) = \frac{\partial}{\partial t}(G_{ik}x_{0k}) + C_{ij}G_{jk}x_{0k} = 0$ which follows from 19.4].

Therefore, the Green's function will be given by

$$\boxed{\mathbf{G}(t) = e^{-\mathbf{C}t}.} \tag{19.5}$$

Now, let the solution for the inhomogeneous equation (19.1) be given by

$$x_i^{inh}(t) = G_{ij}(t)f_j(t) \qquad \text{[ansatz]} \tag{19.6}$$

(Note: the Green's function used is still for the *homogeneous* equation only).
Differentiating both sides by t, we get

$$\dot{x}_i^{inh} = \dot{G}_{ik}f_k + G_{ik}\dot{f}_k$$

Substituting in 19.1, we have

$$\begin{aligned} \dot{G}_{ik}f_k + G_{ik}\dot{f}_k + C_{il}G_{lk}f_k &= \Gamma_i \\ \Rightarrow -C_{ij}G_{jk}f_k + G_{ik}\dot{f}_k + C_{il}G_{lk}f_k &= \Gamma_i \quad \text{(using 19.4)} \end{aligned}$$

$$\Rightarrow \boxed{G_{ik}\dot{f}_k = \Gamma_i} \tag{19.7}$$

Now, from 19.5 we have $\mathbf{G}^{-1} = e^{+\mathbf{C}t} = \mathbf{G}(-t)$

$$\begin{aligned} \mathbf{G}(t)\mathbf{G^{-1}}(t') &= \mathbf{G}(t)\mathbf{G}(-t') = \mathbf{G}(t-t'). \\ \therefore \mathbf{G}(t-t')\mathbf{\Gamma}(t') &= \mathbf{G}(t)\mathbf{G^{-1}}(t')\mathbf{\Gamma}(t') \\ &= \mathbf{G}(t)\dot{f}(t') \quad \text{(using 19.7).} \end{aligned} \tag{19.8}$$

$$\begin{aligned} \therefore \int_0^t G_{ij}(t-t')\Gamma_j(t')dt' &= \int_0^t G_{ik}(t)\dot{f}_k(t')dt' \\ &= \int_0^t \frac{\partial}{\partial t'}\left[G_{ik}(t)f_k(t')\right]dt' \\ &= G_{ik}(t)f_k(t)\big|_0^t \\ &= x_i^{inh}(t). \end{aligned} \tag{19.9}$$

Thus we have

$$\begin{aligned} x_i^{inh}(t) &= \int_0^t G_{ij}(t-t')\Gamma_j(t')dt' \\ &= -\int_t^0 G_{ij}(t')\Gamma_j(t-t')dt' \qquad \text{(changing } t' \to t-t'\text{)} \\ &= \int_0^t G_{ij}(t')\Gamma_j(t-t')dt'. \end{aligned} \tag{19.10}$$

Finally, one gets

$$\begin{aligned} x_i(t) &= x_i^h(t) + x_i^{inh}(t) \\ &= G_{ij}(t)x_{0j}(t) + \int_0^t G_{ij}(t')\Gamma_j(t-t')dt'. \end{aligned} \tag{19.11}$$

19.2 Calculation of the moments

From 19.11, we get

$$M_i(t) = \langle x_i(t) \rangle = G_{ij}(t) x_{0j}(t). \tag{19.12}$$

($\because \langle \Gamma_j(t-t') \rangle = 0$).

The second moment will be given by

$$\sigma_{ij} = \langle [x_i(t) - \langle x_i(t) \rangle][x_j(t) - \langle x_j(t) \rangle] \rangle. \tag{19.13}$$

But,

$$(x_i(t) - \langle x_i(t) \rangle) = \int_0^t G_{ij}(t') \Gamma_j(t-t') dt' \quad \text{(using 19.11)}$$

$$\begin{aligned}
\sigma_{ik}(t) &= \left\langle \int_0^t \int_0^t dt' dt'' G_{ij}(t') \Gamma_j(t-t') G_{kl}(t') \Gamma_l(t-t') \right\rangle \\
&= \int_0^t \int_0^t dt' dt'' G_{ij}(t') G_{kl}(t'') B_{jl} \delta(t'-t'') \quad \text{(using 19.2)} \\
&= \int_0^t dt' G_{ij}(t') G_{kl}(t') B_{jl}. \qquad (19.14)
\end{aligned}$$

$$\therefore \boxed{\dot{\sigma}_{ik} = G_{ij}(t) G_{kl}(t) B_{jl}}\,, \tag{19.15}$$

using the well-known identity $\frac{\partial}{\partial t} \int_0^t f(x) dx = f(t)$.

$$\begin{aligned}
\therefore \ddot{\sigma}_{ik} &= \dot{G}_{ij} G_{kl} B_{jl} + G_{ij} \dot{G}_{kl} B_{jl} \\
&= -C_{im} G_{mj} G_{kl} B_{jl} - G_{ij} C_{km} G_{ml} B_{jl} \qquad (19.16)
\end{aligned}$$

(using 19.4)

$$\text{thus,} \quad \boxed{\ddot{\sigma}_{ik} = -C_{im} \dot{\sigma}_{mk} - C_{km} \dot{\sigma}_{mi}.} \tag{19.17}$$

Integrating 19.17, and using the initial conditions $\dot{\sigma}_{ij} = 0$ and $\sigma_{ij} = 0$, we arrive at

$$\boxed{\dot{\sigma}_{ik} = -C_{im} \sigma_{mk} - C_{km} \sigma_{mi} + B_{ik}.} \tag{19.18}$$

But, we know, $\mathbf{G} = e^{-\mathbf{C}t}$, so that if real part of $\mathbf{C}$ is positive, then $\mathbf{G} \to 0$ as $t \to \infty$. Therefore, 19.14 gives

$$\boxed{\sigma_{ij}(\infty) = \int_0^\infty dt G_{ij}(t) G_{kl}(t) B_{lj}} \tag{19.19}$$

Now, for small t,

$$\mathbf{G} = e^{-\mathbf{C}t} = 1 - \mathbf{C}t + \frac{1}{2} \mathbf{C}^2 t^2 - \cdots$$

From 19.12, $M_i(t) = G_{ij} x_{0j}$, i.e.,

$$M_i(t) = \left[\delta_{ij} - C_{ij} t + \frac{1}{2} C_{ik} C_{kj} t^2 - \cdots \right] x_{0j} \tag{19.20}$$

On the other hand,

$$\begin{aligned}
\sigma_{ij} &= \int_0^t dt' \left[\delta_{ik} - C_{ik}t' + \frac{1}{2}C_{im}C_{mk}t'^2 - \cdots\right]\left[\delta_{kl} - C_{kl}t' + \frac{1}{2}C_{kn}C_{nl}t'^2 - \cdots\right] B_{lj} \\
&= \int_0^t dt' \left[\delta_{ik}\delta_{kl} - (C_{ik}\delta_{kl} + \delta_{ik}C_{kl}) + \cdots\right] B_{lj} \\
&= \int_0^t dt' [B_{ij} - (C_{ik}B_{kj} + C_{il}B_{lj})t' + \cdots] \\
&= B_{ij}t - (C_{ik}B_{kj} + C_{il}B_{lj})t^2 + \cdots \qquad (19.21)
\end{aligned}$$

Equations 19.12 and 19.21, in the limit $t \to 0$, become

$$\begin{aligned}
M_i(t) &\approx x_{0i} - C_{ij}x_{0j}t, \\
\sigma_{ij}(t) &\approx B_{ij}t, \qquad (19.22)
\end{aligned}$$

which are the first and second moments of the solution of the Langevin equation

$$\dot{x}_i(t) + C_{ij}x_j(t) = \Gamma_i(t)$$

with the initial conditions $x_i(0) = x_{0i}$ and noise strength B_{ij}.

20 The Novikov Theorem

It states that [14] if a multivariate Gaussian distribution has zero mean, i.e.,

$$P(\xi) = \sqrt{\frac{\det A}{(2\pi)^n}} \exp\left[-\frac{1}{2}\xi.\mathbf{A}.\xi\right] \qquad (20.1)$$

where $\xi = (\xi_1, \xi_2, \cdots, \xi_n)$ and $\mathbf{A}$ is a square matrix, then the average $\langle \xi_i f(\xi)\rangle$ is given by the relation

$$\boxed{\langle \xi \rangle = \sum_m \langle \xi_i \xi_m \rangle \left\langle \frac{\partial f(\xi)}{\partial m} \right\rangle.} \qquad (20.2)$$

Proof:

Let

$$E(\xi) = \frac{1}{2}\sum_{i,j} \xi_i A_{ij} \xi_j \equiv \frac{1}{2}\xi_i A_{ij}\xi_j$$

following Einstein's summation convention (repeated indices are summed over). Note that $E(\xi)$ is a *scalar*, since the indices have been summed over.

$$\begin{aligned}
\frac{\partial E(\xi)}{\partial \xi_m} &= \frac{1}{2}\frac{\partial}{\partial \xi_m}(\xi_i A_{ij}\xi_j) \\
&= \frac{1}{2}(\delta_{im}A_{ij}\xi_j + \xi_i A_{ij}\delta_{jm}) \\
&= \frac{1}{2}(A_{mj}\xi_j + \xi_i A_{im})
\end{aligned}$$

$$= \quad A_{mj}\xi_j, \tag{20.3}$$

provided the matrix *element* A_{ij} is symmetric.
$\therefore$ It follows that

$$\boxed{\xi_i = (A^{-1})_{im}\frac{\partial E(\xi)}{\partial \xi_m}.} \tag{20.4}$$

Thus we get

$$\begin{aligned}
\langle \xi_i f(\xi)\rangle &\equiv C\int d\xi\ e^{-E(\xi)}\xi_i f(\xi) \\
&= C(A^{-1})_{im}\int d\xi \frac{\partial E(\xi)}{\partial \xi_m} e^{-E(\xi)} f(\xi) \\
&= C(A^{-1})_{im}\int d\xi f(\xi)\left(-\frac{\partial}{\partial \xi_m}\left[e^{-E(\xi)}\right]\right) \\
&= C(A^{-1})_{im}\left[f(\xi)\left(-e^{-E(\xi)}\right)\Big|_{-\infty}^{+\infty} + \int \frac{\partial f(\xi)}{\partial \xi_m} e^{E(\xi)}\right] \\
&= C(A^{-1})_{im}\int \frac{\partial f(\xi)}{\partial \xi_m} e^{E(\xi)} \\
&= (A^{-1})_{im}\left\langle \frac{\partial f(\xi)}{\partial \xi_m}\right\rangle .
\end{aligned} \tag{20.5}$$

Now, putting $F(\xi) = \xi_j$ in the above equation, one gets

$$\boxed{\langle \xi_i\xi_j\rangle = (A^{-1})_{im}\delta_{jm} = (A^{-1})_{ij}} \tag{20.6}$$

Thus, finally we arrive at the relation 20.2:

$$\boxed{\langle \xi_i f(\xi)\rangle = \sum_m \langle \xi_i\xi_m\rangle \left\langle \frac{\partial f(\xi)}{\partial \xi_m}\right\rangle .}$$

Q.E.D.

Example:

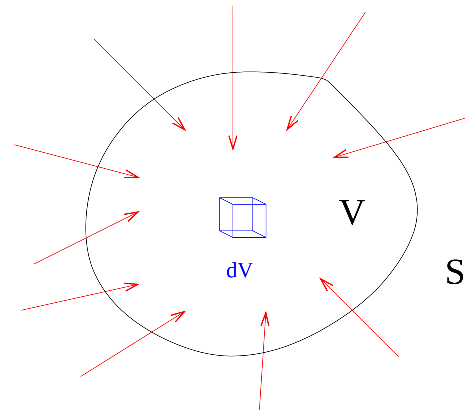
Let $f(\xi) = \xi_j\xi_k\xi_l$.

$$\begin{aligned}
\therefore \langle \xi_i f(\xi)\rangle &= \langle \xi_i\xi_j\xi_k\xi_l\rangle \\
&= \sum_m \langle \xi_i\xi_m\rangle \left\langle \frac{\partial}{\partial \xi_m}(\xi_j\xi_k\xi_l)\right\rangle \\
&= \sum_m \langle \xi_i\xi_m\rangle \langle \delta_{jm}\xi_k\xi_l + \xi_j\delta_{km}\xi_l + \xi_j\xi_k\delta_{lm}\rangle
\end{aligned}$$

$$\boxed{\Rightarrow \langle \xi_i\xi_j\xi_k\xi_l\rangle = \langle \xi_i\xi_j\rangle\langle \xi_k\xi_l\rangle + \langle \xi_i\xi_k\rangle\langle \xi_j\xi_l\rangle + \langle \xi_i\xi_l\rangle\langle \xi_j\xi_k\rangle .} \tag{20.7}$$

which is commonly known as the **Wick formula**.

A The continuity equation



Consider any *conserved* quantity (energy, mass, etc.). Let its *volume* density be ρ. Now consider any *finite* volume as depicted in the figure. Question is: in what way can the total amount of substance, $\int \rho dV$, increase in V? Since the entity is conserved, this increase must be accompanied by the loss of the same amount of substance from *outside* V. Thus, there must have been an influx of stuff through the surface S of the chosen volume V. Keeping in mind that in the case of an *in*flux, the surface area vector is anti-parallel to the flow, we equate

$$\frac{d}{dt}\int_V \rho dV = -\int_S \mathbf{j.dS} \tag{A.1}$$

Using the divergence theorem, one can convert the surface integral into a volume integral:

$$\int_V \frac{\partial \rho}{\partial t}\, dV = -\int_V \boldsymbol{\nabla}\cdot j\; dV. \tag{A.2}$$

Since this will hold for *any* volume V, we can equate

$$\boxed{\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla}\cdot j = 0}. \tag{A.3}$$

This, then, is the continuity equation for a *conserved* quantity. What will be the corresponding equation for a *non-conserved* quantity? Till now, we have been concerned with the volume described in the coordinate frame attached to the laboratory. We have assumed that in a volume element *attached to the fluid* (in the sense of the present context), there is no change in the density. However, if the substance is non-conserved, there is always a probability that the substance gets *created* within any such "material volume" element, and its rate will simply be $(d\rho/dt)dV$, because for a coordinate frame that is attached to the fluid, the corresponding partial derivative becomes a total derivative in the lab frame, the coordinates remaining constant automatically. Thus, instead of (A.2), we will have

$$\int_V \frac{\partial \rho}{\partial t}\, dV = -\int_V \boldsymbol{\nabla}\cdot j\; dV + \int_V \frac{d\rho}{dt}\, dV, \tag{A.4}$$

which in turn gives

$$\boxed{\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla}\cdot j = \frac{d\rho}{dt}}. \tag{A.5}$$

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