Lecture notes on nonequilibrium statistical physics (INCOMPLETE and with possible errors)

Abhishek Dhar, ICTS (TIFR)

[1] Simple random walk in one and higher dimensions

[2] Brownian motion, Langevin equation and Fokker-Planck equations

Einstein's simple proof of relation between fluctuations and dissipation in the motion of a Brownian particle.

Langevin and Fokker-Planck equations.

Simulations

[3] General discussion of Markov processes

Master equations, notion of steady states, detailed balance principle. Examples of disctrete and continuous time Markov processes.

[4]Many particle systems

[5]First passage problem

[6]Linear response theory

[7]Fluctuation theorems and large deviations

[8]Microscopic derivation of the Markov description: Langevin equations

[9]Microscopic derivation of the Markov description: Master equations

Appendix Basic notions of probability theory, examples of probability distributions

1 Random walks

History of the random walk problem: Karl Pearson introduced the term "Random Walk". He was interested in describing the spatial/temporal evolutions of mosquito populations invading cleared jungle regions. He found it too complex to model deterministically, so he conceptualized a simple random model. Pearson posed his problem in Nature (27 July 1905) as follows:

A man starts from a point 0 and walks ℓ yards in a straight line; he then turns through any angle whatever and walks another ℓ yards in a second straight line. He repeats this process n times. I require the probability that after n of these stretches he is at a distance between r and $r + dr$ from his starting point.

The question was answered the following week by Lord Rayleigh, who pointed out the connection between this problem and an earlier paper of his published in 1880* concerned with sound vibrations. Rayleigh pointed out that, for large values of n, the answer is given by:

$$P(r, n)dr = \frac{2}{n\ell^2}\ e^{-r^2/n\ell^2}\ r\ dr\ .$$

1.1 Random walk in one-dimension

Consider a walker on a one dimensional lattice. At every time step the walker tosses an unbiased coin and moves to the left if it is a head and to the right if it is a tail. Thus for every step there are 2 possibilities and the walker chooses either of them with equal probability. After taking n steps the walker can be anywhere between $-n$ to n. Let us denote it's position by X_n. Then we can write

$$X_n = X_{n-1} + \xi_n\ , \tag{1}$$

where ξ_n is an independent random variable chosen from the following distribution

$$\begin{aligned} \xi_n &= 1 \ \text{ with prob. } 1/2 \\ &= -1 \ \text{ with prob. } 1/2. \end{aligned} \tag{2}$$

Evidently the "noise" variable ξ_n satisfies the following properties:

$$\begin{aligned} \langle \xi_n \rangle = 0, \langle \xi_n^2 \rangle = 1, \\ \langle \xi_n \xi_m \rangle = \langle \xi_n \rangle \langle \xi_m \rangle = 0 \ \text{ for } n \neq m, \end{aligned} \tag{3}$$

thus all steps at different times are un-correlated. Assuming $X_0 = 0$ we get after n steps

$$X_n = \sum_{i=1}^{n} \xi_i\ , \tag{4}$$

thus the position is a random variable which is the sum of n iid random variables. From the discussions in the previous section, we expect that for large N the distribution of X_n should be a

Gaussian. We can easily compute the mean and variance exactly

$$\langle X_n \rangle = \sum_{i=1}^{n} \langle \xi_i \rangle = 0, \tag{5}$$

$$\langle X_n^2 \rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \xi_i \xi_j \rangle = \sum_{i=1}^{n} \langle \xi_i^2 \rangle + \sum_{i \neq j} \langle \xi_i \xi_j \rangle = N. \tag{6}$$

What about the exact distribution of the variable X_n ? We now compute the probability $P(X, n)$ that the walker is at some point X ? We note that there are 2^n distinct possible walks, each of which occurs with the same probability. Out of these let us say $T(X, n)$ walks end up at the point X. Then clearly

$$P(X, n) = \frac{T(X, n)}{2^n}. \tag{7}$$

We can find $T(X, n)$ as follows. For any given realization of the walk let n_R be the number of right steps and let n_L be the number of left steps. Then $n_R + n_L = n$ and $n_R - n_L = X$.

Example: One possible realization of a $10-$step walk is $LRRLLRLLRL$. In this case $n = 10,\ n_R = 4,\ n_L = 6$ and $X = -2$. A different realization of the walk which leads to the same values of n, n_R, n_L, X is $LLLLRRRRLL$.

Clearly there are many possible ways of arranging the n_R Rs' and n_L L's and the number of ways would give us $T(X, n)$. This is a combinatorial problem whose answer is:

$$T(X, n) = \frac{n!}{n_R! n_L!}. \tag{8}$$

Prob: Check this formula for $n = 4$.

Now since $n_R = (n + X)/2$ and $n_L = (n - X)/2$ we therefore get, using Eq. (7) and Eq. (8),

$$P(X, n) = \frac{n!}{\frac{n+X}{2}! \frac{n-X}{2}!} \frac{1}{2^n}. \tag{9}$$

Prob: Check normalization: $\sum_{X=-n}^{n} P(X, n) = 1$. Use the fact that $(1/2 + 1/2)^n = 1$.

Now what we would eventually like to get is a "continuum description", that is we want to look at length scales much larger than the lattice spacing (say a) and time scales much larger than time taken for each step (say τ). Let us try to get this.

For this we use Stirling's approximation. This states that for large n we get $n! \approx n^n e^{-n} \sqrt{2\pi n}$. This formula is infact very good even for n as small as 5; in that case $5! = 120$ while the Stirling approximation gives ≈ 118.

Proof of Stirling's approximation: One derivation of the Stirling formula is to use the following result:

$$n! = \int_0^\infty dx\ e^{-x} x^n\ . \tag{10}$$

Let us try to evaluate this integral by finding out where it takes its maximum value and then approximating the integrand by a Gaussian around the maximum. We can write the integrand in the form $e^{-x}\ x^n = e^{-x+n\log x} = e^{f(x)}$, where $f(x) = -x + n\log x$. The point x^* where $f(x)$ and therefore $e^{f(x)}$ is maximum is given by the condition $f'(x^*) = 0$ which gives $x^* = n$. Expanding around this point we get

$$\begin{aligned} f(x) &= f(x^*) + \frac{1}{2}f''(x^*)(x-x^*)^2 + \ldots \\ \text{where } f(x^*) &= -n + n\log n\ , \quad f''(x^*) = -1/n\ . \end{aligned} \tag{11}$$

Using this in Eq. (10) we get

$$\begin{aligned} n! &= \int_0^\infty dx e^{f(x)} \\ &\approx e^{f(x^*)} \int_0^\infty dx\ e^{f''(x^*)(x-x^*)/2} \\ &\approx e^{f(x^*)} \int_{-\infty}^\infty dx\ e^{f''(x^*)(x-x^*)/2} \\ &= e^{f(x^*)} \left(\frac{2\pi}{-f''(x^*)}\right)^{1/2} = e^{-n+n\log n}(2\pi n)^{1/2}\ , \end{aligned} \tag{12}$$

Which is the Stirling formula.

QED

Using Stirling's formula in Eq. (9) we get:

$$P(X,n) = \frac{n^n e^{-n}(2\pi n)^{1/2}}{(\frac{n+X}{2})^{\frac{n+X}{2}} e^{-\frac{n+X}{2}}[2\pi(\frac{n+X}{2})]^{1/2}(\frac{n-X}{2})^{\frac{n-X}{2}} e^{-\frac{n-X}{2}}[2\pi(\frac{n-X}{2})]^{1/2}}\ \frac{1}{2^n}\ .$$

After simplification this reduces to

$$P(X,n) = \frac{(2\pi n)^{1/2}}{(1+\frac{X}{n})^{\frac{n+X}{2}}(1-\frac{X}{n})^{\frac{n-X}{2}}\pi n(1-\frac{X^2}{n^2})^{1/2}}\ .$$

We now consider $X << n$ only or more precisely $X \lesssim O(\sqrt{n})$. In this limit, we get

$$P(X,n) = (\frac{2}{\pi n})^{1/2} e^{-\frac{X^2}{2n}}\ . \tag{13}$$

This is easiest to obtain by taking $\ln P(X,n)$ and expanding. Now let $x = Xa$ and $t = n\tau$. Then the *probability density* for the walker to be between x and $x+dx$ is

$$\begin{aligned} p(x,t) &= P(X,n)/(2a) \\ &= \frac{1}{(4\pi(a^2/2\tau)t)^{1/2}} e^{-\frac{x^2}{4(a^2/2\tau)t}}. \end{aligned} \tag{14}$$

The reason we divide by $2a$ and not a is because after n steps the walker can be located either on even sites (if n is even) or on odd sites (n odd). Now defining the diffusion constant $D = a^2/(2\tau)$ we finally get

$$p(x,t) = \frac{1}{(4\pi Dt)^{1/2}} e^{-\frac{x^2}{4Dt}}. \tag{15}$$

Prob: Check that $\int_{-\infty}^{\infty} dx\ p(x,t) = 1$. Also verify that $\langle x \rangle = 0$ and $\langle x^2 \rangle = 2Dt$.

The moments $\langle x \rangle$ and $\langle x^2 \rangle$ can be obtained more directly. The position of the walker $x(t)$ after $n = t/\tau$ time steps is

$$x(t) = a \sum_{i=1}^{n} \xi_i \tag{16}$$

where ξ_i is $+1$ or -1 with equal probability (thus $\langle \xi_i \rangle = 0$) and ξ_i and ξ_j are uncorrelated or independent, which means that $\langle \xi_i \xi_j \rangle = 0$. Therefore

$$\begin{aligned}
\langle x(t) \rangle &= a \sum_{i=1}^{n} \langle \xi_i \rangle = 0 \\
\langle x^2(t) \rangle &= a^2 \sum_{i,j=1}^{n} \langle \xi_i \xi_j \rangle \\
&= a^2 (\sum_{i=1}^{n} \langle \xi_i^2 \rangle + \sum_{i \neq j} \langle \xi_i \xi_j \rangle) \\
&= a^2 n = 2[a^2/(2\tau)](n\tau) = 2Dt
\end{aligned} \tag{17}$$

Prob: Write a Monte-carlo program to generate $1-D$ random walks and verify the law $\langle x^2 \rangle = 2Dt$.

Prob: Let $\xi_i = 1$ with probability p and -1 with probability $q = 1 - p$. Find $\langle x(t) \rangle$ and $\langle x^2(t) \rangle - \langle x(t) \rangle^2$.

Prob: Let $x_i = 2$ with probability $1/2$ and $x_i = -1$ or 0 with probabilities $1/4$ each. Find $\langle x(t) \rangle$ and $\langle x^2(t) \rangle - \langle x(t) \rangle^2$.

1.2 Random walk and the Diffusion equation

Another method to get Eq. (15) : Since a random walk is like diffusion of particles we expect Eq. (15) to be the solution of the diffusion equation. Let us see how this comes about. As before, $P(X,n)$ is the probability that a particle is at the site X after n steps. It satisfies the following equation

$$P(X, n+1) = \frac{1}{2}\ [\ P(X+1,n) + P(X-1,n)\ ] \tag{18}$$

Subtract $P(X,n)$ from both sides. We then get

$$\begin{aligned}
&P(X,n+1) - P(X,n) = \frac{1}{2}\ [\ P(X+1,n) - 2P(X,n) + P(X-1,n)\ ] \\
&\Rightarrow \frac{p(x,t+\tau) - p(x,t)}{\tau} = \frac{a^2}{2\tau} \frac{[p(x+a,t) - 2p(x,t) + p(x-a,t)]}{a^2} \\
&\Rightarrow \frac{\partial p(x,t)}{\partial t} = D \frac{\partial^2 p(x,t)}{\partial x^2}
\end{aligned} \tag{19}$$

which is the *diffusion equation*. Normally in the diffusion equation we have density of particles $\rho(x,t)$ instead of the probability density $p(x,t)$. But they are simply related by $\rho(x,t) = N\ p(x,t)$ where N is the total number of diffusing particles.

Now Eq. (19) is a linear equation which can be easily solved by Fourier transforming. Solving means: given an initial probability distribution $p(x,t=0)$ find $p(x,t)$ at some later time t. Let us solve for the initial condition $p(x,t=0) = \delta(x)$, which corresponds to the case when the particle is initially located at the origin. Taking the Fourier transform

$$p(x,t) = \int_{-\infty}^{\infty} \widetilde{p}(k,t) e^{ikx} dk; \quad \widetilde{p}(k,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} p(x,t) e^{-ikx} dx$$

gives

$$\begin{aligned}
&\int_{-\infty}^{\infty} \frac{\partial \widetilde{p}(k,t)}{\partial t} e^{ikx} dk = \int_{-\infty}^{\infty} -Dk^2 \widetilde{p}(k,t) e^{ikx} dk \\
&\Rightarrow \frac{\partial \widetilde{p}(k,t)}{\partial t} = -Dk^2 \widetilde{p}(k,t) \\
&\Rightarrow \widetilde{p}(k,t) = e^{-Dk^2 t} \widetilde{p}(k,0) = \frac{1}{2\pi} e^{-Dk^2 t} \qquad (20)
\end{aligned}$$

Taking the inverse Fourier transformation we then get

$$p(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-Dk^2 t} e^{ikx} dk = \frac{1}{(4\pi D t)^{1/2}} e^{-\frac{x^2}{4Dt}} \ . \qquad (21)$$

as before. Note that the diffusion equation can also be written in the following form:

$$\begin{aligned}
&\frac{\partial p(x,t)}{\partial t} + \frac{\partial J(x,t)}{\partial x} = 0 \quad \text{where} \qquad (22) \\
&J(x,t) = -D \frac{\partial p(x,t)}{\partial x}.
\end{aligned}$$

Higher dimensions: We can consider a random walk on a $2-$dimensional, $3-$dimensional or in general a $d-$dimensional lattice and ask the same questions. The combinatorial approach becomes difficult but we get the same diffusion equation which can again be solved quite easily.

To see that we do get the same equation, consider the $2-$dimensional case, where a random walker can move up, down, left or right with equal probabilities. Thus if at some time $t = n\tau$ the walker is at the point $\mathbf{x} = (x,y)$ then, at time $t+\tau$, it can be at either of the 4 points $(x+a,y)$, $(x-a,y)$, $(x,y+a)$, $(x,y-a)$. The probability of it being at any of these 4 points is clearly $1/4$. Let $P(\mathbf{x},t)$ be the probability for the walker to be at $\mathbf{x}$ at time t. Then Eq. (18) gets modified to

$$P(\mathbf{x}, t+\tau) = \frac{1}{4} \ [\ P(x+a,y,t) + P(x-a,y,t) + P(x,y+a,t) + P(x,y-a,t)\ ] \ . \qquad (23)$$

Subtracting $P(\mathbf{x},t)$ from both sides we get:

$$\begin{aligned}
\frac{P(\mathbf{x},t+\tau) - P(\mathbf{x},t)}{\tau} &= \frac{a^2}{4\tau} \frac{[P(x+a,y,t) - 2P(x,y,t) + P(x-a,y,t)]}{a^2} \\
&+ \frac{a^2}{4\tau} \frac{[P(x,y+a,t) - 2P(x,y,t) + P(x,y-a,t)]}{a^2} \\
\Rightarrow \frac{\partial p(\mathbf{x},t)}{\partial t} &= D \left[\frac{\partial^2 p(\mathbf{x},t)}{\partial x^2} + \frac{\partial^2 p(\mathbf{x},t)}{\partial y^2} \right] , \qquad (24)
\end{aligned}$$

which is the 2−dimensional diffusion equation and we have defined $D = a^2/(4\tau)$. Similarly in 3−dimensions we get [with $D = a^2/(6\tau)$]

$$\frac{\partial p(\mathbf{x},t)}{\partial t} = D\nabla^2 P(\mathbf{x},t). \tag{25}$$

To solve this we again Fourier transform

$$p(\mathbf{x},t) = \int_{-\infty}^{\infty} \tilde{p}(\bar{k},t)e^{i\bar{k}.\mathbf{x}}d\bar{k}; \quad \tilde{p}(\bar{k},t) = \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty} p(\mathbf{x},t)e^{-i\bar{k}.\mathbf{x}}d\mathbf{x}.$$

Proceeding exactly as in the $1-D$ case we get

$$p(\mathbf{x},t) = \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty} d\bar{k}e^{-Dk^2t}e^{i\bar{k}.\mathbf{x}} = p(x,t)p(y,t)p(z,t) = \frac{1}{(4\pi Dt)^{3/2}}e^{-\frac{r^2}{4Dt}} \tag{26}$$

The mean square distance traveled by the walker is $\langle r^2\rangle = \langle x^2+y^2+z^2\rangle = 6Dt$. We can verify this directly. Since $\mathbf{x}(t) = a\sum_{i=1}^{n}\bar{\xi}_i$, therefore $\langle \mathbf{x}^2\rangle = a^2\sum_{i=1}^{n}\langle\bar{\xi}_i^2\rangle = na^2 = 6Dt$. Note that the number of walks of length n, from the origin to $\mathbf{x}$ is $6^nP(\mathbf{x},t)$.

1.3 Fourier series exact solution of discrete diffusion equation

1.3.1 One dimensions

The time-evolution equation for the probability distribution is given by

$$P(X,n) = \frac{1}{2}\left[P(X+1,n-1) + P(X-1,n-1)\right]. \tag{27}$$

We want to solve this equation on the infinite lattice for the initial condition $P(X,n=0) = \delta_{X,0}$. The equivalent step of doing Fourier transforms, that we used for the diffusion equation, is to do a Fourier series transform. Thus we define

$$\widetilde{P}(\theta,n) = \sum_{X=-\infty}^{\infty} P(X,n)e^{iX\theta} \ , \tag{28}$$

and the inverse transform is given by

$$P(X,n) = \frac{1}{2\pi}\int_{-\pi}^{\pi} d\theta\widetilde{P}(\theta,n)e^{-iX\theta} \ , \tag{29}$$

Multiplying Eq. (27) by $e^{iX\theta}$ and summing over all X then gives

$$\widetilde{P}(\theta,n) = \cos\theta\tilde{P}(\theta,n-1) = (\cos\theta)^n\tilde{P}(\theta,0) \ . \tag{30}$$

The initial condition $P(x,n=0) = \delta_{X,0}$ gives $\widetilde{P}(\theta,0) = 1$ and so we get from Eq. (29) the following formal solution

$$P(X,n) = \frac{1}{2\pi}\int_{-\pi}^{\pi} d\theta(\cos\theta)^n e^{-iX\theta} \ , \tag{31}$$

1.3.2 Generalization to random walks on hypercubic lattices in arbitrary dimensions

. The evolution equation for a random walker on a d-dimensional hyper-cubic lattice is given by

$$P(\mathbf{X},n)=\frac{1}{2d}\left[\sum_{i=1}^{d}P(\mathbf{X}+\mathbf{e}_i,n-1)+P(\mathbf{X}-\mathbf{e}_i,n-1)\right], \tag{32}$$

where $\mathbf{e}_i$, for $i=1,2,\ldots,d$ are the unit vectors in the d-directions. In this case we define

$$\widetilde{P}(\boldsymbol{\theta},n)=\sum_{\mathbf{X}}P(\mathbf{X},n)e^{i\mathbf{X}.\boldsymbol{\theta}}\ , \tag{33}$$

and the inverse transform is given by

$$P(\mathbf{X},n)=\frac{1}{(2\pi)^d}\int_{-\pi}^{\pi}d^d\theta\widetilde{P}(\boldsymbol{\theta},n)e^{-i\mathbf{X}.\boldsymbol{\theta}}\ . \tag{34}$$

Repeating the steps for the 1D walker we then get

$$P(\mathbf{X},n)=\frac{1}{(2\pi)^d}\int_{-\pi}^{\pi}d^d\theta\left(\frac{1}{d}\sum_{i=1}^{d}\cos\theta_i\right)^n e^{-i\mathbf{X}.\boldsymbol{\theta}}\ , \tag{35}$$

The integral can be performed exactly in $d=2$ to give

$$P(X,Y,n)=\frac{n!}{\frac{n+X+Y}{2}!\frac{n-X-Y}{2}!}\frac{1}{2^n}\frac{n!}{\frac{n+X-Y}{2}!\frac{n-X+Y}{2}!}\frac{1}{2^n}. \tag{36}$$

2 Langevin equations and Brownian motion

2.1 Phenomenological discussion of Brownian motion

As we have seen, the random walk is described by the equation

$$X_{n+1}=X_n+\xi_n$$

where ξ_n is uncorrelated noise with zero mean *i*.e

$$\langle\xi_n\rangle=0;\quad \langle\xi_n\xi_m\rangle=\delta_{nm}.$$

For continuous space and time we write, as usual, $t=n\tau$, $x=X_na$ and the above equation gives

$$\begin{aligned}&\frac{dx(t)}{dt}=\xi(t)\quad\text{with}\\&\langle\xi(t)\rangle=0;\quad \langle\xi(t)\xi(t')\rangle=2D\delta(t-t'),\end{aligned} \tag{37}$$

where $D=a^2/(2\tau)$ is the diffusion constant. This is the equation of motion for a free Brownian particle (a particle whose velocity is a random function of time). If we have a large number of such

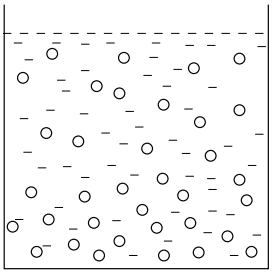

Figure 1: Large number of colloidal particles inside a fluid.

particles then we have seen that their density obeys the diffusion equation which can be written in the form

$$\frac{\partial \rho(x,t)}{\partial t} + \frac{\partial J_{diff}(x,t)}{\partial x} = 0, \quad \text{where} \;\; J_{diff}(x,t) = -D\frac{\partial \rho(x,t)}{\partial x} \tag{38}$$

is usually referred to as Fick's law. Now consider a different situation where a large number of particles are moving with a deterministic (that is non-random) velocity. The equation of motion of each particle is, say

$$\frac{dx(t)}{dt} = f(x). \tag{39}$$

In this case also we can again define the density distribution of particles and ask the question as to how this changes with time ? This is basically determined from the conservation of particles which is given by the following continuity equation:

$$\frac{\partial \rho(x,t)}{\partial t} + \frac{\partial J_{drift}(x,t)}{\partial x} = 0, \quad \text{where} \;\; J_{drift}(x,t) = \dot{x}\rho(x,t) = f(x,t)\rho(x,t). \tag{40}$$

Prob: Derive the continuity equation from the condition for conservation of particles which is $\rho(x,t)dx = \rho(x',t')dx'$ where $t' = t + dt$ and $x' = x + dx$. This is infact just the Liouville's equation in classical mechanics.

The Einstein fluctuation-dissipation relation: we will now use the previous results to derive a formula which will relate the diffusion constant D to real physical properties of the fluid medium in which the Brownian particle is moving.

Consider a large number of colloidal particles inside a fluid as shown in Fig. (2.1). Each colloidal particle is much larger than the fluid particles which constantly bombard it. The net effect of all the forces imparted on the colloid by the fluid particles can effectively be described very accurately by the following forces:

(i) A temporally fluctuating force which causes the particle to move randomly. This causes a diffusive current given by $J_{diff} = -D\frac{\partial \rho(x)}{\partial x}$.

(ii) A deterministic dissipative force: each colloidal particle is acted upon by one is the drag force given by $-\gamma\dot{x}$ where $\gamma = 6\pi\eta a$, with η being the viscosity of the fluid and a the radius of the Brownian particle.

What the fluctuation-dissipation theorem (or Einstein relation) tells us is that the two parts of the forces mentioned above are related to each other. Let us see how this comes about.

Consider the state when the colloidal particles have reached a steady state and are in thermal equilibrium at some temperature T. We know that because of gravity there will be a concentration gradient of colloidal particles in the system and their density will vary as:

$$\rho(x) = \rho(x=0)e^{-\frac{mgx}{k_BT}}, \tag{41}$$

where m is mass of each particle. The steady state can be thought of as maintained by a balance of two currents in the system, of particles falling down under gravity and then diffusing up.

The downward gravitational force acting on the particle is given by mg (we assume that the buoyant force is negligible). The gravitational force and drag force balance to cause the colloidal particle to attain a terminal speed $\dot{x} = mg/\gamma$. This, from Eq. (40), implies a downward drift current given by $J_{drift} = mg\rho(x)/\gamma$. In the equilibrium state there is no net current of particles which means $J_{diff} = J_{drift}$. Hence

$$\frac{\partial \rho(x)}{\partial x} = -\frac{mg}{\gamma D}\rho(x).$$

But from Eq. (41) we get

$$\frac{\partial \rho(x)}{\partial x} = -\frac{mg}{k_BT}\rho(x).$$

Comparing the two equations above we get the Einstein relation

$$D = \frac{k_BT}{\gamma}. \tag{42}$$

Note that it relates the fluctuating (D) and dissipative (γ) parts of the fluid forces acting on the colloid. Since $\gamma = 6\pi\eta a$, everything on the right hand side of Eq. (42) is known, and we can then use it to estimate the value of D.

Prob: Estimate the value of D for a colloid of size $a = 1\mu m$ in water and in air. How far does it travel in a minute? and in an hour?

2.2 Fokker-Planck equation for a Brownian particle in a potential

The full equation of motion for a Brownian particle moving inside a potential $U(x)$ is given by:

$$\begin{aligned} m\frac{dv}{dt} &= -\gamma v + F(x) + \alpha(t) \quad \text{where} \\ F(x) &= -\frac{\partial U(x)}{\partial x} \\ \langle \alpha(t) \rangle &= 0; \quad \langle \alpha(t)\alpha(t') \rangle = 2\gamma k_B T \delta(t-t') \ . \end{aligned}$$

If we are in the high viscosity limit (overdamped, low Reynolds number limit) it can be shown that it is alright (for times $t >> m/\gamma$) to neglect inertial terms, namely the term on the left hand side of the above equation. In that case we get

$$\frac{dx}{dt} = f(x) + \xi(t), \tag{43}$$

where $\xi(t) = \alpha(t)/\gamma$ and $f(x) = F(x)/\gamma$. Hence the noise correlations are given by $\langle \xi(t)\xi(t')\rangle = 2D\delta(t-t')$ with $D = k_BT/\gamma$. This is the Langevin equation of a Brownian particle in the over-damped limit.

If $p(x,t)$ is the probabilty distribution of the particle then, as we saw in the previous section, the probability current corresponding to this Langevin equation is:

$$\begin{aligned} J &= J_{diff} + J_{drift} \\ &= f(x)p(x,t) - D\frac{\partial p(x,t)}{\partial x}. \end{aligned}$$

Using the continuity equation $\partial p/\partial t + \partial J/\partial x = 0$, this then leads to the following *Fokker-Planck* equation for $p(x,t)$:

$$\frac{\partial p(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left[f(x)p(x,t)\right] + D\frac{\partial^2 p(x,t)}{\partial x^2} \ . \tag{44}$$

2.3 A systematic derivation of the Fokker-Planck equation

We now give a derivation of the Fokker-Planck equation corresponding to Eq. (43). We use the fact that the Langevin equation with δ-correlated noise describes a Markov process and hence we can write a evolution equation for the probability density — this will be a generalization of Eq. (18) for the random walk. Let us assume that starting from point x' at time t', the particle can make a transition of size Δx that is chosen from a distribution $\phi(\Delta x; x', t')$. Then we have:

$$p(x,t) = \int_{-\infty}^{\infty} d\Delta x \ p(x-\Delta x, t-\Delta t) \ \phi(\Delta x; x-\Delta x, t-\Delta t) \ .$$

We now do a Taylor-expansion of the function $f(x-\Delta x) = p(x-\Delta x, t-\Delta t) \ \phi(\Delta x; x-\Delta, t-\Delta t)$ around the point x. We then get:

$$\begin{aligned} p(x,t) &= \sum_{n=0}^{\infty} \frac{\partial^n}{\partial x^n}\left[\ p(x,t-\Delta t)\int_{-\infty}^{\infty} d\Delta x \ \frac{(-\Delta x)^n}{n!} \ \phi(\Delta x; x, t-\Delta t) \ \right] \\ &= p(x,t-\Delta t) + \sum_{n=1}^{\infty} \frac{\partial^n}{\partial x^n} \ \left[p(x,t)(-1)^n \frac{\langle (\Delta x)^n\rangle}{n!}\right] \ , \end{aligned} \tag{45}$$

where we have used the fact that $\int \ d\Delta x \ \phi(\Delta x; x, t-\Delta t) = 1$ and defined the moments of the jump distribution $\langle (\Delta x)^n\rangle = \int_{-\infty}^{\infty} \ d\Delta x \ (\Delta x)^n \ \phi(\Delta x; x, t-\Delta t)$. As we will see, for our process described by the Langevin equations, the coefficients $D_n(x,t) = \lim_{\Delta t\to 0}\langle (\Delta x)^n\rangle/(n!\Delta t)$ vanish for $n > 2$. Hence we get

$$\frac{\partial p(x,t)}{\partial t} = -\frac{\partial}{\partial x}[D_1 p(x,t)] + \frac{\partial^2}{\partial x^2}[D_2 p(x,t)] \ . \tag{46}$$

For the overdamped Langevin equation described by Eq. (43) we have:

$$\Delta x = x(t+\Delta t) - x(t) = f(x)\Delta t + \int_t^{t+\Delta t} dt'\xi(t') = f(x)\Delta t + \nu(t) \ ,$$

where $\nu(t)$ is a Gaussian distributed number with zero mean and variance $2D\Delta t$. Hence we get:

$$\begin{aligned} D_1 &= \lim_{\Delta t \to 0} \frac{\langle \Delta x \rangle}{\Delta t} = f(x) \ , \\ D_2 &= \lim_{\Delta t \to 0} \frac{\langle (\Delta x)^2 \rangle}{2\Delta t} = D \ . \end{aligned}$$

Hence we get the Fokker-Planck equation in Eq. (44).

3 General Markov processes

3.1 General description of stochastic processes

3.2 Definition of Markov processes

3.3 Detailed balance condition

4 Interacting particles

4.1 Glauber dynamics

We consider a system of $N = L^d$ spins $\sigma = \{\sigma_1, \sigma_2, \ldots, \sigma_N$ on a hyper-cubic lattice in d-dimensions. Each spin can take two values $\sigma_j = \pm 1$. We consider a general Hamiltonian

$$H = -\sum_{<ij>} J\sigma_i\sigma_j \ , \tag{47}$$

where the sum is over all nearest neigbor pairs.

Heat bath dynamics: We imagine that the spin system is in contact with a thermal environment which causes it to make stochastic jumps between allowed spin configurations. We want to consider a simple possible model for a stochastic dynamics and in particular one which is *Markovian*. Clearly such a dynamics is specified once we specify the W-matrix whose off-diagonal entries gives the rate of transition $W_{\sigma,\sigma'}$ from a spin configuration σ' to another given by σ. One necessary condition is that the steady state of this dynamics should be given by the equilibrium distribution, namely

$$P_{\rm ss}(\sigma) = \frac{e^{-\beta H}}{Z}, \tag{48}$$

where $Z = \sum_\sigma e^{-\beta H}$ is the partition function. One easy way to enforce that this is achieved is to put in the condition that the dynamics satisfies the detailed balance condition:

$$\frac{W_{\sigma',\sigma}}{W_{\sigma,\sigma'}} = \frac{P_{\rm ss}(\sigma')}{P_{\rm ss}(\sigma)} = \frac{e^{-\beta H(\sigma')}}{e^{-\beta H(\sigma)}}. \tag{49}$$

This still leaves us with many possible choices of transition matrices.

Single-spin-flip heat bath dynamics: We now restrict ourselves to a smaller class where transitions occur by the process of a single spin flip. Thus the W-matrix only connects two configurations

if they differ from each other at only one lattice site. Let us denote $w(\sigma_j)$ as the transition rate from the configuration $\sigma = \{\sigma_1, \sigma_2, \ldots, \sigma_j, \ldots, \sigma_N\}$ to the configurtion $\{\sigma_1, \sigma_2, \ldots, -\sigma_j, \ldots, \sigma_N\}$. A little bit of thinking shows that the detailed balance condition then implies

$$\frac{w(\sigma_j)}{w(-\sigma_j)} = \frac{e^{-\beta J \sigma_j \sum_{k\in\langle j\rangle} \sigma_k}}{e^{\beta J \sigma_j \sum_{k\in\langle j\rangle} \sigma_k}}, \tag{50}$$

where $\langle j\rangle$ indicates nearest neighbors of j. Using the fact that $e^{a\sigma} = \cosh a + \sigma \sinh a = \cosh(a)(1 + \sigma \tanh a)$, we can rewrite the above as

$$\frac{w(\sigma_j)}{w(-\sigma_j} = \frac{1 - \sigma_j \tanh(\beta J \sum_{k\in<j>} \sigma_k)}{1 + \sigma_j \tanh(\beta J \sum_{k\in<j>} \sigma_k)}. \tag{51}$$

Let us choose the following *Glauber* rules for the single-spin-flip transition rates satisfying the above detailed-balance condition:

$$w(\sigma_j) = \frac{\alpha}{2}\left[1 - \sigma_j \tanh(\beta J \sum_{k\in\langle j\rangle} \sigma_k)\right], \tag{52}$$

where α is a free constant parameter that allows us to change the the rate of transitions. Note that the transition rate $w(\sigma_j)$ depends not just on the spin at site j but also on the state of the neighboring spins.

The master equation for the general d-dimensional case with spin-flip rates as in Eq. (52) is give by

$$\begin{aligned}&\partial_t P(\sigma_1, \sigma_2, \ldots, \sigma_j, \ldots, \sigma_N)\\ &= \sum_{j=1}^{N} w(-\sigma_j) P(\sigma_1, \sigma_2, \ldots, -\sigma_j, \ldots, \sigma_N) - \sum_j w(\sigma_j) P(\sigma_1, \sigma_2, \ldots, \sigma_j, \ldots, \sigma_N)\ .\end{aligned} \tag{53}$$

The complete equation is difficult to handle analytically so we instead look at equations for the moments and correlations. Let us define

$$m_i(t) = \langle \sigma_i \rangle = \sum_\sigma \sigma_i P(\sigma, t), \tag{54}$$

as the average magnetization at the site i at time t. Multiplying Eq. (53) by σ_l on both sides and summing over all configurations we get

$$\frac{dm_l}{dt} = -2\langle \sigma_l w(\sigma_l)\rangle. \tag{55}$$

In deriving this result we used the fact that

$$\sum_\sigma \sigma_l w(-\sigma_j) p(\sigma_1, \sigma_2, \ldots, -\sigma_j, \ldots, \sigma_N) = \sum_\sigma \sigma_l w(\sigma_j) p(\sigma_1, \sigma_2, \ldots, \sigma_j, \ldots, \sigma_N)$$

for $l \neq j$, a result obtained by changing variable $\sigma_j \to -\sigma_j$. Hence only the term $j = l$ in the summation in Eq. (53) contributes and leads to the result in Eq. (55).

Glauber's rules for $d = 1$: In his 1963 paper, Glauber considers the above dynamics for the case of the one-dimensional Ising model with nearest neigbor interactions, for which things simplify further. We note that for $d = 1$, the sum $\sum_{k\in\langle j\rangle} \sigma_k = \sigma_{j-1} + \sigma_{j+1}$ can take the values $2, 0, -2$. Hence we can write $\tanh(\beta J \sum_{k\in\langle j\rangle} \sigma_k) = (\sum_{k\in\langle j\rangle} \sigma_k) \tanh(2\beta J)/2$. Denoting $\gamma = \tanh(2\beta J)$ we therefore now get the following flip rates

$$w(\sigma_j) = \frac{\alpha}{2}\left[1 - (\gamma/2)\sigma_j \sum_{k\in\langle j\rangle} \sigma_k\right]. \tag{56}$$

In this case, Eq. (55) leads to the following equation for the magnetization:

$$\frac{dm_l}{dt} = -\alpha m_l + \frac{\alpha\gamma}{2}(m_{l-1} + m_{l+1}) \ . \tag{57}$$

This equation has to be solved with appropriate boundary conditions (periodic finite ring, open finite ring or infinite lattice) and initial conditions $m_j(t = 0)$. Since the equations are linear, we can solve them by a Fourier series approach on the ring or on the infinite line. In the thermodynamic limit, we find, for the initial condition $m_l(t = 0) = \delta_{l,0}$,

$$G_l(t) = e^{-\alpha t} J_l(\alpha\gamma t) \ . \tag{58}$$

The linearity of the equations imply that for arbitrary initial conditions, the general solution is given by

$$m_l(t) = \sum_{j=-\infty}^{\infty} G_{l-j}(t) m_j(0) \ . \tag{59}$$

Two-time Correlations: A quantity of great interest in non-equilibrium physics is two time correlations of the form

$$C_{lj}(t) = \langle \sigma_l(t)\sigma(0)\rangle, \tag{60}$$

which can be expressed in terms of the two time joint probability distribution of the spin configuration taking the states σ and σ' at times t and 0 respectively. Thus

$$\begin{aligned} C_{lj}(t) ==& \sum_{\sigma}\sum_{\sigma'} \sigma_l \sigma'_j P(\sigma, t; \sigma', 0) \\ &= \langle \sigma_l(t)\sigma(0)\rangle = \sum_{\sigma}\sum_{\sigma'} \sigma_l \sigma'_j P(\sigma, t|\sigma', 0) P(\sigma', 0). \end{aligned} \tag{61}$$

From our earlier result in Eq. (60) we obtain the following result

$$\sum_{\sigma} \sigma_l P(\sigma, t|\sigma', 0) = m_l(t)|\sigma' = \sum_k G_{l-k}(t)\sigma'_k. \tag{62}$$

Using this we then get

$$C_{lj}(t) = \sum_{\sigma'} \sum_{k} G_{l-k}(t) \sigma'_k \sigma'_j P(\sigma', 0)$$
$$= \sum_{k} G_{l-k}(t) \langle \sigma_k \sigma_j \rangle, \tag{63}$$

where $\langle \sigma_k \sigma_j \rangle$ is now simply an equal time spin correlator. We choose the state at time $t = 0$ as the equilibrium Gibbs state for which it is known that $\langle \sigma_k \sigma_j \rangle = \eta^{|k-j|}$ where $\eta = \tanh \beta J$. We expect that C_{lj} should only depend on $|l - j|$ and so setting $j = 0$ in Eq. (63) we get

$$C_l(t) = \sum_{k} G_{l-k}(t) \eta^k, \tag{64}$$

- **Problem**: Find how the spin-flip rate $w(\sigma_j)$ gets modfied in the presence of an external magnetic field which adds to the Hamiltonian an extra energy equal to $-\mu h \sum_j \sigma_j$.

General $d-$dimensional case: In this case, Eqs. (52,55) lead to the following evolution equation:

$$\frac{dm_l}{dt} = -\alpha m_l + \alpha \left\langle \tanh \left(\beta J \sum_{k \in \langle l \rangle} \sigma_k \right) \right\rangle,$$

which does not form a closed set of equations. In this case we can proceed by making the mean field approximation $\sigma_k \approx m_k$. In which case we get the closed set of equations

$$\frac{dm_l}{dt} = -\alpha m_l + \alpha \tanh \left(\beta J \sum_{k \in \langle j \rangle} m_l \right).$$

These coupled nonlinear equations cannot be solved exactly but we notice that their steady state solution corresponds to the equilibrium mean field equations for the magnetization, namely

$$m = \tanh \left(\beta J z m \right) \ , \tag{65}$$

where z is the coordination number. This gives a non-vanishing solution for $\beta > (Jz)^{-1}$.

- **Problem**: Write a code to simulate the two-dimensional Ising model with the Glauber rules Eq. (52). Starting from a random initial configuration of spins, plot $m(t) = \sum_{i=1}^{N} m_i(t)/N$ as a function of time at temperature $T = 0.8 T_c$, where T_c is the exact equilibrium transition temperature. You need to do an averaging over initial conditions as well as over trajectories. Show results for $N = L^2$ spins with $L = 16, 32, 64$. Compare your results with those obtained by a numerical solution of the mean field dynamical equation for $m_i(t)$. In this case start with a single initial condition which is a small perturbation of the zero magnetization state.

Convergence to the steady state: The dynamical mean field equations correspond to a set of nonlinear ODEs with some known fixed points. To show that the system will converge to a fixed point and not get stuck in periodic cycles, it is useful to construct what is called a Lyapunov function (somewhat like entropy). For the Glauber dynamics one choice for the Lyapunov function is the following:

$$F_G(\{m_l\}) = \beta^{-1} \sum_{i=1}^{N} g(m_i) - J \sum_{\langle i,j \rangle} m_i m_j \ , \tag{66}$$

$$\text{where} \quad g(m) = \frac{1}{2}\left[(1-m)\ln(1-m) + (1+m)\ln(1+m)\right] \ . \tag{67}$$

We note that this is precisely the mean-field free energy expression for the Ising model. The term $g(m)$ can be seen as an entropic contribution coming from defining a coarse-grained magnetization field. We see that

$$\beta \frac{\partial F_G}{\partial m_j} = \tanh^{-1}(m_j) - \beta J \sum_{k \in \langle j \rangle} m_k \ . \tag{68}$$

Setting this to zero gives us the equilibrium mean field equations. Let us compute the rate of change with time of the Lyapunov function. We get

$$\beta \frac{dF_G}{dt} = \sum_j \beta \frac{\partial F_G}{\partial m_j} \dot{m}_j = - \left[\tanh^{-1}(m_j) - \beta J \sum_{k \in <j>} m_k \right] \left[m_j - \tanh(\beta J \sum_{k \in <j>} m_k) \right] \ . \tag{69}$$

The right hand side of the above expression involves terms of the form $-[\tanh^{-1}(u) - v][u - \tanh(v)]$ which is negative definite since the two terms necessarily have the same sign.

Proof:

$$\tanh[\tanh^{-1}(u) - v] = \frac{u - \tanh v}{1 - u \tanh v} \ . \tag{70}$$

We are interested in $|u| < 1$, hence the denominator in the above equation is always positive. Since $\tanh(x)$ and x have the same sign, the above equation then implies that $\tanh^{-1}(u) - v$ and $u - \tanh v$ have the same sign.[QED]

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4.2 Exclusion process

In this case we consider a system of N particles on a lattice with L points. The particles interact strongly such that it's effect is to disallow multiple occupancy at any site (this is refered to as exclusion). A microscopic configuration is then completely specfied by the occupancy list $n = \{n_1, n_2, \ldots, n_L\}$ where $n_j = 0, 1$. We consider a local dynamics where individual particles execute biased random walks while satisfying the exclusion constraint. The hopping rates are taken to be

α_r to the right and α_l to the left. This dynamics is equivalent to the following specification of the W-matrix. Transitions are only allowed between two states n and n' which differ by exchange of particles at any nearest neighbor sites, say j and $j+1$. The transition rate from the state $\{n_1, n_2, \ldots n_j, n_{j+1}, \ldots, n_L\}$ to the state $\{n_1, n_2, \ldots n_{j+1}, n_j, \ldots, n_L\}$ is given by

$$w(n_j, n_{j+1}) = \alpha_r n_j(1 - n_{j+1}) + \alpha_l(1 - n_j)n_{j+1} \ . \tag{71}$$

For the moment we assume that our system is defined on a periodic lattice with L sites. With this specification of the W-matrix, we can proceed, as in the example of the previous section, to write the master equation for the evolution of the probability distribution $P(n, t)$:

$$\begin{aligned} &\partial_t P(n_1, n_2, \ldots, n_L) \\ &= \sum_{j=1}^{N} w(n_{j+1}, n_j) P(n_1, n_2, \ldots, n_{j+1}, n_j, \ldots, n_L) - \sum_j w(n_j, n_{j+1}) P(n_1, n_2, \ldots, n_j, n_{j+1}, \ldots, n_L) \ . \end{aligned} \tag{72}$$

Steady state: Note that for this stochastic process, we did not consider any energy function and the W-matrix was not constructed with the detailed balance condition in mind. It turns out that anyhow we can still find the exact steady state distribution of this system. Noting that the dynamics conserves particle number $N = \sum_{i=1}^{L} n_i$, the W-matrix breaks up into $L+1$ disconnected blocks with each block specified by the total particle number which can take values $N = 0, 1, 2, \ldots, L$. Thus one has $L+1$ possible steady states, the initial condition deciding which state the system will be in. Within a block there are $\binom{L}{N}$ possible configurations and the steady state has a very simple structure — all the $\binom{L}{N}$ configurations occur with the same probability.

Proof: The proof rests on the idea of pairwise balance which is an extension of the idea of detailed balance. This says that, with every configuration n' that is connected to n by the transition matrix, is associated a unique configuration n'' connected to n with the property that in the steady state

$$W_{n',n} P_{\rm ss}(n) = W_{n,n''} P_{\rm ss}(n'') \ . \tag{73}$$

Summing the above equation over n we see that the steady state condition is indeed satisfied. To illustrate this condition for the exclusion process, consider for $L = 6, N = 3$ a configuration $n = \{1, 0, 1, 1, 0, 0\}$. Then the transition to the state $n' = \{1, 0, 1, 0, 1, 0\}$ occurs at a rate α_r and correspondingly theres a transition from $n'' = \{1, 1, 0, 1, 0, 0\}$ to n occuring at the same rate. The uniform probability measure then means that the pair-wise balance condition is satisfied. A bit of thinking convinces us that the construction of the pair is always possible. Note that detailed balance condition is more restrictive and corresponds to $n' = n''$, which in our case is only satisfied for the symmetric exclusion process (with $\alpha_r = \alpha_l$).

Explicit example: Consider the example of two particles moving on a ring with four site, i.e $N = 2$, $L = 4$. We label the allowed configurations as $|1\rangle = (1, 1, 0, 0), |2\rangle = (1, 0, 1, 0), |3\rangle =$

$(1,0,0,1), |4\rangle = (0,1,1,0), |5\rangle = (0,1,0,1), |6\rangle = (0,0,1,1)$. The transition matrix is explicitly given by

$$W = \begin{pmatrix} -(\alpha_l+\alpha_r) & \alpha_l & 0 & 0 & \alpha_r & 0 \\ \alpha_r & -2(\alpha_l+\alpha_r) & \alpha_l & \alpha_l & 0 & \alpha_r \\ 0 & \alpha_r & -(\alpha_l+\alpha_r) & 0 & \alpha_l & 0 \\ 0 & \alpha_r & 0 & -(\alpha_l+\alpha_r) & \alpha_l & 0 \\ \alpha_l & 0 & \alpha_r & \alpha_r & -2(\alpha_l+\alpha_r) & \alpha_l \\ 0 & \alpha_l & 0 & 0 & \alpha_l & -(\alpha_l+\alpha_r) \end{pmatrix} \tag{74}$$

Equations for moments: While the solution of the full master equation is non-trivial we can make some progress by looking at the moments which correspond to physical observables. It is easy to see from the master equation that the evolution of the density field $\rho_i(t) = \langle n_i \rangle = \sum_n n_i P(n,t)$ is given by

$$\frac{d\rho_i}{dt} = \alpha_r \langle n_{i-1}(1-n_i)\rangle + \alpha_l \langle n_{i+1}(1-n_i)\rangle - \alpha_l \langle n_i(1-n_{i-1})\rangle - \alpha_r \langle n_i(1-n_{i+1})\rangle \tag{75}$$

$$= \alpha_r(\rho_{i-1}-\rho_i) + \alpha_l(\rho_{i+1}-\rho_i) + \alpha_r(-C_{i-1,i}+C_{i,i+1}) + \alpha_l(-C_{i,i+1}+C_{i-1,i}) \ , \tag{76}$$

where we have defined the equal time correlator $C_{ij} = \langle n_i n_j \rangle$, and used the obvious identity $C_{ij} = C_{ji}$. It is easy and instructive to understand various terms in the above equation physically. For example consider the process whereby a particle can hop from site $i-1$ to i. This can only occur if $n_{i-1} = 1$ and $n_i = 0$. The probability of this happening is $\langle n_{i-1}(1-n_i)\rangle$ and, given that this is satisfied, the transition rate is α_r. The first term in the right hand side of Eq. (75) precisely corresponds to this process.

Some comments on the structure of the equations for ρ_i:

1. We notice now that unlike the example of the $d = 1$ Glauber model, the equations for ρ_i *do not form a closed set*. The equation involves the higher two-point correlations C_{ij}. We can try to write equations for C_{ij} but those would involve three-point correlations and so on. This is the typical $BBGKY$ hierarchy problem.

2. The equations can be written in the form of a continuity equation:

$$\begin{aligned} \frac{d\rho_i}{dt} &= -J_{i+1} + J_i \\ \text{where} \quad J_i &= \alpha_r(\rho_{i-1} - C_{i-1,i}) - \alpha_l(\rho_i - C_{i-1,i}) \ . \end{aligned} \tag{77}$$

   This corresponds to the fact that particle number is conserved locally.

Symmetric simple exclusion process (SSEP): For the special case $\alpha_l = \alpha_r = \alpha$, the dynamics simplifies considerably and we find that the densities now form a closed set:

$$\frac{d\rho_i}{dt} = \alpha(\rho_{i+1} - 2\rho_i + \rho_{i-1}), \tag{78}$$

which is the same equation that one would have for non-interacting walkers. From our earlier discussion of the random walk we see immediately that the time for the density field to relax to the uniform steady state value is given by

$$\tau_{\rm ssep} \sim L^2/\alpha. \tag{79}$$

As mentioned earlier, the steady state of the exclusion process in each sector is one of uniform measure over allowed states – for SSEP we can easily check that the detailed balance condition is satisfied and so the steady system is in that sense an equilibrium state. Note that we can formally write the steady state in the form $e^{-\beta E(n)}/Z$ where $E(n)$ is zero for all allowed configurations respecting exclusion and ∞ for all disallowed configurations. We also note that the particle current $J = 0$ in the steady state.

Exact mapping to quantum model: The $W-$matrix of the SSEP can be mapped exactly to the $1D$ Heisenberg spin-1/2 ferromagnetic chain, whose eigen-spectrum is known exactly via the formalism of Bethe-Ansatz. In particular it is known that the gap between the ground state (SSEP steady state) and the first excited state scales as $1/L^2$ (for large L), consistent with the result in Eq. (79).

Asymmetric simple exclusion process (ASEP): In this case, a common approach is to again use the mean field approximation and replace $C_{i,j} = \rho_i \rho_j$. We then find the following results for the steady state density and current

$$\rho_i = \rho = N/L, \qquad J_i = J = (\alpha_r - \alpha_l)\rho(1-\rho), \tag{80}$$

for all $i = 1, \ldots, L$. The fact that the particle current is finite is consistent to the fact that the detailed balance condition is not satisfied and we now have a *Non-Equilibrium Steady State* (NESS). The ASEP can be mapped exactly to a quantum non-Hermitian spin chain, whose spectrum can again be obtained using the Bethe Ansatz. From the gap between the ground state and the first excite state one finds that the relaxation time now has a scaling with system size which is different from SSEP. In this case one obtains

$$\tau_{\rm asep} \sim L^{3/2}/\alpha. \tag{81}$$

In general the dependence of relaxation time, in a many body system, on the system size is an important characterization of its dynamics. Typically one finds $\tau_{\rm relax} \sim L^z$ where z is referred to as a *dynamical exponent* of the system. Here we have established that $z = 2$ for SSEP and $z = 3/2$ for ASEP.

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5 Polya's recurrence theorem and first passage problems

We consider a simple random walk on a general hypercubic lattice and ask the question: What is the probability, R_0, that a walker starting from the origin will ever return to the starting point? The walker is allowed to take any amount of time. Polya's theorem states that the walker will return with probanilty one in dimensions $d = 1, 2$ while in higher dimensions, there is a finite probability that the walker will not return.

5.1 Method of generating functions

Proof: We give a simple proof using the idea of generating functions. Let us define the following generating function:

$$G(\mathbf{X}, z) = \sum_{n=0}^{\infty} P(\mathbf{X}, n) z^n.$$

One can show (see below) that $V_0 = G(\mathbf{0}, 1)$ gives the mean number of visits to the origin, $\mathbf{X} = \mathbf{0}$, over infinite time. We can relate R_0 and V_0 using the following result:

$$V_0 = 1.(1 - R_0) + 2.R_0.(1 - R_0) + 3.R_0^2.(1 - R_0) + \dots \tag{82}$$

$$= (1 - R_0)^{-1} \ . \tag{83}$$

The above relation simply sums over cases where there is a single visit, occuring with probability $(1 - R_0)$ (no return), two visits which occur with probability $R_0(1 - R_0)$ (exactly one return), etc. Inverting the above relation we get

$$R_0 = 1 - \frac{1}{V_0} \ . \tag{84}$$

From our earlier exact Fourier-series solution for $P(\mathbf{X}, n)$ we can immediately write the form of the generating function:

$$G(\mathbf{X}, z) = \frac{1}{(2\pi)^d} \int_{-\pi}^{\pi} d^d\theta \frac{e^{-i\mathbf{X}.\boldsymbol{\theta}}}{1 - (z/d)\sum_{j=1}^{d} \cos\theta_j}. \tag{85}$$

Using this we get $V_0 = G(\mathbf{0}, 1) = (2\pi)^{-d} \int_{-\pi}^{\pi} d^d\theta [1 - (z/d)\sum_{j=1}^{d} \cos\theta_j]^{-1}$ and on performing the integrals we find

$$V_0 = \begin{cases} \infty \ , & d = 1, 2 \\ 1.5163860\dots, & d = 3, \end{cases} \tag{86}$$

and finite in other higher dimensions. The integral for V_0 can be performed exactly in $d = 3$ and is easy to compute numerically in higher dimensions, and approaches the value 1 in higher dimensions. From Eq. 84 we then get **Polya's** result:

$$R_0 = \begin{cases} 1 \ , & d = 1, 2 \\ 0.340537\dots, & d = 3, \end{cases} \tag{87}$$

and smaller return probabilities in higher dimensions.

Problem: Prove that on a finite lattice the probability of visit is unity in all dimensions.

Probability of visit to a another site: We can repeat a similar computation to find the probability that, starting from the origin, we will ever visit a particular location $\mathbf{X}$. In this case the mean number of visits $V_{\mathbf{X}} = G(\mathbf{X}, 1)$ can be related to the first visit probability $R_{\mathbf{X}}$ through the equation:

$$V_{\mathbf{X}} = 1.R_{\mathbf{X}}.(1 - R_0) + 2.R_{\mathbf{X}}.R_0.(1 - R_0) + 3.R_{\mathbf{X}}.R_0^2.(1 - R_0) + \dots \tag{88}$$

$$= R_{\mathbf{X}}(1 - R_0)^{-1} = R_{\mathbf{X}}V_0 \ . \tag{89}$$

Hence we have

$$R_{\mathbf{X}} = \frac{V_{\mathbf{X}}}{V_0}. \tag{90}$$

Evaluating the integrals explicitly it is easy to see that in one and two dimensions, we would visit any site (at a finite distance) with probability one. In higher dimension this is less than one and decays with distance from the origin.

We next ask for the distribution of times that the walker takes to visit a given site. Let $P_1(\mathbf{X}, n)$ be the probability that the walker visits $\mathbf{X}$ for the first time at the n^{th} time step. Let us define the corresponding generating function

$$F(\mathbf{X}, z) = \sum_{n=0}^{\infty} P_1(\mathbf{X}, n) z^n. \tag{91}$$

Similar to the expressions in Eqs. (82,88) we can write

$$P(\mathbf{0}, n) = \delta_{n,0} + \sum_{k=0}^{n} P_1(\mathbf{0}, n-k) P(\mathbf{0}, k) \tag{92}$$

$$P(\mathbf{X}, n) = \sum_{k=0}^{n} P_1(\mathbf{X}, n-k) P(\mathbf{0}, k) \ . \tag{93}$$

Multiplying by z^n and summing from $n = 0$ to ∞ we get the relations

$$\begin{aligned} G(\mathbf{0}, z) &= 1 + F(\mathbf{0}, z) G(\mathbf{0}, z) \\ G(\mathbf{X}, z) &= F(\mathbf{X}, z) G(\mathbf{0}, z), \end{aligned} \tag{94}$$

which can be solved for F to give

$$\begin{aligned} F(\mathbf{0}, z) &= 1 - G^{-1}(\mathbf{0}, z) \\ F(\mathbf{X}, z) &= G(\mathbf{X}, z) G^{-1}(\mathbf{0}, z). \end{aligned} \tag{95}$$

Thus since we know the formal exact form of generating function G, the above relations provide us the generating function F for the first passage distribution $P_1(\mathbf{X}, n)$. This can now be obtained by inverting Eq. (91):

$$P_1(\mathbf{X}, n) = \frac{1}{2\pi i} \int dz \frac{F(\mathbf{X}, z)}{z^{n+1}}. \tag{96}$$

In general it is not possible to perform this integral but this form is useful to extract asymptotic properties of the first passage distribution, in particular it's form at large n. We now present a heuristic approach to see how this is done.

Heuristics: Let us consider the following series:

$$A(z) = \sum_{n=0}^{\infty} f(n) z^n \ . \tag{97}$$

For $z \approx 1$, let us set $z = e^{-s}$ with $0 < s << 1$ and let $\tilde{A}(s) = A(z)$. In this case a large number of terms in the sum will contribute and so we can replace the sum by an integral

$$\tilde{A}(s) = \int_0^{\infty} dn' f(n') e^{-n's} \approx \int_0^{1/s} dn' f(n'). \tag{98}$$

Now let us set $s = 1/n$ and differentiate the above equation with respect to n. this leads to the relation

$$f(n) = \frac{d}{dn} \tilde{A}(1/n). \tag{99}$$

Thus by looking at the small s behaviour of $\tilde{G}(\mathbf{X}, s) = G(\mathbf{X}, e^{-s})$ and $\tilde{F}(\mathbf{X}, s) = F(\mathbf{X}, e^{-s})$, we should be able to predict the large n behaviour of $P(\mathbf{X}, n)$ and $P_1(\mathbf{X}, n)$.

Examples: Let us consider the problem of return time distribution, i.e we take $\mathbf{X} = \mathbf{0}$, in dimensions $d = 1, 2$. For $z \approx 1$, the divergent contribution from $\boldsymbol{\theta} = 0$ are most important and we can approximate $\cos\theta = 1 - \theta^2/2$. Then one finds

$$G(\mathbf{0}, z) \approx \begin{cases} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\theta \frac{1}{1 - z + \theta^2/2} \sim (1-z)^{1/2} & d = 1, \\ \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} d\theta\theta \frac{1}{1 - z + \theta^2/2} \sim -\ln(1-z) & d = 2. \end{cases} \tag{100}$$

Hence we get $\widetilde{G}(\mathbf{0}, s) \sim s^{1/2}, \widetilde{F}(\mathbf{0}, s) \sim 1 - c_1/s^{1/2}$ in $d = 1$ and $\widetilde{G}(\mathbf{0}, s) \sim -\ln(s), \widetilde{F}(\mathbf{0}, s) \sim 1 + c_2/\ln(s)$ in $d = 2$, where c_1 and c_2 are constant factors. Using Eq. (99) we then immediately get the large n forms

$$P_1(\mathbf{0}, n) \sim \begin{cases} \frac{1}{n^{3/2}} & d = 1, \\ \frac{1}{n \ln^2(n)} & d = 2. \end{cases} \tag{101}$$

Exact results in $d = 1$: In dimension $d = 1$ we can compute $P_1(X, n)$ exactly. In this case the Generating function can be obtained by contour integration and one gets

$$G(X, z) = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \frac{e^{-iX\theta}}{1 - z\cos\theta} = \frac{[z^{-1} - (z^{-2} - 1)^{1/2}]^{|X|}}{(1 - z^2)^{1/2}} \ . \tag{102}$$

For $X = 0$ we get $G(0,z) = (1-z^2)^{-1/2}$ and performing a Taylor expansion around $z = 0$ gives $G(0,z) = \sum_{n=0}^{\infty} \frac{(2n)!}{2^{2n}n!n!} z^{2n}$, which gives us the expected known result for $P(0,n)$. Next we note that $F(0,z) = 1 - G^{-1}(0,z) = 1 - (1-z^2)^{1/2}$ so that

$$\frac{dF}{dz} = zG(z) = \sum_{n=0}^{\infty} \frac{(2n)!}{2^{2n}n!n!} z^{2n+1}.$$

$$\text{Hence } F(0,z) = \sum_{n=0}^{\infty} \frac{(2n)!}{(2n+2)2^{2n}n!n!} z^{2n+2} = \sum_{n=0}^{\infty} \frac{(2n-2)!}{(2n)2^{2(n-1)}(n-1)!(n-1)!} z^{2n}$$

$$= \sum_{n=0}^{\infty} \frac{(2n)!}{(2n-1)2^{2n}n!n!} z^{2n}. \tag{103}$$

From this series form we can read off

$$P_1(0,2n) = \frac{(2n)!}{(2n-1)2^{2n}n!n!} \ , \tag{104}$$

for $n > 0$.

Problem: Verify by exact enumeration the above formula for $P_1(0,2) = 1/2,\ P_1(0,4) = 1/8,\ P_1(0,6) = 1/16,\ P_1(0,4) = 5/128$.

Finding $P_1(X,n)$ for $X \neq 0$ by inverting $F(X,z)$ is not trivial and we now discuss a second approach for the first passage problem.

5.2 Method of absorbing boundary condition

First passage from 0 **to** Y: Since we are asking for the time for first passage from $\mathbf{0}$ to $\mathbf{Y}$, this means that we are looking at trajectories which end at bfY. Hence let us consider the problem where we put the absorbing boundary condition $P(\mathbf{Y},n) = 0$ so that there is no probability of transitions out of the site $\mathbf{Y}$. Suppose we solve the diffusion equation with this boundary condition and the initial condition $P(\mathbf{Y}, n=0) = \delta_{\mathbf{Y},\mathbf{0}}$ and let us indicate the solution as $P^{A_Y}(\mathbf{X},n)$. This probability gets contributions from all paths of length n which do not cross the point $\mathbf{X}$. Hence it is clear that we can obtain, for $d > 1$

$$P_1(\mathbf{Y},n) = \frac{1}{2d} \sum_{\mathbf{X} \in <\mathbf{Y}>} P^{A_Y}(\mathbf{X}, n-1), \tag{105}$$

where $<\mathbf{Y}>$ denotes all the $2d$ neigboring sites of $\mathbf{Y}$. For $d = 1$, we have

$$P_1(Y,n) = \frac{1}{2} P^{A_Y}(Y-1, n-1). \tag{106}$$

Solution in $d = 1$: In this case it is easy to see, by the method of images, that

$$P^{A_Y}(X,n) = P(X,n) - P(2Y - X, n), \tag{107}$$

where $P(X,n)$ is the solution of the free random walk on the infinite lattice with initial condition $X=0$. Hence from Eq. (106) we get

$$\begin{aligned} P_1(Y,n) &= \frac{1}{2}\left[P(Y-1,n-1) - P(Y+1,n-1)\right] \\ &= \frac{1}{2^n}\left[\frac{(n-1)!}{\frac{n-Y}{2}!(\frac{n+Y}{2}-1)!} - \frac{(n-1)!}{(\frac{n-Y}{2}-1)!\frac{n+Y}{2}!}\right] \\ &= \frac{Y}{n}P(Y,n). \end{aligned} \tag{108}$$

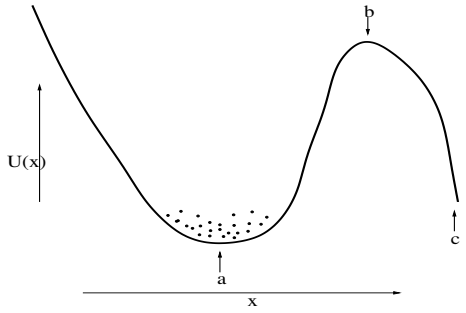
This formula is valid for $Y>0$. For $Y=0$, we can consider the first step to be either to the left or right and then ask for the first passage in the remaining $n-1$ steps from 0 to $Y=1$. Thus

$$P_1(0,2n) = P_1(1,2n-1), \tag{109}$$

which agrees with the result in Eq. (104).

5.3 Kramer's escape rate: a physical derivation

Consider a collection of independent Brownian particles in a potential $U(x)$ which has the shape shown in the figure below. Let us assume that the well is very deep and initially the particles are within the well. Physically we expect that the particles will reach a close-to-equilibrium state but will leak out slowly across the barrier. What is the rate at which this escape takes place ? This is the Kramer's escape rate problem.



Let us first write the Langevin equation for the particles. We will work in the overdamped limit where it is ok to drop the inertial term $m\dot{v}$. Thus we have the equation:

$$\gamma\dot{x} = -\frac{\partial U(x)}{\partial x} + \eta. \tag{110}$$

The corresponding Fokker-Planck equation for the probability density $P(x,t)$ is given by

$$\begin{aligned}\frac{\partial P(x,t)}{\partial t} &= \frac{\partial}{\partial x}\left[\frac{1}{\gamma}\frac{\partial U}{\partial x}P(x,t)\right] + D\frac{\partial^2 P(x,t)}{\partial x^2} \\ &= \frac{\partial}{\partial x}\left[\frac{1}{\gamma}\frac{\partial U}{\partial x}P(x,t) + D\frac{\partial P(x,t)}{\partial x}\right] = -\frac{\partial J}{\partial x} \qquad (111)\end{aligned}$$

$$\text{where} \quad J = -\frac{1}{\gamma}\frac{\partial U}{\partial x}P(x,t) - D\frac{\partial P(x,t)}{\partial x} \quad \text{and} \quad D\gamma = k_B T \qquad (112)$$

We can rewrite the current in the following form:

$$J = -De^{-\frac{U(x)}{k_B T}}\frac{\partial}{\partial x}\left[e^{\frac{U(x)}{k_B T}}P\right] \qquad (113)$$

If the system was completely in equilibrium there would be no currents $J = 0$ and we would therefore get

$$P(x) = e^{-\frac{U(x)}{k_B T}}P_0 \qquad (114)$$

where W_0 can be determined from normalization. This is the expected equilibrium distribution. However with the given form of $U(x)$ the system cannot be exactly in equilibrium (WHY!!!). Let us thus assume that the particles are approximately in equilibrium at the bottom of the well and there is a small current J across the barrier. With $\partial P/\partial t \approx 0$, the current J will be independent of x and from Eq. 113 we get

$$\frac{\partial}{\partial x}\left[e^{\frac{U(x)}{k_B T}}P\right] = -\frac{J}{D}e^{\frac{U(x)}{k_B T}} \qquad (115)$$

Integrating this between the points a and c gives

$$\left[e^{\frac{U(x)}{k_B T}}P\right]_a^c = -\frac{J}{D}\int_a^c e^{\frac{U(x')}{k_B T}}dx' \qquad (116)$$

But $P(x)$ is very small at c. Hence we get

$$\begin{aligned}-e^{\frac{U(a)}{k_B T}}P(x=a) &= -\frac{J}{D}\int_a^c e^{\frac{U(x')}{k_B T}}dx' \\ \Rightarrow J &= \frac{De^{\frac{U(a)}{k_B T}}P(a)}{\int_a^c e^{\frac{U(x')}{k_B T}}dx'} \qquad (117)\end{aligned}$$

The escape rate r can now be obtained by noting that this gives the *conditional* probability of escape per unit time, given that the particle is initially inside the well near $x = a$. Thus if we define p as the probability of the particle being inside the well then $J = pr$. To evaluate p we first note that if the barrier is high then we have (approximately) the equilibrium relation:

$$P(x) = P(a)e^{-\frac{U(x)-U(a)}{k_B T}} \qquad (118)$$

The probability of finding a particle in the well is thus

$$p = \int_{a-\Delta}^{a+\Delta} P(x)dx = P(a)e^{\frac{U(a)}{k_BT}} \int_{a-\Delta}^{a+\Delta} e^{-\frac{U(x)}{k_BT}} \tag{119}$$

where Δ is of the order of the size of the well. Again the integrand is peaked about the point $x = a$ and expanding about it gives

$$p = P(a)(\frac{2\pi k_BT}{|U''(a)|})^{1/2} \tag{120}$$

In Eq. 117 the integrand in the denominator is peaked about the point $x = b$. Expanding about this point then gives

$$\int_a^c e^{\frac{U(x')}{k_BT}} dx' = \int_a^c e^{[U(b)+U''(b)(x-b)^2/2+...]/(k_BT)} dx' \approx e^{\frac{U(b)}{k_BT}} \int_{-\infty}^{\infty} e^{-\frac{|U''(b)|(x-b)^2}{2k_BT}} dx' = (\frac{2\pi k_BT}{|U''(b)|})^{1/2} e^{\frac{U(b)}{k_BT}} \tag{121}$$

Using this and Eq. 120 we finally get, from $r = J/p$, the Kramer's escape rate formula:

$$r = \frac{D}{2\pi k_BT}[U''(a)|U''(b)|]^{1/2} e^{-\frac{E_b}{k_BT}} \tag{122}$$

where $E_b = U(b) - U(a)$ is the barrier height. Thus the escape rate falls exponentially with the barrier height. It also depends on how flat the potential is at the points $x = a$ and $x = b$. As expected the escape rate increases with increasing temperature ($D/k_BT = 1/\gamma$) depends weakly on temperature). Also note that the formula can only be applied for $E_b >> k_BT$ because the assumptions that have been made while deriving it hold only in this regime.

REFERENCES:

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6 Linear response theory

We consider a system described by a microscopic Hamiltonian H_0 that is in thermal equilibrium at temperature T at some time t_0. Let the system be described by the phase space variables $\mathbf{q} = \{x_1, x_2, \ldots, x_N, p_1, p_2, \ldots, p_N\}$. Let us imagine that at time t_0 we switch on a time-dependent perturbation in the system. We want to study the response of the system to the perturbation. For this we measure the expectation value of some observable, say $A(\mathbf{q})$.

Let us assume that the perturbation can be described as a change in the Hamiltonian of the form $H_1 = -f(t)B(\mathbf{q})$ and the full Hamiltonian for time $t > t_0$ is given by $H = H_0 + H_1$. We then expect that for a small perturbation the response at time t would be linear in the perturbing field and would depend on the field values at all past times. The general form of the response would thus be

$$\langle \delta A(t) \rangle = \langle A \rangle_H - \langle A \rangle_{H_0} = \int_{t_0}^{t} dt' \chi_{AB}(t - t')\ f(t')\ , \tag{123}$$

and this defines the response function χ_{AB}. We will now try to obtain an expression for this nonequilibrium response function in terms of equilibrium correlation functions.

6.1 Linear response theory for classical Hamiltonian systems

At time t_0 the system is described by the canonical phase space distribution function $\rho_0(\mathbf{q}) = e^{-\beta H_0}/Z_0$. On applying a perturbation of the form $H_1 = -f(t)B(\mathbf{x},\mathbf{p})$ this distribution evolves through the Liouville equation given by

$$\begin{aligned}
\frac{\partial \rho(\mathbf{x},\mathbf{p})}{\partial t} &= \{H,\rho\} = \{H_0,\rho\} - f(t)\{B,\rho\} \\
&= \mathcal{L}_0\rho + f(t)\mathcal{L}_1\rho \\
\text{where } \mathcal{L}_0 &= \sum_{i=1}^{N}\left(\frac{\partial H_0}{\partial x_i}\frac{\partial}{\partial p_i} - \frac{\partial H_0}{\partial p_i}\frac{\partial}{\partial x_i}\right) \ , \quad \mathcal{L}_1 = -\sum_{i=1}^{N}\left(\frac{\partial B}{\partial x_i}\frac{\partial}{\partial p_i} - \frac{\partial B}{\partial p_i}\frac{\partial}{\partial x_i}\right) \ . \qquad (124)
\end{aligned}$$

In the above we have expressed the Poisson brackets explicitly in the form of linear operators. A formal solution of the linear equation can be written as

$$\rho(t) = e^{\mathcal{L}_0(t-t_0)}\ \rho(t_0) + \int_{t_0}^{t} dt' f(t') e^{\mathcal{L}_0(t-t')}\mathcal{L}_1\rho(t') \ . \qquad (125)$$

The distribution at time t_0, $\rho(t_0) = \rho_0$ is invariant under the unperturbed dynamics, hence $\mathcal{L}_0\rho_0 = 0$ and this means that the first term on the *rhs* of above equation gives $e^{\mathcal{L}_0(t-t_0)}\ \rho(t_0) = \rho_0$. In the second term, we follow the usual approach of perturbation theory and replace $\rho(t')$ by ρ_0 to get, after setting $t_0 = -\infty$,

$$\rho(t) = \rho_0 + \int_{-\infty}^{t} dt' f(t') e^{\mathcal{L}_0(t-t')}\mathcal{L}_1\rho_0 \ . \qquad (126)$$

We rewrite $\mathcal{L}_1\rho_0$ in the following way:

$$\mathcal{L}_1\rho_0 = -\{B,\rho_0\} = \beta\{B,H_0\}\ \rho_0 = -\beta(\mathcal{L}_0 B)\rho_0. \qquad (127)$$

The expectation value of any observable $A(\bar{q})$ at time t is therefore given by

$$\begin{aligned}
\langle A(t)\rangle_H &= \int d\mathbf{q}\ A(\mathbf{q})\rho(\mathbf{q},t) \\
&= \langle A\rangle_{\rm eq} - \beta \int_{-\infty}^{t} dt'\ f(t') \int d\mathbf{q}\ A(\mathbf{q},0)\ e^{\mathcal{L}_0(t-t')}\mathcal{L}_0 B\ \rho_0(\mathbf{q}) \ . \qquad (128)
\end{aligned}$$

Hence

$$\chi_{AB} = \frac{\delta\langle A\rangle(t)}{\delta f(t')} = -\beta \int d\mathbf{q}\ A(\mathbf{q},0)\ e^{\mathcal{L}_0(t-t')}\mathcal{L}_0 B\ \rho_0(\mathbf{q}) \ . \qquad (129)$$

Now we make the following two observations:
(i) The operator $\mathcal{L}_0$ is anti-Hermitian, so that for any two normalizable functions g and h, we have

$$\int d\mathbf{q}\ g^*(\mathbf{q})\mathcal{L}_0 h(\mathbf{q}) = -\int d\mathbf{q}\ h(\mathbf{q})[\mathcal{L}_0 g(\mathbf{q})]^*. \qquad (130)$$

(ii) The rate of change of any phase space function, say C, under evolution with H_0 is given by

$$\begin{aligned} dC(\mathbf{q})/dt &= \sum_i \dot{x}_i \; \partial C(\mathbf{q})/\partial x_i + \dot{p}_i \; \partial C(\mathbf{q})/\partial p_i \\ &= -\{H_0, C\} = -\mathcal{L}_0 C. \end{aligned} \tag{131}$$

Hence we have $C(t) = e^{-\mathcal{L}_0 t} \; C$.

Example: Consider the simple harmonic oscillator with $H = p^2/2 + \omega^2 x^2/2$. We know that for initial conditions $x(t) = x, p(t) = p$, the solution at time t is $x(t) = \cos(\omega t)x + \sin(\omega t)p/\omega$. Let us verify if we are able to get this also from the form $x(t) = e^{-\mathcal{L}_0 t}x$. Explicitly we get

$$e^{-\mathcal{L}_0 t}x = x - \mathcal{L}_0 t x + \frac{\mathcal{L}_0^2 t^2}{2}x^2 - \frac{\mathcal{L}_0^3 t^3}{3!}x^3 + \frac{\mathcal{L}_0^4 t^4}{4!}x^4 \ldots \tag{132}$$

From the definition of the Liouville operator, one has $\mathcal{L}_0 x = -p, \; \mathcal{L}_0 p = \omega^2 x$, and by repeatedly acting with $\mathcal{L}_0$, we then get

$$\begin{aligned} e^{-\mathcal{L}_0 t}x &= x + pt - \frac{\omega^2 t^2}{2}x - \frac{\omega^2 t^3}{3!}p^3 + \frac{\omega^4 t^4}{4!}x^4 \ldots \\ &= \cos(\omega t)x + \frac{\sin(\omega t)}{\omega}p, \end{aligned} \tag{133}$$

in agreement with the known exact formula.

Using (i) and (ii) we then get from Eq. (129)

$$\begin{aligned} \chi_{AB}(t - t') &= -\beta \int d\mathbf{q} \; A(\mathbf{q}, 0) \; e^{\mathcal{L}_0 (t-t')} \mathcal{L}_0 B \; \rho_0(\mathbf{q}) \\ &= \beta \int d\mathbf{q} \; \mathcal{L}_0 (e^{-\mathcal{L}_0 t} A \;) \; (e^{-\mathcal{L}_0 t'} B) \; \rho_0(\mathbf{q}) \\ &= -\beta \frac{d}{dt} \langle A(t) B(t') \rangle_{\text{eq}}. \end{aligned} \tag{134}$$

This is one of the central results of linear response theory. We note some important points.

- Since the response function only depends on the time difference we can write:

$$\chi_{AB}(t) = -\beta \; \frac{d}{dt} \langle A(t) \; B(0) \rangle_{\text{eq}} \; = -\beta \; \langle \dot{A}(t) B(0) \rangle_{\text{eq}} \; , \tag{135}$$

  where we should remember that the average is with respect to initial conditions chosen from $\rho_0(\mathbf{q}) = e^{-\beta H_0}/Z_0$.

- The quantity $\dot{A}$ is again some function of phase-space variables. In this equation, to find $A(t)$ or $\dot{A}(t)$, we evolve with the *unperturbed* Hamiltonian H_0.

- We can write the linear response formula in a slightly different form. Let $\Delta A(t) = A(t) - \langle A \rangle_{\text{eq}}, \Delta B(t) = B(t) - \langle B \rangle_{\text{eq}}$. Then it is easy to see that $\langle \Delta A(t) \Delta B(0) \rangle_{\text{eq}} = \langle A(t) B(0) \rangle_{\text{eq}} - \langle A \rangle_{\text{eq}} \langle B \rangle_{\text{eq}}$, hence it is clear that

$$\chi_{AB}(t) = -\beta \frac{d}{dt} \; \langle \Delta A(t) \Delta B(0) \rangle \; , \tag{136}$$

  where $\Delta A = A - \langle A \rangle$.

Problem: Consider a single particle described by a Hamiltonian $H_0 = p^2/2 + U(x)$, with two different choices of the potential (a)$U(x) = x^2/2$ and (b)$U(x) = x^2/2 + x^4/4$. Choosing initial conditions from the distribution $\rho_0(x,p) = e^{-\beta H_0}/Z_0$ (you need to figure out how to draw random number z from a specified distribution $p(z)$), and using a 4th order Runga-Kutta code to evolve the system, compute the correlation function $C(t) = \langle x(0)x(t)\rangle_{\rm eq}$. For the harmonic case, compare with the exact result. Take temperature $T = 1$.
Next, from the simulation directly compute the response $\delta\langle x(t)\rangle$ to a small external force of the form $f(t) = \epsilon$ for $0 < t < 10$. Compare the response with what you get from the linear response formulam using the numerical $C(t)$ obtained in previous part.

Reference: `https://web.stanford.edu/~hca/c276autumn2009/`

6.2 Linear response theory for Markov processes

Let us consider a general system which is described by coordinates $\mathbf{q}$, and with the probability $P(\mathbf{q})$'s evolution given by the linear Fokker-Planck equation

$$\frac{\partial P(\mathbf{q})}{\partial t} = \mathcal{L}P = [\mathcal{L}_0 + f(t)\mathcal{L}_1]\, P, \tag{137}$$

where $\mathcal{L}_0$ is the unperturbed operator whose steady state solution is the equilibrium state, *i.e* $\mathcal{L}_0\rho_0 = 0$, and $f(t)\mathcal{L}_1$ represents a time dependent perturbation of the dynamics. Standard perturbation theory, as detailed in the previous section, then leads to the result for the response

$$\begin{aligned}\chi(t-t') = \frac{\delta A(t)}{\delta f(t')} &= \int d\mathbf{q} A(\mathbf{q}) e^{\mathcal{L}_0(t-t')}[\mathcal{L}_1\rho_0(\mathbf{q})] \\ &= \int d\mathbf{q} A(\mathbf{q}) e^{\mathcal{L}_0(t-t')}[\rho_0^{-1}(\mathbf{q})\mathcal{L}_1\rho_0(\mathbf{q})\rho_0(\mathbf{q})] \\ &= \int d\mathbf{q} A(\mathbf{q}) e^{\mathcal{L}_0(t-t')}[C(\mathbf{q})\rho_0(\mathbf{q})], \end{aligned} \tag{138}$$

$$\text{where} \quad C(\mathbf{q}) = \rho_0^{-1}(\mathbf{q})\mathcal{L}_1\rho_0(\mathbf{q})\ . \tag{139}$$

Form of equilibrium correlations: We note that the two-time correlation function between any two observables A and C, in the equilibrium state ρ_0, is given by

$$\begin{aligned}\langle A(t)C(t')\rangle_{\rm eq} &= \int d\mathbf{q} \int d\mathbf{q})' A(\mathbf{q}) C(\mathbf{q}') P(\mathbf{q}t|\mathbf{q}'t')\rho_0(\mathbf{q}') \\ &= \int dq \int dq' A(\mathbf{q}) C(\mathbf{q}') e^{\mathcal{L}_0(t-t')}\delta(\mathbf{q}-\mathbf{q}')\rho_0(\mathbf{q}') \\ &= \int d\mathbf{q} A(\mathbf{q}) e^{\mathcal{L}_0(t-t')}[C(\mathbf{q})\rho_0(\mathbf{q})]. \end{aligned} \tag{140}$$

Hence comparing the forms in Eq. (138) and Eq. (140) we get the general relation between response and correlations

$$\chi(t-t') = \langle A(t)C(t')\rangle_\beta, \quad \text{where} \quad C = \rho_0^{-1}\mathcal{L}_1\rho_0. \tag{141}$$

Let us now look at some specific examples.
(i) Single-particle overdamped Langevin equation: We consider the dynamics $dx/dt = -(1/\gamma)\partial U/\partial x + \sqrt{2D}\xi + f(t)/\gamma$, so that

$$\mathcal{L}_0 = D\partial_x^2 + \partial_x \frac{1}{\gamma}\partial U/\partial x,$$
$$\mathcal{L}_1 = -\frac{1}{\gamma}\partial_x \ , \quad \rho_0 = e^{-\beta U}/Z_0 \ . \tag{142}$$

Hence one gets

$$C = \frac{\beta}{\gamma}\partial U/\partial x. \tag{143}$$

Next we use the relation $\mathcal{L}_0(x\rho_0) = -U'\rho_0/\gamma$ (**Verify**) to get

$$\chi = \int dx A(x) e^{\mathcal{L}_0(t-t')}(\beta U'/\gamma)\rho_0(x) = -\beta \int dx A(x) e^{\mathcal{L}_0(t-t')}\mathcal{L}_0(x\rho_0)$$
$$= -\beta \frac{d}{dt}\langle A(t)x(t')\rangle. \tag{144}$$

More generally let us suppose that the external time-dependent force is of the form $-\partial_x[-f(t)B(x)] = f(t)B'(x)$. Then we have $\mathcal{L}_1 = -(1/\gamma)\partial_x B'(x)$ and hence we get

$$C = -\rho_0(1/\gamma)\partial_x B'\rho_0 = -B''/\gamma + (\beta/\gamma)B'U'. \tag{145}$$

Again it can be easily checked that this precisely equals $-\beta\mathcal{L}_0(B\rho_0)$ (**Verify**). Hence we then get the response to this perturbation as

$$\chi_{AB} = -\beta \int dx A(x) e^{\mathcal{L}_0(t-t')}\mathcal{L}_0[B(x)\rho_0(x)]$$
$$= -\beta \frac{d}{dt}\langle A(t)B(t')\rangle. \tag{146}$$

(ii) Single-particle under-damped Langevin equation: We consider the dynamics $dx/dt = p/m, dp/dt = -U'(x) - \gamma p/m + \sqrt{2\gamma k_B T}\xi + f(t)B'(x)$, so that

$$\mathcal{L}_0 = \gamma k_B T\partial_p^2 + (\gamma/m)\partial_p p + \partial_p(U') - (1/m)\partial_x p,$$
$$\mathcal{L}_1 = -B'(x)\partial_p \ , \quad \rho_0 = e^{-\beta(p^2/2m+U)}/Z_0 \ . \tag{147}$$

Hence

$$C = -\rho_0\partial_p B'\rho_0 = \beta/mpB'(x) = -\beta\mathcal{L}_0[B(x)\rho_0(x,p)], \tag{148}$$

where the last step is easy to verify explicitly (**Do so**). Thus we finally get

$$\chi_{AB} = -\beta \int dxdp A(x,p) e^{\mathcal{L}_0(t-t')}\mathcal{L}_0 B(x)\rho_0(x,p)$$
$$= -\beta \frac{d}{dt}\langle A(t)B(t')\rangle_{\rm eq}. \tag{149}$$

Problem: Consider a set of N interacting Brownian particle described by the overdamped Langevin equations

$$\dot{x}_i = -(1/\gamma)\partial_{x_i}[U(\mathbf{x}) - f(t)B(\mathbf{x})] + \sqrt{D}\eta_i, \tag{150}$$

where $U = U(x_1, x_2, \ldots, x_N)$ is a general interaction potential and the Gaussian noise terms have zero mean and correlations $\langle \eta_i(t)\eta_j(t')\rangle = \delta_{ij}\delta(t-t')$. Using the above approach, show that

$$\frac{\delta\langle A\rangle(t)}{\delta f(t')} = -\beta\frac{d}{dt}\langle A(t)B(t')\rangle_{\rm eq}. \tag{151}$$

In particular this gives for the choice $A = x_i, B = x_j, f(t) = f_j(t)$

$$\chi_{ij}(t-t') = \frac{\delta\langle x_i\rangle(t)}{\delta f_j(t')} = -\beta\frac{d}{dt}\langle x_i(t)x_j(t')\rangle_{\rm eq}. \tag{152}$$

Perform simulations for a single particle in a potential well with (a) $U(x) = x^2/2$, (b) $U(x) = x^2/2 + x^4/4$ to compute the correlation $\langle x(0)x(t)\rangle$. For the harmonic case, also compute this analytically and compare with the simulation result. Plot the results for the harmonic and anharmonic cases together and comment on the qualitative differences.

Reference: Chapter 7, The Fokker-Planck equation - H Risken.

6.3 Response functions in frequency domain

Let us consider an oscillatory perturbation of the form $f(t) = Re[\tilde{f}(\omega)\ e^{-i\omega t}]$ acting from time $t_0 = -\infty$. Then from Eq. (123) the response is given by the real part of

$$\begin{aligned}\int_{-\infty}^{t} dt'\chi_{AB}(t-t')\tilde{f}(\omega)e^{-i\omega t'} &= \int_{-\infty}^{\infty} dt'\chi_{AB}(t-t')\ \theta(t-t')\ e^{i\omega(t-t')}\ \tilde{f}(\omega)e^{-i\omega t} \qquad (153)\\ &= \widetilde{\chi}_{AB}(\omega)\tilde{f}(\omega)e^{-i\omega t}\ ,\\ \text{where}\ \ \widetilde{\chi}_{AB}(\omega) &= \int_0^{\infty} dt\ \chi_{AB}(t)\ e^{i\omega t}\ . \qquad (154)\end{aligned}$$

Thus the response has the same oscillatory time-dependence. In general $\widetilde{\chi}_{AB}(\omega)$ is complex, meaning that there is a phase-lag between the driving and the response.

We now consider the special case $A = B$. Let the real and imaginary parts of the frequency response function be denoted by $\widetilde{\chi}'_{AA}(\omega)$ and $\widetilde{\chi}''_{AA}(\omega)$ respectively so that $\widetilde{\chi}_{AA}(\omega) = \widetilde{\chi}'_{AA}(\omega) + i\widetilde{\chi}''_{AA}(\omega)$. Also let us define $C_{AA}(t) = \langle \Delta A(t)\Delta A\rangle$ and

$$\widetilde{C}_{AA}(\omega) = \int_{-\infty}^{\infty} dt\ C_{AA}(t)\ e^{i\omega t} = 2\int_0^{\infty} dt\ C_{AA}(t)\ \cos(\omega t) \tag{155}$$

where we used the fact that time translational invariance implies $C_{AA}(t) = C_{AA}(-t)$. Using Eq. (136) we then get

$$\widetilde{\chi}_{AA}(\omega) = -\beta \int_0^\infty dt \ \frac{d}{dt} \ \langle \Delta A(t) \Delta A(0) \rangle \ e^{i\omega t} = \beta \langle \Delta A^2(0) \rangle + i\omega\beta \int_0^\infty dt C_{AA}(t) \ e^{i\omega t} \ . \tag{156}$$

Comparing the real and imaginary parts of both sides we get

$$\widetilde{\chi}'_{AA}(\omega) = \beta \langle \Delta A^2(0) \rangle - \beta\omega \ \int_0^\infty dt \ C_{AA}(t) \ \sin(\omega t) \tag{157}$$

$$\widetilde{\chi}''_{AA}(\omega) = \frac{\beta\omega}{2} \widetilde{C}_{AA}(\omega) \ . \tag{158}$$

As we will show now, the imaginary part of the frequency response function, is related to the dissipation in the system. The relation Eq. (158) relates the dissipation to the fluctuations in the system and is refered to as a *fluctuation-dissipation-theorem*.

6.4 Power dissipation

Since the external perturbation is driving the system, it is performing work on the system which must eventually be dissipated as heat. To find the rate of dissipation we find the average rate at which the internal energy of the system changes. This is given by

$$\begin{aligned} W = \frac{d\langle H_0 \rangle}{dt} &= \frac{d}{dt} \int d\mathbf{q} \ H_0(\mathbf{q}) \rho(\mathbf{q}, t) \\ &= \frac{d}{dt} \int d\mathbf{q} H_0(\mathbf{q}) \ e^{Lt} \rho(\mathbf{q}, 0) \\ &= \frac{d}{dt} \int d\mathbf{q} [e^{-Lt} H_0(\mathbf{q})] \rho(\mathbf{q}, 0) \\ &= \int d\mathbf{q} \frac{dH_0(\mathbf{q}_t)}{dt} \rho_0(\mathbf{q}), \end{aligned} \tag{159}$$

where we used the antihermiticity of L and the interpretation of the operator $e^{-Lt}A(\mathbf{q})$ discussed earlier. Now $dH_0/dt = (d/dt) \ [H + f(t)A] = \partial H/\partial t + \dot{f}A + f\dot{A} = f\dot{A}$. Hence we get

$$W = \frac{d\langle H_0 \rangle}{dt} = \int d\mathbf{q} \ f \ \dot{A}\rho = f(t) \ \langle \dot{A} \rangle \ . \tag{160}$$

Now consider the oscillatory force $f(t) = Re[\tilde{f}e^{-i\omega t}] = (\tilde{f}e^{-i\omega t} + \tilde{f}^* e^{i\omega t})/2$. As seen from Eq. (153) the response is given by $\langle \delta A(t) \rangle = (\widetilde{\chi} \ \tilde{f}e^{-i\omega t} + \widetilde{\chi}^* \ \tilde{f}^* e^{i\omega t})/2$ and hence

$$\langle \dot{A} \rangle = -\frac{i\omega}{2} \ [\ \widetilde{\chi} \ \tilde{f}e^{-i\omega t} - \widetilde{\chi}^* \ \tilde{f}^* e^{i\omega t} \ ] \ . \tag{161}$$

To find the average dissipation rate we average $W = f(t)\langle \dot{A} \rangle$ over the time period $2\pi/\omega$. This then gives

$$\overline{W} = \frac{\omega}{2} \ |\tilde{f}(\omega)|^2 \ \widetilde{\chi}(\omega) \ . \tag{162}$$

Thus we see that the power dissipation rate is proportional to the imaginary part of the frequency response function.

6.5 Green-Kubo formula for electrical conductivity

We consider the effect of applying a time-dependent electric field to a system in equilibrium. For an electric field applied along the x-direction the perturbation of the Hamiltonian is given by $H' = -eE(t)\sum_{i=1}^{N} x_i$ where e is the charge of each particle. According to our earlier notation we then have $f(t) = E(t)$ and $B(\mathbf{x}) = e\ \sum_{i=1}^{N} x_i$. The observable of interest here is the charge current $j(x,t)$. The charge density is given by $\rho(x,t) = e\sum_i \delta(x - x_i)$. From the continuity equation $\partial\rho/\partial t + \partial j/\partial x = 0$ it follows that the current density is given by $j(x,t) = e\ \sum_i\ \dot{x}_i\ \delta(x - x_i)$. The total current is given by $J = \int_0^L dx j(x,t) = \sum_i \dot{x}_i$. Here we will be interested finally in the current response to a constant electric field hence we look at the observable $A = J$. From our general linear response formula in Eq. (134), and noting that in the present case $\dot{B} = J$, we immediately get

$$\langle J(t)\rangle = \beta \int_{-\infty}^{t} dt' E(t')\langle J(t-t')J(0)\rangle\ . \tag{163}$$

We now note the following important point: if we apply a constant electric field to a closed finite system then eventually at long times the system will settle to a new equilibrium state with zero current and a non-uniform charge distribution. To set up a steady current in a closed system we need to switch on the field at a rate such that the system is not able to equilibrate — since the equilibration time increases with system size, this is achieved by setting $E(t') = e^{\epsilon t'}E$. We obtain the required steady current at time $t = 0$ by first setting $L \to \infty$ and then taking $\epsilon \to 0$. The average current density is then given by

$$j = \frac{\langle J\rangle}{L} = \beta\ E\ \lim_{\epsilon\to 0}\ \int_0^\infty dt\ e^{-\epsilon t}\ \lim_{L\to\infty}\frac{1}{L}\langle J(t)J(0)\rangle\ . \tag{164}$$

Comparing with the expected form $j = \sigma\ E$ where σ is the electrical conductivity of the system we get the *Green-Kubo* formula

$$\sigma = \beta\ \lim_{\epsilon\to 0}\int_0^\infty dt\ e^{-\epsilon t}\ \lim_{L\to\infty}\frac{1}{L}\langle J(t)J(0)\rangle\ . \tag{165}$$

7 Flutuation theorems and large deviations

8 Microscopic derivation of the Langevin equation

We describe now the simplest derivation of the Langevin equation where the environment is modelled as a collection of harmonic oscillators. Eliminating the environment degrees of freedom leads to an effective equation for the Brownian particle which has noise and dissipation terms, and that are related by the fluctuation dissipation theorem. In fact this approach lead to what is called the generalized Langevin equation which we first describe.

8.1 The generalized Langevin equation

In the simple Langevin equation that we wrote in Sec. [2], the disipative part is instantaneous and the noise is uncorrelated in time. This is not a very good model of real heat baths and a more appropriate description is in terms of the generalized Langevin equation. This is given by the equation

$$m\ddot{x} = -k\ x - \int_{-\infty}^{t} dt' \alpha(t-t') u(t') + \eta(t)\ , \tag{166}$$

where $\eta(t)$ is again a Gaussian noise but with the following correlations:

$$\begin{aligned} \langle \eta(t) \rangle &= 0 \\ \langle\ \eta(t)\eta(t')\ \rangle &= k_B T \alpha(t-t')\ . \end{aligned} \tag{167}$$

Thus the friction term involves *memory* and the noise is now *correlated*.

To get steady state properties, we can Fourier transform Eq. (166) to get

$$\begin{aligned} \tilde{x}(\omega) &= \frac{\tilde{\eta}(\omega)}{-m\omega^2 + k - i\omega\alpha^+(\omega)} \\ \text{with} \quad \langle \tilde{\eta}(\omega)\tilde{\eta}(\omega') \rangle &= \frac{k_B T}{2\pi}\tilde{\alpha}(\omega) = \frac{k_B T}{\pi} Re[\alpha^+(\omega)] \\ \text{and} \quad \alpha^+(\omega) &= \int_0^\infty dt\ \alpha(t)\ e^{i\omega t}\ , \qquad \tilde{\alpha}(\omega) = \int_{-\infty}^{\infty} dt\ \alpha(t)\ e^{i\omega t}\ . \end{aligned} \tag{168}$$

Using these we get the following expressions:

$$\begin{aligned} \langle x^2(t) \rangle &= \frac{k_B T}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{\tilde{\alpha}(\omega) + \tilde{\alpha}^*(\omega)}{[-m\omega^2 + k - i\omega\tilde{\alpha}(\omega)][-m\omega^2 + k + i\omega\tilde{\alpha}^*(\omega)]} \\ &= \frac{k_B T}{\pi} Im \left[\int_{-\infty}^{\infty} \frac{d\omega}{\omega} \frac{1}{(-m\omega^2 + k - i\omega\tilde{\alpha}(\omega))} \right] = \frac{k_B T}{k}\ , \end{aligned} \tag{169}$$

$$\langle u^2(t) \rangle = \frac{k_B T}{\pi} Im \left[\int_{-\infty}^{\infty} d\omega \frac{\omega}{(-m\omega^2 + k - i\omega\tilde{\alpha}(\omega))} \right] = \frac{k_B T}{m}\ , \tag{170}$$

$$\tag{171}$$

where the integrals have been performed by taking appropriate contours in the complex ω plane. In performing the integral we use the fact that $\tilde{\alpha}(\omega)$ is an analytic function in the upper half ω-plane and also *assume* that $-m\omega^2 + k - i\omega\tilde{\alpha}(\omega)$ does not have zeros in this region.

8.2 Microscopic derivation of the generalized Langevin equation

As our system (for which we want to derive a Langevin equation) we consider a single harmonic oscillator described by the phase space variables (x, p) and with a natural frequency $\omega_0 = k/m$. The oscillator is coupled to a heat bath (environent) modelled by N independent oscillators described

by $\{X_\alpha, P_\alpha\}$ and which have frequencies $\{\omega_\alpha\}$. To generate dissipation one eventually needs to take the limit $N \to \infty$. The full Hamiltonian of system and bath is taken to be:

$$\begin{aligned} H &= \frac{p^2}{2m} + \frac{m\omega_o^2 x^2}{2} + \sum_{\alpha=1}^{N}[\ \frac{P_\alpha^2}{2} + \frac{\omega_\alpha^2 X_\alpha^2}{2}\ ] - \sum_{\alpha=1}^{N} c_\alpha x X_\alpha \\ &= H_s + H_b + H_{sb}\ . \end{aligned} \tag{172}$$

The last term represents the coupling between the system and the bath. Introducing the shifted frequency $m\omega_s^2 = m\omega_o^2 - \sum_\alpha c_\alpha^2/\omega_\alpha^2$, we can rewrite Eq. (172) in the following equivalent form

$$H = \frac{p^2}{2m} + \frac{m\omega_s^2 x^2}{2} + \sum_{\alpha=1}^{N}[\ \frac{P_\alpha^2}{2} + \frac{\omega_\alpha^2 (X_\alpha - \frac{c_\alpha x}{\omega_\alpha^2})^2}{2}\ ]\ . \tag{173}$$

Let us now write the equations of motion for the system and bath variables. These are given by:

$$m\ddot{x} = -m\omega_o^2 x + \sum_\alpha c_\alpha X_\alpha\ , \tag{174}$$

$$\ddot{X}_\alpha = -\omega_\alpha^2 X_\alpha + c_\alpha x\ . \tag{175}$$

We assume that the reservoir and system interaction is switched on at time $t = t_0$. The solution of the equations of motion, for $t > t_0$, of the reservoir variables is given by:

$$X_\alpha(t) = \cos\omega_\alpha(t-t_0)X_\alpha(t_0) + \frac{\sin\omega_\alpha(t-t_0)}{\omega_\alpha}\dot{X}_\alpha(t_0) + \int_{t_0}^{t} dt' \frac{\sin\omega_\alpha(t-t')}{\omega_\alpha} c_\alpha x(t')\ . \tag{176}$$

Plugging these into the system's equation of motion Eq. (174) we get the following effective equation of motion for the system:

$$m\ddot{x} = -m\omega_o^2 x + \int_{t_0}^{t} dt' \Sigma(t-t')x(t') + \eta(t)\ , \tag{177}$$

$$= -m\omega_o^2 x + \int_{t_0}^{t} dt' \frac{d\alpha(t-t')}{dt'} x(t') + \eta(t)\ , \tag{178}$$

$$\text{where} \quad \Sigma(t) = \sum_\alpha \frac{c_\alpha^2}{\omega_\alpha}\sin(\omega_\alpha t)\ , \quad \alpha(t) = \sum_\alpha \frac{c_\alpha^2}{\omega_\alpha^2}\cos(\omega_\alpha t)\ , \tag{179}$$

$$\eta(t) = \sum_\alpha c_\alpha[\cos\omega_\alpha(t-t_0)X_\alpha(t_0) + \frac{\sin\omega_\alpha(t-t_0)}{\omega_\alpha}\dot{X}_\alpha(t_0)]\ . \tag{180}$$

The above equation looks like a generalized Langevin equation with $\eta(t)$ as the noise term. This is a random variable since it depends on the initial values of the bath degrees of freedom which are chosen from a thermal equilibrium distribution. We thus use the fact that at $t = t_0$ the reservoir (isolated) is prepared in equilibrium and hence we know the statistical properties of the bath variables $\{X_\alpha(0),\ \dot{X}_\alpha(0)\}$. Using equipartition we immediately get:

$$\begin{aligned} \langle\omega_\alpha^2 X_\alpha^2\rangle &= \langle\dot{X}_\alpha^2\rangle = k_B T \\ \langle X_\alpha \dot{X}_\alpha\rangle &= 0 \end{aligned}$$

From these properties of the bath one can work out the correlations of the noise $\eta(t)$ in Eq. (180). We get (for $t, t' > t_0$) the following fluctuation-dissipation relation

$$\langle \eta(t)\eta(t') \rangle = k_B T \alpha(t - t') \ . \tag{181}$$

Finally, after a partial integration, we can rewrite Eq. (178) in the following standard form

$$m\ddot{x} = -m\omega_s^2 x - \alpha(t - t_0)x(t_0) - \int_{t_0}^{t} dt' \alpha(t - t')u(t') + \eta(t) \tag{182}$$

where, as before, we have $m\omega_s^2 = m\omega_o^2 - \alpha(0)$. Setting $t_0 \to -\infty$ and using the fact that $\lim_{t\to\infty} \alpha(t) \to 0$ (true whenever the frequencies ω_α form a continuous spectrum) the above equation reduces to the generalized Langevin equation Eq. (166)

$$m\ddot{x} = -kx - \int_{-\infty}^{t} dt' \alpha(t - t')u(t') + \eta(t) \ , \tag{183}$$

where we made the identification $k = m\omega_s^2$. Note that the natural frequency of the system has got shifted from ω_o to ω_s because of coupling to the heat bath. This can be made to go to zero by taking the limit of vanishing coupling between system and bath.

In the case of finite coupling between system and heat bath it is good to have a clear idea of what exactly we mean when we say that at long times we want that the system should equilibrate. Suppose we consider the phase space distribution function $\rho(x, p, X_\alpha, P_\alpha, t)$ of the system plus bath at time t. At time $t = 0$ we start with $\rho = \rho_s(x, p)\ \rho_b^{eq}(X_\alpha, P_\alpha)$ where $\rho_b^{eq} = e^{-\beta H_b}/Z_b$ is the equilibrium canonical distribution function for the isolated bath while ρ_s is an arbitrary distribution function describing the initial state of the system. Let $\rho_r(x, p, t) = \int \prod_\alpha dX_\alpha dP_\alpha \rho(x, p, \{X_\alpha, P_\alpha\}, t)$ be the reduced distribution function for the system at time t. Also let $\rho^{eq}(x, p, X_\alpha, P_\alpha) = e^{-\beta H}/Z$ be the equilibrium distribution function for the coupled system and reservoir and $\rho_r^{eq}(x, p) = \int \prod dX_\alpha dP_\alpha \rho^{eq}$ be the corresponding reduced equilibrium distribution. Then for *approach to equilibrium* in the long time limit we will require:

$$\lim_{t\to\infty} \rho_r(x, p, t) = \rho_r^{eq}(x, p) \ . \tag{184}$$

Note that, instead of Eq. (185), we can use the following equivalent form:

$$m\ddot{x} = -m\omega_o^2 x + \int_{-\infty}^{t} dt' \Sigma(t - t')x(t') + \eta(t) \ . \tag{185}$$

8.3 Quantum Langevin equation

Let us try to see how we would go about writing a quantum Langevin equation. We start with the same model of a single harmonic oscillator coupled to an oscillator bath and described by the same Hamiltonian as in Eq. (172). The equations of motion Eq. (174,175) still hold once we interpret the variables $\{x, p, X_\alpha, P_\alpha\}$ as operators in the Heisenberg represenation. An operator O satisfies the equation of motion $\dot{O} = -i\ [O, H]$ and applying these it is easily seen that we recover Eq. (174,175).

In fact the discussion till Eq. (180) is valid both clasically and quantum mechanically. However the bath correlations and consequently the noise properties will be different. In the quantum case we get

$$\begin{aligned} \langle\ \omega_\alpha^2 X_\alpha^2(0)\ \rangle = \langle\ \dot{X}_\alpha^2(0)\ \rangle &= \frac{\hbar\omega_\alpha}{2}\coth\frac{\hbar\omega_\alpha}{2k_BT}\ , \\ \langle\ [\ X_\alpha(0)\dot{X}_\alpha(0) + \dot{X}_\alpha(0)X_\alpha(0)\ ]\ \rangle &= 0\ , \end{aligned} \tag{186}$$

and from Eq. (180) the noise correlations follow:

$$\begin{aligned} \langle\ \eta(t)\ \rangle &= 0\ , \\ \frac{1}{2}\langle\ \eta(t)\eta(t') + \eta(t')\eta(t)\ \rangle &= k_BTK(t-t')\ , \end{aligned} \tag{187}$$

$$\text{where}\quad K(t) = \sum_\alpha \frac{c_\alpha^2}{\omega_\alpha^2}\cos\omega_\alpha t\ (\frac{\hbar\omega_\alpha}{2k_BT}\ \coth\frac{\hbar\omega_\alpha}{2k_BT})\ . \tag{188}$$

Note that $K(t)$ reduces to $\alpha(t)$ in the classical limit $\hbar\omega_\alpha/(k_BT) \to 0$. In Fourier space we get:

$$\begin{aligned} \frac{1}{2}\langle\ \eta(\omega)\eta(\omega') + \eta(\omega')\eta(\omega)\ \rangle &= \frac{k_BT}{2\pi}\tilde{K}(\omega)\ \delta(\omega+\omega') \\ &= \frac{k_BTRe[\alpha^+(\omega)]}{\pi}\ (\frac{\hbar\omega}{2k_BT}\coth\frac{\hbar\omega}{2k_BT})\ \delta(\omega+\omega')\ , \end{aligned} \tag{189}$$

which is the quantum version of the fluctuation-dissipation theorem and which reduces to Eq. (168) in the classical limit. One can also show that

$$\langle\ \eta(\omega)\eta(\omega')\ \rangle = Re[\alpha^+(\omega)]\frac{\hbar\omega}{2\pi}\ [\ 1 + f(\omega,T)\ ]\ ,$$

where $f(\omega,T) = 1/[e^{\beta\hbar\omega}-1]$ is the phonon distribution function.

8.4 Examples of heat baths

The only property of the heat bath that we really need is the spectral function $\alpha^+(\omega)$. This function gives us the dissipation kernel $\alpha(t)$ and because of the FD theorem also specifies the noise. Alternatively we may specify the function $\Sigma^+(\omega)$. From the relation $\Sigma(t) = -d\alpha(t)/dt$ we get $\Sigma^+(\omega) = i\omega\alpha^+(\omega) + \alpha(0)$. Let us also make the definition:

$$Im[\Sigma^+(\omega)] = \omega\ Re[\alpha^+(\omega)] = \Gamma(\omega)\ . \tag{190}$$

In terms of the bath and coupling variables $\{\omega_\alpha, c_\alpha\}$ the spectral function $\Sigma^+(\omega)$ is given by:

$$\Sigma^+(\omega) = Re[\Sigma^+(\omega)] + i\Gamma(\omega)\ ,$$

$$\text{where}\quad Re[\Sigma^+(\omega)] = \sum_\alpha \frac{c_\alpha^2}{\omega_\alpha^2 - \omega^2}\ , \tag{191}$$

$$\Gamma(\omega) = \pi\sum_\alpha \frac{c_\alpha^2}{2\omega_\alpha}[\delta(\omega-\omega_\alpha) - \delta(\omega+\omega_\alpha)]\ . \tag{192}$$

8.4.1 Drude model and Ohmic bath

This corresponds to the choice

$$\alpha(t) = \frac{\gamma}{\tau} e^{-|t|/\tau} \ . \tag{193}$$

Hence we get

$$\begin{aligned} \alpha^+(\omega) &= \frac{\gamma}{1+\omega^2\tau^2} + i\frac{\omega\tau\gamma}{1+\omega^2\tau^2} \\ \text{and} \ \ \Sigma^+(\omega) &= \alpha(0) + i\omega\alpha^+(\omega) = \frac{\gamma}{\tau(1+\omega^2\tau^2)} + i\frac{\omega\gamma}{1+\omega^2\tau^2} \ . \end{aligned} \tag{194}$$

The Ohmic bath is obtained by taking the limit $\tau \to 0$ in which case we get

$$\alpha(t) \to 2\gamma\delta(t), \qquad \alpha^+(\omega) = \gamma \ . \tag{195}$$

In this case $\alpha(0) \to \infty$ but we absorb it within the definition of the spring constant of the system (*i.e* define $k = m\omega_s^2 = m\omega_o^2 - \alpha(0)$. In the quantum-mechanical case the noise-noise correlation can be obtained from Eq. (187-188) and is given by:

$$\frac{1}{2}\langle\ \eta(t)\eta(t') + \eta(t')\eta(t)\ \rangle = k_B T K(t-t') = \frac{\gamma}{\pi}\int_0^\infty d\omega\hbar\omega\coth\left(\frac{\hbar\omega}{2k_BT}\right)\ \cos\omega(t-t') \ . \tag{196}$$

8.4.2 Rubin model

In this model the heat bath is taken to be a one-dimensional harmonic chain and the end particle is connected to the system. Thus we have:

$$\begin{aligned} H_s &= \frac{p^2}{2m} + \frac{1}{2}m\omega_o^2 x^2 \\ H_b &= \sum_{l=1,N_b}\frac{p_l^2}{2} + \sum_{l=0,N_b+1} k_0\frac{(x_{l+1}-x_l)^2}{2} \qquad \text{with} \ \ x_0 = x_{N+1} = 0 \\ H_{sb} &= -k' x x_1 \ . \end{aligned}$$

We transform to normal-mode coordinates using $x_l = \sum_\alpha U_{l\alpha}X_\alpha$ and $p_l = \sum_\alpha U_{l\alpha}P_\alpha$. The normal modes for the one-dimensional chain are given by:

$$\begin{aligned} U_{l\alpha} &= \left(\frac{2}{N_b+1}\right)^{1/2}\sin(lq_\alpha) \qquad \text{where} \quad q_\alpha = \frac{\pi\alpha}{(N_b+1)}, \quad \alpha = 1,2,...N_b \\ \omega_\alpha &= 4k_0\sin^2\left(\frac{q_\alpha}{2}\right) \ . \end{aligned} \tag{197}$$

We then get the same form of the full Hamiltonian as given by Eq. (172) with

$$c_\alpha = k'\left(\frac{2}{N_b+1}\right)^{1/2}\sin(q_\alpha) \ . \tag{198}$$

The required spectral properties can then be found. It is clear from the definition that $\Gamma(\omega)$ is non-vanishing only in the range $|\omega| < 2\sqrt{k_0}$. In this range we have:

$$\begin{aligned}\Gamma(\omega) = -\Gamma(-\omega) &= \pi k'^2 \sum_q \frac{2}{N_b+1}\frac{\sin^2(q)}{2\omega_q}\delta(\omega-\omega_q) \\ &= k'^2 \int_0^\pi dq \frac{\sin^2(q)}{\omega_q}\delta(\omega-\omega_q) \\ &= \frac{k'^2}{k_0}\sin(q) \quad \text{where} \quad \sin(q) = \frac{\omega}{\sqrt{k_0}}(1-\frac{\omega^2}{4k_0})^{1/2} \ .\end{aligned}$$

The real part of $\Sigma^+(\omega)$ is given by

$$\begin{aligned}Re[\Sigma^+(\omega)] &= \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega' \frac{\omega'}{\omega'^2-\omega^2}\Gamma(\omega') \\ &= \frac{k'^2}{k_0}\frac{1}{2\pi}\int_0^\pi dq' \frac{\sin^2(q')}{1-\frac{\omega^2}{2k_0}-\cos(q')} \\ &= \frac{k'^2}{k_0}\cos(q) \quad \text{for} \ \ 0<\omega<2\sqrt{k_0} \\ &= -\frac{k'^2}{k_0}e^{-\sigma} \quad \text{for} \ \ |\omega|>2\sqrt{k_0} \\ \text{where} \quad \cos(q) &= 1-\frac{\omega^2}{2k_0} \qquad \cosh(\sigma) = \frac{\omega^2}{2k_0}-1 \ . \end{aligned} \tag{199}$$

Thus we finally have:

$$\begin{aligned}\Sigma^+(\omega) &= \frac{k'^2}{k_0}e^{iq} \quad \text{for} \ \ 0<\omega<2\sqrt{k_0} \\ &= -\frac{k'^2}{k_0}e^{-\sigma} \quad \text{for} \ \ |\omega|>2\sqrt{k_0} \ ,\end{aligned} \tag{200}$$

with $q,\ \sigma$ given by Eq. (199).

9 Quantum master equations

9.1 Derivation of the Redfield equation

We consider the general Hamiltonian

$$H = H_S + H_B + H_{SB}. \tag{201}$$

We switch on H_{SB} at $t = t_0$. Let χ_t denote the full density matrix of the system and bath at time t. At $t = t_0$ we assume $\chi_{t_0} = \rho_B^{\rm eq} \otimes \rho_0$, where $\rho_B^{\rm eq} = e^{-\beta H_B}/Z_B$ denotes the equilibrium bath density matrix while ρ_0 denotes the system density matrix which is taken to be arbitrary. The evolution of the density matrix χ for $t > t_0$ is given by

$$\chi_t = e^{-iH(t-t_0)}\chi_{t_0}e^{iH(t-t_0)}. \tag{202}$$

We then get

$$\frac{\partial \chi_t}{\partial t} = -\frac{i}{\hbar}[H, \chi_t]. \tag{203}$$

Let us transform to the interaction picture and define

$$\chi_t^I = e^{i(H_S+H_B)t/\hbar}\chi_t e^{-i(H_S+H_B)t/\hbar}. \tag{204}$$

It is easy to see then that this satisfies the equation

$$\frac{\partial \chi_t^I}{\partial t} = \frac{i}{\hbar}[(H_S + H_B), \chi_t^I] - \frac{i}{\hbar}e^{i(H_S+H_B)t/\hbar}[H, \chi_t]e^{-i(H_S+H_B)t/\hbar} \tag{205}$$

$$= -\frac{i}{\hbar}[H_{SB}^I, \chi_t^I], \tag{206}$$

where for any operator A we define $A^I(t) = e^{i(H_B+H_S)t/\hbar}Ae^{-i(H_B+H_S)t/\hbar}$. We next write the following formal solution:

$$\chi_t^I == \chi_{t_0}^I - \frac{i}{\hbar}\int_{t_0}^t dt'[H_{SB}^I(t'), \chi_{t'}^I]. \tag{207}$$

Plugging this back into Eq. (206), we get:

$$\frac{\partial \chi_t^I}{\partial t} = -\frac{i}{\hbar}[H_{SB}^I(t), \chi_{t_0}^I] + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \left[H_{SB}^I(t), [H_{SB}^I(t'), \chi_{t'}^I]\right]. \tag{208}$$

We now trace over the bath degrees of freedom and define $\rho^I = Tr_B[\chi^I]$. For our choice of initial χ_{t_0} and many physical choices of system-bath coupling, H_{SB} and the bath Hamiltonian H_B, it will turn out that $Tr_B\{[H_{SB}^I, \chi_{t_0}]\} = 0$. Hence we get:

$$\frac{\partial \rho_t^I}{\partial t} = \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' Tr_B \left\{\left[H_{SB}^I(t), [H_{SB}^I(t'), \chi_{t'}^I]\right]\right\}. \tag{209}$$

So far we have not made any approximations. We now make the **first approximation**. This is the so-called Born approximation which makes the assumption

$$\chi_t^I = \rho_t^I \otimes \rho_B(t_0) \ , \tag{210}$$

thus we assume that the bath does not change much. This then gives:

$$\frac{\partial \rho_t^I}{\partial t} = \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' Tr_B \left\{\left[H_{SB}^I(t), [H_{SB}^I(t'), \rho_{t'}^I \otimes \rho_B^{eq}]\right]\right\}. \tag{211}$$

We note that the above equation involves the density matrix ρ^I at time t' and in that sense it is non-Markovian. The **second approximation** is to take the Markovian assumption and replace $\rho_{t'}^I$ by ρ_t^I and so the above equation takes the form

$$\frac{\partial \rho_t^I}{\partial t} = \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' Tr_B \left\{\left[H_{SB}^I(t), [H_{SB}^I(t'), \rho_t^I \otimes \rho_B^{eq}]\right]\right\}. \tag{212}$$

We choose the interaction, quite common, to be of the form

$$H_{SB}^I(t) = \sum_i S_i^I(t) \otimes B_i^I(t). \tag{213}$$

Let us open up the commutators in Eq. (212). This gives

$$\begin{aligned}
&\left[H_{SB}^I(t), [H_{SB}^I(t'), \rho_t^I \otimes \rho_B^{eq}]\right] && (214)\\
&= \left[S_i^I(t)B_i^I(t), \left(S_j^I(t')B_j^I(t')\rho_t^I\rho_B^{eq} - \rho_t^I\rho_B^{eq}S_j^I(t')B_j^I(t')\right)\right] && (215)\\
&= S_i^I(t)B_i^I(t)S_j^I(t')B_j^I(t')\rho_t^I\rho_B^{eq} - S_j^I(t')B_j^I(t')\rho_t^I\rho_B^{eq}S_i^I(t)B_i^I(t) && (216)\\
&- S_i^I(t)B_i^I(t)\rho_t^I\rho_B^{eq}S_j^I(t')B_j^I(t') + \rho_t^I\rho_B^{eq}S_j^I(t')B_j^I(t')S_i^I(t)B_i^I(t) && (217)\\
&= S_i^I(t)S_j^I(t')\rho_t^I B_i^I(t)B_j^I(t')\rho_B^{eq} - S_j^I(t')\rho_t^I S_i^I(t)B_j^I(t')\rho_B^{eq}B_i^I(t) && (218)\\
&- S_i^I(t)\rho_t^I S_j^I(t')B_i^I(t)\rho_B^{eq}B_j^I(t') + \rho_t^I S_j^I(t')S_i^I(t)\rho_B^{eq}B_j^I(t')B_i^I(t). && (219)
\end{aligned}$$

Taking a trace over the bath degrees of freedom and re-inserting the above into Eq. (212) we get:

$$\begin{aligned}
\frac{\partial\rho_t^I}{\partial t} = -\frac{1}{\hbar^2}\int_{t_0}^t dt'\Big\{ &\left[S_i^I(t)S_j^I(t')\rho_t^I - S_j^I(t')\rho_t^I S_i^I(t)\right]\langle B_i^I(t)B_j^I(t')\rangle_B \\
&+ \left[\rho_t^I S_j^I(t')S_i^I(t) - S_i^I(t)\rho_t^I S_j^I(t')\right]\langle B_j^I(t')B_i^I(t)\rangle\Big\}.
\end{aligned} \tag{220}$$

Finally let us go back to the Schrodinger representation. Noting that $\chi_t = e^{-i(H_S+H_B)t/\hbar}\chi_t^I e^{i(H_S+H_B)t/\hbar}$, we get

$$\dot\chi = -\frac{i}{\hbar}[(H_S+H_B),\chi] + e^{-i(H_S+H_B)t/\hbar}\dot\chi^I e^{i(H_S+H_B)t/\hbar}. \tag{221}$$

Taking a trace over the bath degrees, and setting $t_0 \to \infty$ then gives

$$\begin{aligned}
\dot\rho = -\frac{i}{\hbar}[H_S,\rho] - \frac{1}{\hbar^2}\int_{-\infty}^t dt'\Big\{ &\left[S_iS_j(t'-t)\rho_t - S_j(t'-t)\rho_t S_i\right]\langle B_i(t)B_j(t')\rangle_B \\
&+ \left[\rho_t S_j(t'-t)S_i - S_i\rho_t S_j(t'-t)\right]\langle B_j(t')B_i(t)\rangle_B\Big\}.
\end{aligned} \tag{222}$$

Finally, making a change of variables $s = t - t'$ we get

$$\begin{aligned}
\dot\rho = -\frac{i}{\hbar}[H_S,\rho] - \frac{1}{\hbar^2}\int_0^\infty ds\Big\{ &\left[S_i, S_j(-s)\rho_t\right]\langle B_i(s)B_j(0)\rangle_B \\
&+ \left[\rho_t S_j(-s), S_i\right]\langle B_j(0)B_i(s)\rangle_B\Big\}.
\end{aligned} \tag{223}$$

9.2 Example of a single oscillator coupled to a bosonic bath

We consider the following example:

$$\begin{aligned}
H_S &= \hbar\omega_c a^\dagger a, && (224)\\
H_B &= \sum_j \hbar\omega_j b_j^\dagger b_j, && (225)\\
H_{SB} &= \hbar(\kappa_j a b_j^\dagger + \kappa_j^* a^\dagger b_j) = (S_1B_1 + S_2B_2) && (226)\\
\text{where } S_1 &= a,\ S_2 = a^\dagger,\ B_1 = \hbar\sum\kappa_j b_j^\dagger = B^\dagger,\ B_2 = \hbar\sum\kappa_j^* b_j = B. && (227)
\end{aligned}$$

Then we get the following Redfield equation:

$$\begin{aligned}\dot{\rho} &= -\frac{i}{\hbar}[H_S,\rho] - \frac{1}{\hbar^2}\int_0^\infty ds\,\Big\{\big[a,a^\dagger(-s)\rho_t\big]\,\langle B^\dagger(s)B(0)\rangle_B + \big[a^\dagger,a(-s)\rho_t\big]\,\langle B(s)B^\dagger(0)\rangle_B \\ &+ \big[\rho_t a(-s),a^\dagger\big]\,\langle B^\dagger(0)B(s)\rangle_B + \big[\rho_t a^\dagger(-s),a\big]\,\langle B(0)B^\dagger(s)\rangle_B\Big\} \qquad (228)\\ &= -\frac{i}{\hbar}[H_S,\rho] \\ &- \int_0^\infty ds\,\Bigg\{\big[a,a^\dagger(-s)\rho_t\big]\sum_j|\kappa_j|^2e^{i\omega_j s}n_j + \big[a^\dagger,a(-s)\rho_t\big]\sum_j|\kappa_j|^2e^{-i\omega_j s}(n_j+1) \\ &+ \big[\rho_t a(-s),a^\dagger\big]\sum_j|\kappa_j|^2e^{-i\omega_j s}n_j + \big[\rho_t a^\dagger(-s),a\big]\sum_j|\kappa_j|^2e^{i\omega_j s}(n_j+1)\Bigg\}, \qquad (229)\end{aligned}$$

where $n_j = [e^{\beta\hbar\omega_j}-1]^{-1}$. We note that the time dependence of the isolated oscillator is trivial and given by $a(s) = e^{i\omega_c s}a$. Using this, the above equation takes the form

$$\begin{aligned}\dot{\rho} &= -\frac{i}{\hbar}[H_S,\rho] \\ &- \Bigg\{\big[a,a^\dagger\rho\big]\int_0^\infty ds\sum_j|\kappa_j|^2e^{i(\omega_j-\omega_c)s}n_j + \big[a^\dagger,a\rho\big]\int_0^\infty ds\sum_j|\kappa_j|^2e^{-i(\omega_j-\omega_c)s}(n_j+1) \\ &+ \big[\rho a,a^\dagger\big]\int_0^\infty ds\sum_j|\kappa_j|^2e^{-i(\omega_j-\omega_c)s}n_j + \big[\rho a^\dagger,a\big]\int_0^\infty ds\sum_j|\kappa_j|^2e^{i(\omega_j-\omega_c)s}(n_j+1)\Bigg\}. \qquad (230)\end{aligned}$$

Note that this equation does not have any memory term, even though it might appear in the beginning that there is an integral over time. The integrals in the above equations give complex numbers that depend on bath properties and on the system frequency ω_c. These can be obtained using the result

$$\int_0^\infty dt\; e^{i\omega t} = \frac{i}{\omega+i\epsilon} = iP\left(\frac{1}{\omega}\right) + \pi\delta(\omega). \qquad (231)$$

If we ignore the principal part, then it can be shown that for this single oscillator example, the Redfield equation reduces to the so-called Lindblad form.

Problem: Prove the last statement.

We now discuss the Lindblad equation which was originally derived without taking course to a microscopic model, of system and bath, as the starting point.

9.3 Lindblad equation

The most general form of the Lindblad equation is:

$$\begin{aligned}\dot{\rho} &= -\frac{i}{\hbar}[H_S,\rho] + \sum\gamma_m\left(D_m\rho D_m^\dagger - \frac{1}{2}\{D_m^\dagger D_m,\rho\}\right), \qquad (232)\\ &= -\frac{i}{\hbar}[H_S,\rho] + \sum\frac{\gamma_m}{2}\left([D_m\rho,D_m^\dagger] + [D_m,\rho D_m^\dagger]\right), \qquad (233)\\ & \qquad (234)\end{aligned}$$

where $\{A,B\}$ denotes the anti-commutator $AB+BA$, γ_m are c-numbers while D_m are arbitrary system operators.