Physics 127b: Statistical Mechanics

Fokker-Planck Equation

The Langevin equation approach to the evolution of the velocity distribution for the Brownian particle might leave you uncomfortable. A more formal treatment of this type of problem is given by the Fokker-Planck equation. We can either formulate the question in terms of the evolution of a nonstationary probability distribution from a defined initial condition, or in terms of the evolution of the conditional probabilities for a stationary random process. I will choose the latter approach.

Remember the *conditional probability*

$$P_n(y_1, t_1; y_2, t_2; \ldots \mid y_n, t_n) dy_n \tag{1}$$

is the probability (in the ensemble sense) that *if* $y(t)$ takes on the values y_1 at t_1, y_2 at t_2 ... y_{n-1} at t_{n-1} then it will lie between y_n and $y_n + dy_n$ at time t_n (where $t_1 > t_2 > t_3 \ldots > t_n$). Note the notation for conditional probability is distinguished from the probabilities p_n through the case, and the | notation. Also note in $P_2(y, t \mid y', t')$ the notation is y, t implies y', t' with $t' > t$; unfortunately *Reif* uses the reverse order, i.e. y', t' implies y, t. (For higher order P_n there is less possibility of confusion.)

The probability distributions p_n and the conditional probabilities P_n are related through

$$p_n(y_1, t_1; \ldots; y_n, t_n) = p_{n-1}(y_1, t_1; \ldots; y_{n-1}, t_{n-1}) \times P_n(y_1, t_1; \ldots; y_{n-1}, t_{n-1} \mid y_n, t_n). \tag{2}$$

A *Markoff process* is one for which future probabilities are determined by the most recently known value, and do not depend on the previous history

$$P_n(y_1, t_1; y_2, t_2; \ldots; y_{n-1}, t_{n-1} \mid y_n, t_n) = P_2(y_{n-1}, t_{n-1} \mid y_n, t_n). \tag{3}$$

Stationary Markoff processes are therefore completely characterized by $p_1(y)$ and $P_2(y_1 \mid y_2, t) = p_2(y_1, 0; y_2 t)/p_1(y_1)$ (where we use the convenient notation $P_2(y_1 \mid y_2, t)$ for $P_2(y_1, t_1 \mid y_2, t_1 + t)$). The importance of Markoff processes is not that all physical processes are Markoff, but that the analysis of Markoff processes is considerably simpler. For example in the description of Brownian motion in terms sharp molecular kicks the x-velocity of the particle is Markoff (the probability of $u(t + \delta t)$ depends only on $u(t)$ and the molecular collisions in time δt; on the other hand the position $x(t)$ is *not*, because $x(t + \delta t)$ depends on $x(t)$ and $u(t)\delta t \simeq x(t) - x(t - \delta t)$, as well as the molecular collisions. It is of course easy to formulate the problem in terms of $u(t)$ and then derive properties of $x(t)$ from this. The question of whether a random process is Markoff or not might depend on the level of the description. For example, in the coarse grained description of Brownian motion where we discuss $x(t)$ as a random walk (i.e. on a time scale large compared to the relaxation time of the velocity), the random process $x(t)$ becomes a Markoff one.

Time Evolution

From general probability theory the two point conditional probability distribution satisfies the *Chapman-Kolmogorov* equation

$$P_2(y_1, t_1 \mid y_3, t_3) = \int_{-\infty}^{\infty} dy_2 \, P_2(y_1, t_1 \mid y_2, t_2) P_3(y_1, t_1; y_2, t_2 \mid y_3, t_3) \tag{4}$$

where $t_1 < t_2 < t_3$. This corresponds to integrating over all possibilities at the intermediate time t_2.

For a Markoff process the P_3 is given by P_2 and the equation reduces to the *Smoluchowski equation*

$$P_2(y_1, t_1 \mid y_3, t_3) = \int_{-\infty}^{\infty} dy_2 \, P_2(y_1, t_1 \mid y_2, t_2) P_2(y_2, t_2 \mid y_3, t_3). \tag{5}$$

This is effectively an integral equation for the time evolution of P_2.

If in a small time interval only small changes in y can occur, this time evolution of a Markoff random process can be rewritten as a differential equation known as the *Fokker-Planck* equation. An example where this is the case is the Brownian motion of a heavy particle: in a small time interval the velocity of the heavy particle is only changed by a small amount by the small number of molecular collisions. On the other hand for the velocity distribution of molecules in a gas, each binary collision can change the velocity by a large amount, and the Fokker-Planck equation does not apply. Thus the Fokker-Planck equation is appropriate for the fluctuations of *macroscopic degrees of freedom.*

Writing in terms of $P_2(y_0|y, t)$ for starting at y_0 and ending at y a time t later the Fokker-Planck equation is

$$\frac{\partial}{\partial t} P_2 = -\frac{\partial}{\partial y} [A(y) P_2] + \frac{1}{2} \frac{\partial^2}{\partial y^2} [B(y) P_2] \tag{6}$$

which is to be solved with the initial conditions $P_2(y_0|y, 0) = \delta(y - y_0)$. In this expression A and B are given by the rate of growth of the mean and standard deviation

$$A(y) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_{-\infty}^{\infty} (y' - y) P_2(y|y', \Delta t) dy', \tag{7a}$$

$$B(y) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_{-\infty}^{\infty} (y' - y)^2 P_2(y|y', \Delta t) dy'. \tag{7b}$$

The first term is a *drift* of the distribution corresponding to a systematic bias, and the second to a *diffusion* of the distribution, corresponding to the residual average effect of positive and negative jumps. (Higher moments of P_2 increase less rapidly than Δt, and do not give higher order derivative terms in the equation.)

We have already encountered a Fokker-Planck equation: the diffusion equation for the probability distribution of a random walk is a simple example.

Derivation

The derivation from the Smoluchowski equation is elementary, albeit a little tricky. Write Eq. (5) in the form (with $y_1 \to y_0$, $y_3 \to y$, $y_2 \to y - \xi$ and $t_2 - t_1 \to t$, $t_3 - t_2 \to \tau$)

$$P_2(y_0 \mid y, t + \tau) = \int_{-\infty}^{\infty} d\xi \, P_2(y_0 \mid y - \xi, t) P_2(y - \xi \mid y, \tau), \tag{8}$$

where τ will be a small time increment. In this equation we are studying the conditional probability of getting to y at time $t + \tau$ in terms of the probability of getting "nearby" to $y - \xi$ at time t and then to y in the small time increment τ. Now expand the left hand side in a Taylor expansion in τ

$$P_2(y_0 \mid y, t + \tau) \simeq P_2(y_0 \mid y, t) + \frac{\partial P_2(y_0|y, t)}{\partial t} \tau \tag{9}$$

to give

$$\frac{\partial P_2(y_0|y, t)}{\partial t} \tau = -P_2(y_0 \mid y, t) + \int_{-\infty}^{\infty} d\xi \, P_2(y_0 \mid y - \xi, t) P_2(y - \xi \mid y, \tau). \tag{10}$$

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Note that the first term on the right hand side could be written

$$-\int_{-\infty}^{\infty} d\xi\, P_2(y_0 \mid y, t) P_2(y \mid y - \xi, \tau) \tag{11}$$

since $\int d\xi\, P_2(y \mid y - \xi, \tau) = 1$. The form of the equation is then a "scattering out" term and a "scattering in" term, as in the Boltzmann equation. This sort of equation is known as a *Master Equation*. The difference from the Boltzmann equation is that here we assume that only small changes in y are possible in small τ, and we expand the dependence on the "from" value $z = y - \xi$ in the scattering-in term in small ξ. Note that we are not expanding $P_2(y - \xi \mid y, \tau)$ in small ξ—for fixed y this function decreases rapidly with ξ, and it is precisely because of this that we only need to know $P_2(y_0 \mid z, t) P_2(z \mid z + \xi, \tau)$ for z near y. Thus write

$$P_2(y_0 \mid y - \xi, t) P_2(y - \xi \mid y, \tau) = P_2(y_0 \mid z, t) P_2(z \mid z + \xi, \tau)|_{z = y - \xi} \tag{12}$$

$$= \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \xi^n \frac{\partial^n}{\partial y^n} \left[P_2(y_0 \mid y, t) P_2(y \mid y + \xi, \tau) \right]. \tag{13}$$

This gives

$$\frac{\partial P_2(y_0 \mid y, t)}{\partial t} \tau = -P_2(y_0 \mid y, t) + \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial y^n} \left[P_2(y_0 \mid y, t) \int_{-\infty}^{\infty} d\xi\, \xi^n P_2(y \mid y + \xi, \tau) \right]. \tag{14}$$

The zeroth order terms cancel, leaving (taking $\tau \to 0$)

$$\frac{\partial P_2(y_0 \mid y, t)}{\partial t} = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial y^n} \left[P_2(y_0 \mid y, t) \lim_{\tau \to 0} \frac{1}{\tau} \int_{-\infty}^{\infty} d\xi\, \xi^n P_2(y \mid y + \xi, \tau) \right]. \tag{15}$$

If the random process evolves through the effect of many small changes, only the first two moments $n = 1, 2$ pf P_2 will contribute, with higher moments increasing as τ^p with $p > 1$ giving no contribution as $\tau \to 0$.

Fokker-Plank Equation for the Brownian Velocity

Derivation

The Fokker-Planck approach Eq. (6) and Eq. (7) is really quite independent of the Langevin equation, and in many ways is preferable from a formal point of view, since the Langevin equation is rather pathological and needs careful treatment. We should therefore calculate A, B directly from thinking about the molecular collisions, and indeed this can be done. But here I will just get them by integrating the Langevin equation from a known velocity u over a small time interval

$$M \Delta u + \gamma u \Delta t = \int_t^{t + \Delta t} F'(t') dt'. \tag{16}$$

Using $\langle F' \rangle = 0$ gives

$$A = \lim_{\Delta t \to 0} \frac{\langle \Delta u \rangle}{\Delta t} = -\frac{u}{\tau_r}, \qquad \tau_r = \frac{M}{\gamma}, \tag{17}$$

$$B = \lim_{\Delta t \to 0} \frac{\langle \Delta u^2 \rangle}{\Delta t} = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \frac{1}{M^2} \int_t^{t + \Delta t} \int_t^{t + \Delta t} \langle F'(t_1) F'(t_1) \rangle dt_1 dt_2. \tag{18}$$

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You should be familiar with this sort of double integral by now! Note that although Δt is small, we assume it to be large compared to the molecular collision time, so that the force correlation function is nonzero only over time differences short compared to Δt. In the usual way we have

$$\lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_t^{t+\Delta t} \int_t^{t+\Delta t} \langle F'(t_1)F'(t_1)\rangle \, dt_1 dt_2 = \lim_{\Delta t \to 0} \frac{2}{\Delta t} \int_t^{t+\Delta t} dt_1 \int_0^\infty \langle F'(0)F'(\tau)\rangle \, d\tau \quad (19)$$

$$= \frac{1}{2} G_F(0) = 2kT\gamma \quad (20)$$

so that

$$B = \frac{2\gamma kT}{M^2}. \quad (21)$$

Solution

To study the decay of the velocity to the equilibrium Maxwellian we solve the Fokker-Planck for $P_2(u_0 \mid u, t)$ with the initial condition $P_2(u_0|u, t = 0) = \delta(u - u_0)$. You can find a "forward" solution in *Reif* §15.12. I will just show the solution and let you verify that it satisfies the differential equation by substitution:

$$P_2(u_0 \mid u, t) = \frac{1}{\sqrt{2\pi\sigma_u^2(t)}} \exp\left[-\frac{(u - \bar{u}(t))^2}{2\sigma_u^2(t)}\right] \quad (22)$$

where the time dependent mean $\bar{u}(t)$ and variance $\sigma_u^2(t)$ are what we found before

$$\bar{u}(t) = u_0 e^{-t/\tau_r} \quad (23)$$

$$\sigma_u^2(t) = \frac{kT}{M}(1 - e^{-2t/\tau_r}). \quad (24)$$

Example

As an example of how to use the solution, consider the calculation of the correlation function

$$C_u(\tau) = \langle u(0)u(t)\rangle = \int_{-\infty}^\infty \int_{-\infty}^\infty p_2(u_1, 0; u_2, t)u_1 u_2 du_1 du_2. \quad (25)$$

For the stationary random process $u(t)$ we have

$$p_2(u_1, 0; u_2, t) = p_1(u_1)P_2(u_1 \mid u_2, t) \quad (26)$$

and

$$p_1(u) = \lim_{t \to \infty} P_2(u_0 \mid u, t) \quad (27)$$

so that

$$C_u(\tau) = \int_{-\infty}^\infty \int_{-\infty}^\infty \frac{1}{\sqrt{2\pi\sigma_m^2}} e^{-u_1^2/2\sigma_m^2} \frac{1}{\sqrt{2\pi\sigma_u^2(t)}} \exp\left[-\frac{(u_2 - \bar{u}(t))^2}{2\sigma_u^2(t)}\right] u_1 u_2 du_1 du_2, \quad (28)$$

with $\sigma_m^2 = kT/M$ and $\bar{u}(t) = u_1 e^{-t/\tau_r}$. The u_2 integration just gives $\bar{u}(t)$, so that

$$C_u(\tau) = e^{-t/\tau_r} \int_{-\infty}^\infty \frac{1}{\sqrt{2\pi\sigma_m^2}} e^{-u_1^2/2\sigma_m^2} u_1^2 \, du_1 \quad (29)$$

$$= \frac{kT}{M} e^{-t/\tau_r}. \quad (30)$$

From this the spectral density is given by Fourier transform

$$G_u(f) = \frac{4kT}{M\tau_r} \frac{1}{(2\pi f)^2 + (1/\tau_r)^2}. \quad (31)$$

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Stationary, Gaussian, Markoff Processes

Results very similar to the ones we have just calculated actually apply to a large class of random processes namely those that are stationary, Gaussian, and Markoff. For such a process $y(t)$ all the statistical properties are determined by the mean $\bar{y}$, the variance σ_y^2, and the two point correlation time τ_r. This is known as Doob's theorem. Remember that a stationary Markoff process is characterized by $p_1(y)$ and $P_2(y_1|y_2, t)$ or $p_2(y_1, 0; y_2, t)$. For a Gaussian process p_1 is characterized by $\bar{y}$ and σ_y^2, and for p_2 we need in addition the α_{12} parameter of the Gaussian distribution, which is determined by the two point correlation function $C_y(t)$. Further, since the behavior in each successive time increment does not depend on the history, the decay of correlations must be a simple exponential

$$C_y(\tau) = \sigma_y^2 e^{-t/\tau_r}. \tag{32}$$

The spectral density is then *Lorenzian*

$$G_y(f) = \frac{(4/\tau_r)\sigma_y^2}{(2\pi f)^2 + (1/\tau_r)^2}. \tag{33}$$

This appears white for $f \ll \tau_r^{-1}$, and falls off as f^{-2} for high frequencies. The complete characterization also involves

$$p_1(y) = \frac{1}{\sqrt{2\pi\sigma_y^2}} \exp\left[-\frac{(y-\bar{y})^2}{2\sigma_y^2}\right] \tag{34}$$

and

$$P_2(y_1|y_2, t) = \frac{1}{\sqrt{2\pi\sigma^2(t)}} \exp\left[-\frac{(y_2 - \bar{y}(t))^2}{2\sigma^2(t)}\right] \tag{35}$$

using the notation

$$\bar{y}(t) = \bar{y} + e^{-t/\tau_r}(y_1 - \bar{y}) \tag{36a}$$

$$\sigma^2(t) = (1 - e^{-2t/\tau_r})\sigma_y^2 \tag{36b}$$

showing how the mean and the variance of the conditional probability relaxes from the initial value set by the "initial condition" $y = y_1$ to the long time asymptotic forms set by p_1. I will not derive these general results here.

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