Physics 127b: Statistical Mechanics

Langevin Equation

To understand the Brownian motion more completely, we need to start from the basic physics, i.e. Newton's law of motion. The most direct way of implementing this is to recognize that there is a stochastic component to the force on the particle, which we only know through a probabilistic description. This gives us a *Langevin equation* for the velocity $u(t)$ (which is a random process)

$$M\frac{du}{dt} + \gamma u = F(t). \tag{1}$$

Here γu (with $\gamma = \mu^{-1}$) is the systematic part of the molecular force, and $F(t)$ is the random component with $\langle F \rangle = 0$. (We could also include a nonstochastic external force, but will not do so here.) We also assume there is no causal connection of $F(t)$ with the velocity, i.e. $F(t)$ is uncorrelated with the velocity $u(t')$ for $t > t'$. Since the time scale of the molecular collisions is small compared to the time scale M/γ set by the dynamics of the particle, F is a series of randomly spaced spikes or delta functions—a very nasty looking function! However we are interested in the effect on the time scale M/γ during which many molecular collisions occur, and on this sort of time scale the noise force behaves as a Gaussian random process.

Solution of the Langevin Equation

Spectral Method

If we are just interested in the stationary random process $u(t)$ a long time after any initial transients have died out it is easy to solve the Langevin equation by taking Fourier transforms. Without being too careful we can write for $T \to \infty$

$$\tilde{u}_T(f) = \frac{\tilde{F}_T(f)}{(-2\pi i f M) + \gamma} \tag{2}$$

so that the spectral density of the velocity is

$$G_u(f) = \frac{1}{(2\pi f M)^2 + \gamma^2} g. \tag{3}$$

But we know that the integral of G_u over all frequencies is just the variance $\langle u^2 \rangle$ of u, which by equipartition is kT/M. This allows us to fix the strength of the stochastic force

$$g = G_F(f) = 4kT\gamma. \tag{4}$$

Thus the stochastic force is completely determined by the dissipation γ and the temperature, again a manifestation of the common origin of dissipative and stochastic forces in the molecular collisions. This result is analogous to the Johnson noise term in electrical circuits, and is an example of a general result relating stochastic forcing terms to dissipation coefficients. Note that our derivation here has been purely classical, and so we get the classical limit of the Nyquest expression.

Solution in the time domain

The Langevin equation is a complete description (in the stochastic sense!) of the Brownian motion, but is a nasty equation to deal with, since the forcing term is a random sequence of delta functions—very singular!

However, we are usually interested in mean values or low order correlation functions, and we can proceed by constructing appropriate quantities and taking expectation values.

Write the equation in the form

$$\frac{du}{dt} + \frac{u}{\tau_r} = A(t) \tag{5}$$

where $\tau_r = M/\gamma$ is a relaxation time of the macroscopic motion of the particle and $A(t) = F(t)/M$ is the stochastic driving. Physically, we expect the stochastic driving to be unaffected by the position and velocity of the particle (remember the average part of the force, which will act in the opposite direction to the particle velocity, is the u/τ_r term). Loosely we would say the force is "uncorrelated with the velocity". However, the velocity responds to the force, so we must be careful:

$$\left\langle A(t)u(t')\right\rangle \begin{cases} = 0 & t > t' \quad \text{"force uncorrelated with velocity"} \\ \neq 0 & t < t' \quad \text{"velocity correlated with earlier force"} \end{cases} \tag{6}$$

Velocity First lets look at the statistics of the velocity $u(t)$. This is given by formally integrating the Langevin equation. We again suppose we have a tagged particle that at $t = 0$ has a velocity that is known precisely. Then

$$u(t) = u(0)e^{-t/\tau_r} + e^{-t/\tau_r} \int_0^t e^{t'/\tau_r} A(t')dt'. \tag{7}$$

Now take averages as desired. Since $\langle A \rangle = 0$ this immediately gives for the mean

$$\langle u(t)\rangle = u(0)e^{-t/\tau_r}. \tag{8}$$

For the mean square velocity

$$\left\langle u^2(t)\right\rangle = u^2(0)e^{-2t/\tau_r} + e^{-2t/\tau_r} \int_0^t \int_0^t e^{(t_1+t_2)/\tau_r} \left\langle A(t_1)A(t_2)\right\rangle, \tag{9}$$

where we have used $\langle u(0)A(t > 0)\rangle = 0$ to eliminate the cross term. This is the same type of double integral we evaluated in the previous lecture. Writing $t_2 = t_1 + \tau$ and proceeding as there

$$\left\langle u^2(t)\right\rangle = u^2(0)e^{-2t/\tau_r} + 2e^{-2t/\tau_r} \int_0^t dt_1 e^{2t_1/\tau_r} \int_0^{t-t_1} d\tau \, e^{\tau/\tau_r} \left\langle A(t_1)A(t_1+\tau)\right\rangle, \tag{10}$$

$$\simeq u^2(0)e^{-2t/\tau_r} + \tau_r(1 - e^{-2t/\tau_r}) \int_0^\infty d\tau \, \left\langle A(0)A(\tau)\right\rangle. \tag{11}$$

Writing $\int_0^\infty d\tau \, \langle A(0)A(\tau)\rangle$ as $\frac{1}{4}G_A(0) = \frac{1}{4}g_A$ and using Eq. (8) this finally gives for the variance of $u(t)$

$$\sigma_u^2(t) = \left\langle (u(t) - \langle u(t)\rangle)^2\right\rangle = \frac{g_A \tau_r}{4}(1 - e^{-2t/\tau_r}). \tag{12}$$

We can evaluate $g_A = 4kT\gamma/M$ or note that σ_u^2 must approach the equipartition value at large times, so that

$$\sigma_u^2(t) = \frac{kT}{M}(1 - e^{-2t/\tau_r}). \tag{13}$$

Position To follow the position we can multiply the Langevin equation by x and average. Use

$$xu = x\frac{dx}{dt} = \frac{1}{2}\frac{dx^2}{dt}, \tag{14a}$$

$$x\frac{du}{dt} = \frac{d(xu)}{dt} - u^2 = \frac{1}{2}\frac{d^2x^2}{dt^2} - u^2. \tag{14b}$$

On averaging, since the force is uncorrelated with the position $\left\langle A(t)x(t')\right\rangle = 0$, this gives

$$\frac{d^2\left\langle x^2\right\rangle}{dt^2} + \frac{1}{\tau_r}\frac{d\left\langle x^2\right\rangle}{dt} = 2\left\langle u^2\right\rangle. \tag{15}$$

We could study the behavior of a Brownian particle originally at rest, using the results of the previous section for how $\left\langle u^2\right\rangle$ relaxes to the equilibrium value, but instead of going into this complication, lets suppose that the particle already has this mean square speed $\left\langle u^2\right\rangle = kT/M$. Integrating from the initial values $\left\langle x^2(0)\right\rangle = d\left\langle x^2(0)\right\rangle/dt = 0$ gives

$$\left\langle x^2(t)\right\rangle = \frac{2kT}{M}\tau_r^2\left[\frac{t}{\tau_r} - (1 - e^{-t/\tau_r})\right]. \tag{16}$$

For small $t \ll \tau_r$ this gives propagation at the thermal speed

$$\sqrt{\left\langle x^2(t)\right\rangle} \simeq t\sqrt{kT/M} \tag{17}$$

and at long times $t \gg \tau_r$ diffusion

$$\left\langle x^2(t)\right\rangle \simeq \frac{2kT\tau_r}{M}t \tag{18}$$

again relating the diffusion constant to the dissipation (here expressed in terms of τ_r).