Statistical Physics
Section 15: The Langevin Approach and The Dynamics of Fluctuations

15. 1. The Random Walk

Let us revisit the random walk and the diffusion limit of section 14.5

$$\frac{\partial p}{\partial t} = D\frac{\partial^2 p}{\partial x^2} \tag{1}$$

This is the equation for the time evolution of the *probability distribution* of x. Such an equation (second order in space derivatives, first order in time) is generally known as a *Fokker-Planck equation.*

The *Langevin equation*, on the other hand is a stochastic equation for the position x.

To see what's involved let us try to write directly an equation for the time evolution of x in the random walk. We consider a small time interval Δt

$$x(t + \Delta t) = x(t) + \Delta x(t) \tag{2}$$

The step $\Delta x(t)$ is a random variable and when the lattice spacing is $|\Delta x| = a$

$$\Delta x(t) = \begin{cases} +a & \text{probability} \quad \nu\Delta t \\ -a & \text{probability} \quad \nu\Delta t \\ 0 & \text{probability} \quad (1 - 2\nu\Delta t) \end{cases} \tag{3}$$

Note that $\langle \Delta x\rangle = 0$ and $\langle (\Delta x)^2\rangle = 2a^2\nu\Delta t = 2D\Delta t$. Also note that $\Delta x(t)$ are uncorrelated for different t. What we want to do now is take the 'continuum limit' i.e. let Δx and Δt go to zero in some prescribed way. There are some mathematical subtleties involved... suffice to say that to make things work we should have the lattice spacing a scale as

$$a \propto (\Delta t)^{1/2}$$

when we take the limit $\Delta t \to 0$

Let us take on trust that an appropriate equation to describe the continuum limit of (2) is

$$\dot{x} = \eta(t) \tag{4}$$

where

$$\begin{aligned} \langle \eta(t)\rangle &= 0 & (5)\\ \text{and} \quad \langle \eta(t)\eta(t')\rangle &= \Gamma\delta(t - t') & (6) \end{aligned}$$

A random variable $\eta(t)$ with statistics (5,6) is known as 'white noise'.

By specifying the statistics for $\eta(t)$, we therefore specify a *stochastic process* $x(t)$, whose relation to η is through a *stochastic differential equation* commonly referred to as a Langevin equation. We can formally integrate (4) to obtain

$$x(t) - x_0 = \int_0^t \mathrm{d}t'\eta(t') \tag{7}$$

To extract useful information from this solution we should take averages. Using the properties (5,6)

$$\begin{aligned} \langle x(t) - x_0 \rangle &= 0 & (8) \\ \langle (x(t) - x_0)^2 \rangle &= \int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \langle \eta(t')\eta(t'') \rangle = \Gamma \int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \delta(t' - t'') = \Gamma t & (9) \end{aligned}$$

We identify the diffusion constant D by

$$\Gamma = 2D \tag{10}$$

Actually one can show that the two descriptions, diffusion equation and Langevin equation are equivalent i.e. the Langevin equation (with rapidly decaying noise) generates not only the same mean square displacement but the same probability distribution $p(x)$ as calculated from the diffusion equation. A proof of this statement lies beyond the course; see e.g. Stochastic Processes in Physics and Chemistry, by N. G. Van Kampen. (North Holland, 1981). As some justification of the equivalence we consider (7) as a sum of uncorrelated random variables which under general conditions has a gaussian probability distribution. This concurs with the solution of the diffusion equation which we have seen in section 14 gives a gaussian probability distribution.

15. 2. Brownian Motion

We now consider *Brownian Motion* originally studied as the motion of a suspended colloidal particle in a fluid. This particle is constantly being bombarded by collisions with the (smaller) fluid molecules; if we don't keep track of these collisions, the effect is *as if* the particle is being buffeted by 'random' forces. The resulting motion of the colloidal particle is in effect a random walk: this 'Brownian motion' was first reported by a certain Reverend Brown. It was later analysed by Einstein (in his most cited research paper) who realised that, among other things, it proved that the suspending fluid was indeed made of discrete molecules, an idea which up to then had remained controversial.

This approach is in fact a form of coarse-graining and is another way to introduce irreversibility into macroscopic physics. That is, in principle we could keep track of all the (reversible) molecular dynamics which gives rise to the collision but we cannot practically do this. Instead we postulate the existence of *random forces* that are not derived from any Hamiltonian. Langevin was the first to give an explicit analysis of the effect of random forces. Consider a particle of mass m (which we'll set to 1 later) immersed in a fluid. According to Langevin, its equation of motion is (in one dimension)

$$m\ddot{x} = -\gamma\dot{x} + f(t) \tag{11}$$

The first term on the right is a damping force caused by friction between the particle and the fluid. Note that often $\mu \equiv 1/\gamma$ is used and this is called the *mobility* of such a sphere (warning: it has nothing to do with chemical potential!). The final term f is a *random force.*

In principle the random forces are *correlated* in time since the molecular collisions which cause them are correlated and have some definite duration. But if we assume that there is some correlation time t_c over which

$$\langle f(t_1)f(t_2) \rangle = g(t_1 - t_2)$$

Figure 1: Sketch of $g(t_1 - t_2)$ against $|t_1 - t_2|$

decays rapidly then as long as we consider timescales $\gg t_c$ we can safely replace $g(t_1 - t_2)$ by a delta function. Thus the statistics of the random forces are given by

$$\begin{aligned} \langle f(t) \rangle &= 0 & (12) \\ \langle f(t_1) f(t_2) \rangle &= \Gamma \delta(t_1 - t_2) & (13) \end{aligned}$$

Now let us integrate (11) taking $m = 1$. Introducing an integrating factor gives

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[v \mathrm{e}^{\gamma t}\right] = \mathrm{e}^{\gamma t} f(t)$$

which we can integrate up to obtain

$$v - v_0 \mathrm{e}^{-\gamma t} = \int_0^t \mathrm{d}t' \mathrm{e}^{-\gamma(t-t')} f(t') \tag{14}$$

Thus

$$\langle v \rangle = v_0 \mathrm{e}^{-\gamma t} \tag{15}$$

Note that in the short time limit $\gamma t \ll 1$, we have $v \simeq v_0$ and friction has not yet taken effect. In the long time limit, $\gamma t \gg 1$, $v \rightarrow 0$

Now consider the mean squared velocity

$$\begin{aligned} \langle v^2 \rangle &= v_0^2 \mathrm{e}^{-2\gamma t} + \int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \mathrm{e}^{-\gamma(t-t') - \gamma(t-t'')} \langle f(t') f(t'') \rangle \\ &= v_0^2 \mathrm{e}^{-2\gamma t} + \Gamma \int_0^t \mathrm{d}t' \mathrm{e}^{-2\gamma(t-t')} \\ &= v_0^2 \mathrm{e}^{-2\gamma t} + \frac{\Gamma}{2\gamma}\left[1 - \mathrm{e}^{-2\gamma(t-t')}\right] & (16) \end{aligned}$$

Again we can inspect the short time limit $\langle v^2 \rangle \simeq v_0^2$ and the long time limit

$$\langle v^2 \rangle \rightarrow \frac{\Gamma}{2\gamma} \quad \text{for} \quad \gamma t \gg 1 \tag{17}$$

Thus after a sufficiently long time the particle forgets its initial velocity and comes into thermal equilibrium with the fluid. But, by equipartition, a particle in equilibrium, should have kinetic energy

$$\frac{m}{2} \langle v^2 \rangle = \frac{1}{2} kT \tag{18}$$

Therefore we deduce

$$\boxed{\Gamma = 2\gamma kT} \tag{19}$$

This equation relates the magnitude of the noise fluctuations Γ to the viscous term controlled by γ. On reflection, this should not come as a surprise since the same microscopic dynamics involving molecular collisions gives rise to both the deterministic viscosity term and the stochastic force term in (11).

In the tutorial you are invited to integrate (14) once again and the result is (inserting (19))

$$\langle (x(t)-x_0)^2\rangle = \frac{(v_0^2 - kT)}{\gamma^2}(1-\mathrm{e}^{-\gamma t})^2 + \frac{2kT}{\gamma}\left(t - \frac{1}{\gamma}\left[1-\mathrm{e}^{-\gamma t}\right]\right) \tag{20}$$

One can work out the short and long time limits

$$\begin{aligned} \langle (x(t)-x_0)^2\rangle &\simeq v_0^2 t^2 \quad \text{for} \quad \gamma t \ll 1 && (21)\\ &\simeq \frac{2kTt}{\gamma} \quad \text{for} \quad \gamma t \gg 1 && (22)\end{aligned}$$

Thus initially the particle moves ballistically with the initial velocity v_0 and after a long time the Brownian particle performs diffusive motion with diffusion constant

$$\boxed{D = \frac{kT}{\gamma}} \tag{23}$$

This relation is known as the *Einstein Relation* and relates the diffusion constant of the particle to the dissipation. It is useful as it allows an explicit expression for the diffusion constant if one knows γ. A famous example is a sphere: equation for fluid flow past a moving sphere may be solved and yields $\gamma = 6\pi\eta a$ where a is the radius of the sphere and here η the fluid viscosity. This gives

$$D = \frac{kT}{6\pi\eta a}$$

which is the *Stokes-Einstein formula* for the diffusion constant of a colloidal particle.

Finally we can consider a particle with charge q say and the effect of an external field E. The external field will produce a systematic force qE to add into (11) and the equation for the mean velocity becomes

$$m\langle\dot{v}\rangle = -\gamma\langle v\rangle + qE \tag{24}$$

The terminal drift velocity is then

$$\langle v\rangle = \frac{qE}{\gamma} = \frac{qED}{kT}$$

If we define the mobility μ through $\langle v\rangle = \mu qE$ we have

$$\boxed{\mu = \frac{D}{kT}} \tag{25}$$

which is known as the *Nernst-Einstein relation.* Note that it relates the *response* to an external perturbation (here μ measures the response of the drift velocity to the electric field) to *fluctuations* in the equilibrium state (when the field is zero).

15. 3. Dynamics of fluctuations

Consider some thermodynamic variable x of mean zero, that can fluctuate in time. (This could be a local magnetisation, or the local density in a fluid, or anything similar.) x is measured as a departure from the global mean value i.e. it is a *fluctuation* about the mean value. We are interested in the *correlations* of these fluctuations in an equilibrium state. For example, if the value of x at time t is positive, then it is more likely to be positive than negative, a short while later. These effects are characterised by a *correlation function*

$$\langle x(\tau)x(\tau+t)\rangle \tag{26}$$

In equilibrium (steady state) this must be independent of the initial time τ, hence

$$\langle x(\tau)x(\tau+t)\rangle = M_{xx}(t) \tag{27}$$

i.e. M_{xx} is only a function of the time difference t.

A typical $M_{xx}(t)$ looks like this: We expect a correlation time t_c so that for large t

Figure 2: Sketch of $M_{xx}(t)$ against t

$$M_{xx}(t) \sim \exp(-t/t_c) \tag{28}$$

Different fluctuating variables can also be correlated with each other, for example the magnetisation at two nearby places is correlated. To study this, we can define similarly

$$\langle x(\tau)y(\tau+t)\rangle = M_{xy}(t) \tag{29}$$

for any pair of variables, x and y. $M_{xy}(t)$ is the *dynamic correlation matrix*, of which $M_{xx}(t)$ is a diagonal element.

Now the principle of detailed balance (which as we saw arises from microscopic reversibility) implies that there are no probability currents flowing in equilibrium. This in turn means that, once equilibrium is reached, there is no arrow of time since there is no probability current flowing which would distinguish the forward and backward time directions. Thus detailed balance implies that the fluctuations arising in equilibrium are time-reversal symmetric:

$$M_{xx}(t) = \langle x(\tau)y(\tau+t)\rangle = \langle x(\tau)y(\tau-t)\rangle = M_{xx}(-t) \tag{30}$$

Moreover, $M_{xy}(-t)$ obeys

$$M_{xy}(-t) = \langle y(\tau-t)x(\tau)\rangle = \langle y(\tau)x(\tau+t)\rangle \tag{31}$$

since there is no dependence on the initial time τ in the steady state average (so we can shift $\tau \to \tau+t$). Combining this with the previous result, we find that *the dynamic correlation matrix is symmetric in the indices x and y*:

$$M_{xy}(t) = M_{yx}(t) \tag{32}$$

This is a rather nontrivial consequence of microscopic time reversal symmetry.

15. 4. Linear response theory and the Fluctuation-dissipation theorem

Suppose we now perturb our system a little. To do this, we can imagine having a small "thermodynamic force" f_x acting on it: a local applied h field, say, if x is a local magnetisation. (Formally, as in section 3 one adds to the Hamiltonian a perturbation $-f_x x$.)

There are various experimental 'protocols' for studying the effect of such perturbations see figure. Usually we consider a perturbation which remains turned on for a long time (say from $t = -\infty$) and is then switched off at (say) $t = 0$. For $t > 0$ the resulting average response of y decays away, irreversibly, as

Figure 3: Effect of perturbation on a quantity which is zero in equilibrium

$$\langle y(t)\rangle_f = R_{yx}(t)\, f_x \tag{33}$$

This defines the *response function matrix* $R_{yx}(t)$, where $t \geq 0$.

Aside: Another protocol is to give the system a sharp 'kick' at $t = 0$ then see how it relaxes. This gives the interpretation of a Green function to $R_{yx}(t)$.

In either case if the perturbation is small enough, it will (at least in each local neighbourhood) produce a change so weak that *this could anyway have arisen by a spontaneous fluctuation.* If that is the case, the perturbation $y(t)$ will on average decay in time just as if it were such a fluctuation, which happened by chance to be present at $t = 0$.

This idea that the perturbation can be treated as an 'honorary fluctuation' lies behind the *fluctuation-dissipation theorem.*

$$\boxed{k_B T\, R_{yx}(t) = M_{yx}(t)} \tag{34}$$

This results simply states that the response function $R_{xy}(t)$ contains exactly the same information as provided by the correlation function $M_{xy}(t)$. To motivate the factor kT one can check that it gives both side of the equation the same dimensions.

We do not attempt a proof here as it would be lengthy and involve either the machinery of classical mechanics through Poisson Brackets etc or quantum mechanics through the density matrix (see final chapter of Chandler for a relatively simple exposition).

In the next section we shall look at a particular example

Finally, a remarkable theorem can be obtained by combining two results given already above the Fluctuation-dissipation theorem (34) and (32) which expresses the symmetry, with respect to its indices, of the correlation matrix.

Accordingly we have

$$\boxed{R_{xy}(t) = R_{yx}(t)} \tag{35}$$

that is, *the response function matrix is itself symmetric in x, y indices.* This, in essence, is Onsager's theorem, which states that the mean response of a variable x to a small thermodynamic force f_y acting on some other variable y, is entirely determined by the mean response of y to f_x. (To use this quantitatively, one has to take care to define the forces and displacements according to certain rules.)

Onsager's theorem is a remarkably subtle result, in which the *time reversibility* of microphysics strongly constrains the *time irreversible* relaxation of a macroscopic system perturbed away from equilibrium. Onsager's achievement was not so much to prove the result (which we have done in outline above) but to realise that such a connection could possibly exist in the first place! This is the same Lars Onsager who solved the 2d Ising Model and he was awarded the Nobel prize (in Chemistry) in 1968.

Example: thermoelectricity [not covered in lectures]

Suppose you have a system consisting of two blocks of metal in contact. Let the left hand block be hotter than the right one. In that case, not only heat *but also particles* (in this case, electrons) will cross from left to right. This is easy to understand: hotter electrons, on the left, are more likely to travel to the right than the cold ones on the right are, to travel to the left. This is the *thermoelectric effect.*

Now take a different experiment where the temperatures are the same but the chemical potentials of the electrons are not. That can be arranged by having a voltage difference between the two blocks. Onsager's theorem states that *not only particles, but also heat energy* will flow from one block to the other. That is not so easy to understand! It is called the *Peltier effect*, and is widely used to make solid-state heat pumps. (These can, if desired, be of minuscule dimensions with no moving parts.) Onsager's theorem correctly predicts the magnitude of the Peltier effect from measurements of the thermoelectric effect. There are many similar, and equally unintuitive, applications of the theorem.

15. 5. Example: Over Damped Brownian Motion

Let us return to the Brownian motion of a colloidal particle suspended in a fluid acted upon by a systematic external force F_{ex}. For convenience we shall also add a harmonic restoring force (think of the particle tethered by a weak spring to the origin) with spring constant κ. This is basically a trick to keep the displacement of the particle bounded as $t \to \infty$. The Langevin equation now reads

$$m\ddot{x} = -\gamma\dot{x} + F_{ex} - \kappa x + f(t) \tag{36}$$

where the statistics of the random force f are taken to be (12,13).

To simplify things we consider the *overdamped* regime where we can ignore the acceleration term on the lhs of (36). This 'Aristotlean' view of dynamics may seem a bit dangerous but is an adequate description in a strongly viscous medium (γ large). Then

$$\dot{x} = \mu \left[F_{ex} - \kappa x + f(t)\right] \quad \text{where} \quad \mu = \frac{1}{\gamma} \tag{37}$$

We consider the protocol of the external force switched on up to $t = 0$ then switched off. Integrating (37) gives

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t}\left[x\mathrm{e}^{\mu\kappa t}\right] &= \mu\mathrm{e}^{\mu\kappa t}\left(F_{ex} + f(t)\right) \\ \Rightarrow \quad x(t) &= \mu\int_{-\infty}^{0}\mathrm{d}t'\mathrm{e}^{-\mu\kappa(t-t')}\left(F_{ex} + f(t')\right) + \mu\int_{0}^{t}\mathrm{d}t'\mathrm{e}^{-\mu\kappa(t-t')}f(t') \end{aligned} \tag{38}$$

The average displacement is

$$\langle x(t)\rangle = \frac{F_{ex}}{\kappa}\mathrm{e}^{-\mu\kappa t} \simeq \frac{F_{ex}}{\kappa} - F_{ex}\mu t \quad \text{when} \quad \mu\kappa t \ll 1 \tag{39}$$

i.e. the particle moves back from F_{ex}/κ to zero. We read off

$$R_{xx} = \frac{1}{\kappa}\mathrm{e}^{-\mu\kappa t} \tag{40}$$

Next we consider the correlation function

$$M_{xx}(t) = \langle x(\tau)x(\tau + t)\rangle \tag{41}$$

when there is no external force. In this case (38) becomes

$$x(t) = \mu\int_{-\infty}^{t}\mathrm{d}t'\mathrm{e}^{-\mu\kappa(t-t')}f(t') \tag{42}$$

and the correlation function can be computed

$$\begin{aligned} M_{xx}(t) &= \mu^2\int_{-\infty}^{\tau}\mathrm{d}t'\mathrm{e}^{-\mu\kappa(\tau-t')}\int_{-\infty}^{\tau+t}\mathrm{d}t''\mathrm{e}^{-\mu\kappa(\tau+t-t'')}\langle f(t')f(t'')\rangle \\ &= \mu^2\Gamma\int_{-\infty}^{\tau}\mathrm{d}t'\mathrm{e}^{-\mu\kappa(t+2\tau-2t')} \\ &= \frac{\mu\Gamma}{2\kappa}\mathrm{e}^{-\mu\kappa t} \end{aligned} \tag{43}$$

Comparing (40) and (43), the fluctuation-dissipation theorem (34) tells us that

$$kT = \frac{\mu\Gamma}{2} \tag{44}$$

which is consistent with our previous identifications from section 15.2 i.e. the Einstein Relation (23) and (19).