14. The Langevin equation

In the first part of the course we studied the statistical properties of a physical system *in thermodynamic equilibrium*: in other words the system could sample all its microscopic states. The fundamental quantity of interest was the partition function, from which all thermodynamic observables can be derived. In these last series of lectures we will consider the time evolution of a system which is *approaching* thermodynamic equilibrium starting from an initial state. There are several complementary ways to describe the dynamics of approach to equilibrium. In this lecture we will analyse in some detail the Langevin equation description, which you should have already seen in the Statistical Physics course (year 4).

14.1. Langevin's description of the dynamics of a particle in water

We begin by considering a single particle (a hard sphere) which is immersed in a fluid. The particle feels a force due to the collisions from the particles in the liquid. Such a force is constituted of two parts: (i) a systematic (or deterministic) hydrodynamic drag, which resists motion, and (ii) a fluctuating stochastic force, which has zero mean, and which may only be characterised through a *probabilistic* description. The equation of motion governing the dynamics of the sphere (of mass m and instantaneous velocity v) is thus:

$$m\frac{d\vec{v}}{dt} = -\gamma\vec{v} + \vec{\eta}(t), \tag{1}$$

where we have indicated with γ the particle friction, and with $\vec{\eta}(t)$ the stochastic component of the collision driven force (note that vectors are identified by their being written in bold face). Eq. 1 is known as a Langevin equation (LE), in this case valid for a single colloidal particle. Generalisations to a particle subject to conservative forces as well as to collisional forces, and to many particles, are easily done (at least formally).

From hydrodynamics we know (Stokes' law):

$$\gamma = 6\pi\eta R \tag{2}$$

where R is the particle radius and η is the viscosity of the solvent.

Eq. 1 can formally be solved as a first-order inhomogeneous differential equation (even though the inhomogeneous term is *random*), to yield (henceforth $m = 1$):

$$\vec{v}(t) = \vec{v}(0)\exp(-\gamma t) + \int_0^t d\tau \exp\left[-\gamma(t-\tau)\right]\vec{\eta}(\tau). \tag{3}$$

Usually, this is as far as one can go when treating a Langevin equation analytically. More commonly, to solve a Langevin equation one can use a numerical method (see below), or switch to the equivalent Fokker-Planck equation (see Section 15).

Given the stochastic nature of the LE, in order to get some useful information out of this formal solution, we need to take averages over the possible realisations of $\eta(t)$. Given this, we now need to make some assumptions on the nature of η. Because collision forces arise from the chaotic movements of the molecules in the liquid solvent, which bang into the moving sphere, it is usually assumed that forces at different times (and if appropriate acting on different particles) are uncorrelated. It is also common to assume that the probability distribution from which the random forces are drawn is Gaussian. In formulas, the ansatz (known as white noise assumption) is:

$$\langle \vec{\eta}(t) \rangle = \vec{0} \tag{4}$$

$$\langle \eta_\mu(t) \eta_\nu(t') \rangle = \Gamma \delta_{\mu\nu} \delta(t - t'), \tag{5}$$

where Γ controls the strength of noise, μ and ν indicate Cartesian components (x, y, z as we are in 3D), and where the first and second δ are Kronecker and Dirac deltas respectively.

By taking the average of Eq. 3, we obtain that:

$$\langle \vec{v}(t) \rangle = \vec{v}(0) \exp\left(-\gamma t\right), \tag{6}$$

so that the average of $\vec{v}$ obeys the classical (deterministic) dynamics of a Stoke sphere without an external forcing.

Are there any constraints on the values of Γ ? The next section shows that Γ is indeed fixed, due to the equipartition theorem. This is an (example of an) important result which goes under the name of fluctuation-dissipation theorem.

14.2. Tuning the strength of noise and the fluctuation-dissipation theorem

Let us consider the average of $\vec{v}^2$:

$$\begin{aligned} \langle \vec{v}(t) \cdot \vec{v}(t) \rangle &= \vec{v}(0) \cdot \vec{v}(0) \exp(-2\gamma t) + 2 \int_0^t d\tau \exp\left[-\gamma(2t - \tau)\right] \vec{v}(0) \cdot \langle \vec{\eta}(\tau) \rangle \\ &+ \int_0^t d\tau \int_0^t d\tau' \exp\left[-\gamma(2t - \tau - \tau')\right] \langle \vec{\eta}(\tau) \cdot \vec{\eta}(\tau') \rangle. \end{aligned} \tag{7}$$

Considering Eqs. 4,5, one arrives at the following equality:

$$\langle \vec{v}(t) \cdot \vec{v}(t) \rangle = \vec{v}(0) \cdot \vec{v}(0) \exp(-2\gamma t) + \frac{3\Gamma}{2\gamma} \left[1 - \exp(-2\gamma t)\right]. \tag{8}$$

For large t this average should be equal to $3 k_B T$, by the equipartition theorem, therefore the value of C is fixed to be

$$\Gamma = 2 k_B T \gamma. \tag{9}$$

This relation between the strength of the fluctuations of the stochastic forces and the hydrodynamic drag γ, which is a dissipative term, is an example of a more general result known as fluctuation-dissipation theorem. In the next

Lecture on Fokker-Planck equation we will see other examples of this theorem at work.

14.3. Overdamped Langevin equation

For micron sized colloids (or smaller globular objects such as proteins – which are typically $\sim 5-10$ nm in size), the Reynolds number is very small so that inertial effects (captured by the term $m\frac{d\vec{v}}{dt}$) may safely be disregarded. The Langevin equation of a colloidal sphere subject to collisions in a viscous solvent and to a conservative force coming from a potential $V(x)$ is then (in 1D, note that $v \equiv dx/dt$):

$$\frac{dx}{dt} = \frac{F}{\gamma} + \eta(t) \tag{10}$$

$$F = -\frac{\partial V}{\partial x} \tag{11}$$

(Note that η has been rescaled by γ so that the fluctuations $\langle \eta(t)\eta(t')\rangle = 2k_BT/\gamma$ – the factor of 2 instead of 6 comes from the fact that here we are working in 1D.) In this form, the LE forms the basis of Brownian Dynamics (BD), which is arguably the most popular model to simulate on a computer the dynamics of polymers and/or a set of colloidal particles in a solvent (the solvent is sometimes referred to as implicit in this formulation as it only enters via the stochastic forcing). It is useful to stress that BD has an important drawback when used in this way, as it disregards the onset of a non-zero average velocity field in the solvent, which is equivalent to the onset of correlations between the velocities of different spheres (or beads or monomers in a polymer). In this way while the equilibrium is captured correctly the transient dynamics might be incorrect (indeed the scaling laws describing the relaxation dynamics from a non-equilibrium state of a polymer change when hydrodynamic correlations are included so that the BD is not in the same universality class of the hydrodynamic theory - and it is thus incorrect in this respect).

This particular LE is also a very common example of relaxational dynamics, which describes the approach to thermodynamic equilibrium (governed by the potential V), in this simplified case of a single particle.

If we fix $F = 0$, then the particle performs a random walk, and in 1D, we know that $\langle (x(t) - x(0))^2 \rangle = 2Dt$. On the other hand, by integrating Eq. 10 and computing its second moment, we obtain that:

$$\langle (x(t) - x(0))^2 \rangle = \frac{2k_BT}{\gamma} t. \tag{12}$$

By equating the two expression we obtain Stokes-Einstein's formula for diffusion:

$$D = \frac{k_BT}{\gamma} = \frac{k_BT}{6\pi\eta R}. \tag{13}$$

(Note that $\frac{1}{\gamma}$ is also referred to as inverse mobility.)

As an application, we can apply Eq.13 to compute the diffusion of a colloidal sphere of radius 1 micron in water. If we use a value of $\eta = 1$ cP (or equivalently 10^{-3} Pa s in SI units) for the viscosity of water and we plug in the value of k_BT, e.g. as 4.1 pN nm, we find that the diffusion coefficient of this sphere is about 0.2 $\mu\mathrm{m}^2\mathrm{s}^{-1}$.

The run-tumble-run motion of the *E. coli* bacterium, which is a similar size, may also be schematised by a random walk, i.e. diffusion, but in this case the diffusion coefficient at room temperature is about $500 - 1000$ $\mu\mathrm{m}^2\mathrm{s}^{-1}$. Why do you think we cannot use the Stokes-Einstein formula in this case?

14.4. The LE as an SDE and its handling on a computer

Let us now consider a slightly more general case of the LE written down in Eq. 10:

$$\frac{dx(t)}{dt} = f(x(t),t) + g(x(t),t)\eta'(t), \tag{14}$$

where $\langle \eta'(t)\eta'(t')\rangle = \delta(t-t')$. This is how physicists write down a stochastic differential equation (SDE). Let us introduce for later convenience the quantity:

$$W^\epsilon(t) = \int_t^{t+\epsilon} \eta(t')dt', \tag{15}$$

which gives the total force due to collisions with the liquid molecules in a time interval ϵ. In the simplest case, each collision gives a contribution to the force, and contributions coming from different collisions are uncorrelated (see above). Note that $\langle W^\epsilon(t)\rangle = 0$, and

$$\begin{aligned} \langle W^\epsilon(t)^2\rangle &= \langle \int_t^{t+\epsilon}\int_t^{t+\epsilon} \eta(t')\eta(t'')dt'dt''\rangle \\ &= \int_t^{t+\epsilon}\int_t^{t+\epsilon} \delta(t'-t'')dt'dt'' = \epsilon \end{aligned} \tag{16}$$

Mathematicians prefer to write down Eq. 10 as:

$$\begin{aligned} dx &= f(x,t)dt + g(x,t)dW(t) && (17) \\ \langle dW(t)dW(t'=t+dt)\rangle &= dt && (18) \end{aligned}$$

so that formally one may note that "$dW(t)/dt = \eta(t)$".

To understand the LE more in depth, it is useful to explicitly think of how to solve this on the computer. Let us take a small $\epsilon > 0$, and let us take $g(x(t),t) \equiv \sqrt{2D}$ for the time being. The discretized LE is:

$$x(t_{N+1}) = x(t_N) + \epsilon f(x(t_N),t_N) + \sqrt{2D}W^\epsilon(t_N). \tag{19}$$

We now have to specify how to simulate $\sqrt{2D}W^\epsilon(t_N)$. Let us call $t = N\epsilon$, $dt = n\epsilon$, with $1 \ll n \ll N$. We have:

$$x(t+dt) = x(t) + \sum_{i=N}^{N+n} \epsilon f(x(t_i),t_i) + \sum_{i=N}^{N+n} \sqrt{2D}W^\epsilon(t_i). \tag{20}$$

For $n \gg 1$, assuming integrability (e.g. a-la-Riemann) of f in the first term, and using the central limit theorem in the second term, we get:

$$x(t+dt) = x(t) + dt f(x(t),t) + \sqrt{dt}\sqrt{2D}\tilde{\eta}(t) \tag{21}$$

with $\tilde{\eta}(t)$ a gaussian random variable with mean 0 and variance 1. This equation can now be solved explicitly on a computer. Note that because η is a derivative of dW, it would be $\sim dt^{-1/2}$ (hence formally divergent) by what we have just shown.

*14.5. *The Ito-Stratonovich dilemma*

If $g(x,t)$ is not constant, the LE written above may be ambiguous. To see why this is so, let us consider the following integral version of the LE:

$$x(t) - x(0) = \int_0^t f(x(t'),t')dt' + \int_0^t g(x(t'),t')dW(t'). \tag{22}$$

It is thus natural to introduce the integral defined by the measure dW. However, due to the stochastic nature of the "measure" dW, this integral has some very peculiar properties. Note first that if f=0 and g=$\sqrt{2D}$ then:

$$x(t) - x(0) = \sqrt{2D}\int_0^t dW(t') = \sqrt{2D}W(t) \tag{23}$$

where $W(t)$ is a random walk of diffusion constant D. $W(t)$ is also known as the *Wiener process*. Consider now the definition:

$$\int_0^T g(t)dW(t) \equiv \lim_{N\to\infty}\sum_{i=0}^{N-1} g(\tau_i)\left(W(t_{i+1}) - W(t_i)\right) \tag{24}$$

$$\tau_i \equiv (1-\alpha)t_i + \alpha t_{i+1}, \tag{25}$$

where we have chosen a succession $0 = t_0 < \ldots < t_N = T$. If dW were a continuous measure, the result would be independent of α, with $0 < \alpha < 1$. If dW is the differential of the Wiener process, this is no longer true. The following case is an important example: consider the average of a Wiener process, namely

$$\langle \int_0^T W(t)dW(t)\rangle \left(= \langle \int_0^T (\int_0^t \eta(t')dt')\eta(t)dt\rangle \right) = \alpha. \tag{26}$$

Two conventions are common: if $\alpha = 0$ then the corresponding SDE is of "Ito form", whereas if $\alpha = 1/2$ it is of Stratonovich form. The first choice means that the function is independent of the successive increment in the random walk, and is more common in finance and mathematics. However note that it would imply "$W(t)dW(t) = 0$". Stratonovich's form is more common among physicists: note that it would imply "$W(t)dW(t) = d(W(t)^2)/2$". In general, if an SDE is written a-la-Stratonovich, the common rules of calculus formally apply, while there are corrections if it is written a-la-Ito. Note that this is *not* an issue with common LEs with constant g, or equivalently with thermal noise. It becomes important in the case of multiplicative noise (see below).

*14.6. *Non-potential systems and multiplicative noise: epidemics spreading and stock prices*

A notable strength of the LE is that it is not limited to the description of the approach to equilibrium in systems which can be described in equilibrium by a free energy. It can equally well describe the non-equilibrium dynamics of a system which is far from equilibrium. As a case study, let us consider the following example, a toy model for epidemics spreading (a similar situation may be encountered in some reaction-diffusion models).

Let us consider, in one spatial dimension, a ring made up by N sites (so that there are N links between nearest neighbours). The sites in the ring are characterised by a state σ_i, with $i = 1, \cdots, N$, which can take on the values 0 or 1. Let 0 denote a healthy individual and 1 denote a sick one. The sites are updated according to the following microscopic stochastic dynamics:

$$\sigma_i = 1 \quad \rightarrow \quad \sigma_i = 0 \qquad \text{with probability } 1-p \tag{27}$$

$$\sigma_{i\pm1} = 0 \quad \rightarrow \quad \sigma_{i\pm1} = 1 \qquad \text{if } \sigma_i = 1\,, \text{with probability } 1-p. \tag{28}$$

In other words, the disease spreads to the nearest neighbours and its spreading is probabilistic. This microscopic dynamics (other slightly different versions are qualitatively equivalent) *cannot* be derived starting from a potential or a Hamiltonian (as we do not know how to write $H(\{\sigma_i\}_i)$). It leads to a non-equilibrium phase transition between a "passive" phase in which all individuals/agents are healthy ($\sigma_i = 0\ \forall i$), and another one in which there is a non-zero density of sick individuals (i.e. a number of sick individuals which is extensive in the thermodynamic limit). This transition occurs at a critical value of the probability p, p_c. Note that this system cannot come from a potential because it does not satisfy *detailed balance*. It is easy to understand why this is the case, as there is an absorbing state in which all the individuals are healthy. Given the dynamical rules which we have postulated, this state will not evolve in time. As a result the probability of exiting this state is 0, while the probability of reaching it is non-zero, hence detailed balance does not hold.

This model for epidemics is an example of far-from-equilibrium system which shows a phase transition (for which a set of critical exponents can be defined in close analogy to conventional equilibrium statistical mechanics). Nevertheless we can write down a "coarse-grained" Langevin dynamics, with not much more work than for the case of systems which possess a thermodynamic potential. In this case our coarse grained dynamic variable is $\psi_a(x,t)$, which is a scalar field, giving the spatio-temporal density/fraction of sick individuals ($0 < \psi_a(x,t) < 1$ for any x and t). The generic form for the LE for ψ is:

$$\frac{\partial \psi(x,t)}{\partial t} = f(\psi(x,t)) + g(\psi(x,t))\eta(x,t) \tag{29}$$

On the basis of symmetry alone, and close to the phase transition at $p = p_c$, we can expand the observables, f and g^2, in powers of ψ and $\nabla\psi$, to obtain:

$$\begin{aligned} f &= c_1 + r\psi(x,t) + u\psi(x,t)^2 + \cdots + c_2\nabla\psi + c_3\left(\nabla^2\psi\right) && (30) \\ g^2 &= c_1' + r'\psi(x,t) + u'\psi(x,t)^2 + \cdots + c_2'\nabla\psi + c_3'\left(\nabla^2\psi\right). && (31) \end{aligned}$$

Now: $c_1 = 0$ as the system is closed (otherwise the activity would systematically increase or decrease in time), $r, u \neq 0$ in general, $c_2 = 0$ as in a ring there is left/right symmetry, and $c_3 \neq 0$. For the second equation, $c_2' = 0$ for the same reason, and $c_1' = 0$ as when $\psi(x,t) = 0$ there should be no noise. As a result the simplest non zero term for g^2 is proportional to ψ. In this case thus the noise is not thermal as before, but it is "multiplicative". As a general rule, non-equilibrium systems with absorbing states *should be described* by a Langevin equation with multiplicative noise. In our case the minimal LE to describe the coarse grained dynamics of ψ is:

$$\frac{\partial\psi(x,t)}{\partial t} = c\left(\nabla^2\psi(x,t)\right) + r\psi(x,t) - u\psi(x,t)^2 + \sqrt{r'\psi(x,t)}\eta(x,t). \quad (32)$$

It is interesting to note that Eq. 32 also comes up in different contexts, as a reaction-diffusion equation (without the noise term it is equivalent to the Fisher equation, which may describe the wave of advance of an advantageous genetic trait in a population).

Another context in which a non-constant g appears (we have multiplicative noise) is in a LE description of stock market fluctuation. A commonly used LE to describe the dynamics of the price of a stock, S, is:

$$\frac{dS}{dt} = \mu S dt + \sigma S dW \quad (33)$$

with $\sigma > 0$. This equation derives from the assumption that the rate of change of a stock price are themselves random. (LEs like these are commonly interpreted a-la-Ito).