Nonequilibrium Statistical Mechanics - Lecture notes

I. INTRODUCTION

Non-equilibrium statistical mechanics is the formalism that allows us to understand and quantify time dependent phenomena in macroscopic systems. These notes give a brief introduction to some of the key ideas in the simplest context of the motion of a tagged particle in a fluid. Recommended additional reading includes the last chapter in Chandler's book "Introduction to Modern Statistical Mechanics" , Robert Zwanzig's book entitled "Non-equilibrium Statistical Mechanics" and Van Kampen's seminal book "Stochastic processes in physics and chemistry".

II. BROWNIAN MOTION - LANGEVIN DYNAMICS

Let us consider a micron sized particle of mass m in one spatial dimension in a fluid of viscosity η. The equation of motion of this particle will be

$$\frac{\partial x}{\partial t} = v; m\frac{\partial v}{\partial t} = F$$

where F is a force exerted by the fluid molecules on this particle. Identifying the exact form of the force requires us to confront the Newton's equations associated with the very large number of fluid particles. Instead, as a first step, we take a phenomenological approach. Empirical facts suggest that the dominant force exerted by the fluid on the particle is a friction force proportional to the velocity of the Brownian particle with the friction given by the Stokes drag $\zeta = 6\pi a\eta$ for a spherical particle of radius a in a fluid of viscosity η. If this was the entire effect of the fluid, the equation of motion for the Brownian particle becomes

$$m\frac{\partial v}{\partial t} = -\zeta v$$

Solving for the velocity for a given initial condition we have,

$$v\left(t\right) = e^{-\frac{\zeta}{m}t}v\left(0\right)$$

According to this, the velocity of the Brownian particle at long times becomes zero. But this is not satisfactory because we should expect that the Brownian particle comes to equilibrium with the fluid and hence its mean square velocity should correspond to the temperature of the surrounding fluid, i.e., $\left\langle v^2\right\rangle = k_BT/m$. The appropriate modification to the fluid force is to add a random force in addition to the deterministic friction force given above. Then the equation of motion of the Brownian particle becomes

$$m\frac{\partial v}{\partial t} = -\zeta v + \eta$$

where η is now a stochastic force. The above equation is called the Langevin equation for a Brownian particle (and is a particular realization of the fundamental dynamical equation underlying all stochastic processes in physics and chemistry). The stochastic part of the force arises because of occasional imbalance in the impacts of the fluid particles with the Brownian particle. So we should expect the such a force lasts for a very short time (of the order of the molecular collision) and successive events are uncorrelated. Given this physical context, we assume that the random force is a "one step Markov process", i.e., η is drawn from a Gaussian distribution such that

$$\left\langle \eta\left(t\right)\right\rangle_c = 0$$

$$\left\langle \eta\left(t\right)\eta\left(t'\right)\right\rangle_c = 2B\delta\left(t-t'\right)$$

and all higher cumulants vanish. This is the mesoscopic description of a Brownian particle that will be the focus of the rest of this section.

For a given initial condition we can solve for the velocity as a function of time to get

$$v\left(t\right) = e^{-\frac{\zeta}{m}t}v\left(0\right) + \frac{1}{m}\int_0^t dt' e^{-\frac{\zeta}{m}\left(t-t'\right)}\eta\left(t'\right)$$

When averaged over noise this decays to zero at long times as should be expected. The mean square velocity on the other hand takes the form

$$\left\langle v^2\left(t\right)\right\rangle = e^{-2\frac{\zeta}{m}t}v\left(0\right) + \frac{B}{\zeta m}\left(1-e^{-2\frac{\zeta}{m}t}\right)$$

Given the fact that the Brownian particle comes to equilibrium with a thermal bath we should expect that $\lim_{t\to\infty}\left\langle v^2(t)\right\rangle = \frac{k_BT}{m}$ This together with the equation above identifies the magnitude of the noise in the system as

$$B = \zeta k_B T$$

This relationship is a particular case of a fluctuation-dissipation theorem. The frictional damping provided by the medium is an example of dissipation, representative of the tendency of macroscopic systems to approach thermodynamic equilibrium. The stochastic force is an example of a fluctuation, a fast time scale dynamics that is a remnant of the detailed microdynamics of the system. Both of them have their origin in the same phenomena, in this case that of collisions of the Brownian particle with the fluid particle. So, we should expect that they are related to each other. The way the relationship is uncovered is to see the consequence of the two forces to the asymptotic (i.e., long time limit) state of the system. If the asymptotic state is an equilibrium state of temperature T, then the relationship between fluctuation and dissipation is as given above. When the asymptotic state is something different (as happens in inherently out of equilibrium systems such as those that occur in Biology or in systems maintained in a non-equilibrium steady state due to external driving such as in shear flows), the relationship can be quite different and complex.

Finally, we can use the Langevin dynamics above to estimate the mean square displacement of a Brownian particle. Note that

$$x(t) = x(0) + \int_0^t ds v(s)$$

Defining $\Delta x = x(t) - x(0)$, we have

$$\left\langle \Delta x(t)^2 \right\rangle = \int_0^t ds \int_0^t ds' \left\langle v(s) v(s') \right\rangle$$

Substituting the form of the velocities given earlier and carrying out the various time integrals we get

$$\left\langle \Delta x(t)^2 \right\rangle = \frac{2k_BT}{\zeta}\left[t - \frac{m}{\zeta} + \frac{m}{\zeta}e^{-\frac{\zeta t}{m}}\right]$$

where the initial velocities $v(0)$ of the Brownian particle as assumed to be drawn from an equilibrium distribution, i.e., $\left\langle v(0)^2 \right\rangle = \frac{k_BT}{m}$. The above expression indicates that at times $t >> \frac{m}{\zeta}$ the mean square displacement grows linearly with the velocity. This linear dependence is considered the signature of diffusive behavior or the fact that the Brownian particle is a random walker. This is in contrast to ballistic dynamics in which case $x \sim vt$ and therefore $x^2 \sim t^2$ and square of the displacement grows quadratically. It is easy to see by taylor expanding the above expression that on time scales $t << m/\zeta$ the Brownian particle exhibits a ballistic behavior as well and only at long times do we cross over to a diffusive behavior.

III. BROWNIAN MOTION - MACROSCOPIC PHENOMENOLOGY

The macroscopic phenomenon that emerges from the considerations of Brownian motion discussed in the previous section is that of diffusion. A prototypical scenario is to to release a dye of heavy molecules at one point in a clear fluid and watch the color spread as a function of time. Such a process is phenomenologically described by a diffusion equation. In one dimension, the diffusion equation is given by

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}$$

where $C(x,t)$ is the concentration of particles at a point x at a time t. It is a probability distribution but for the fact that the normalization now is the number of particles in the system rather than unity. From the above macroscopic equation, we can calculate the mean square displacement of a particular particle as

$$\begin{aligned}\frac{\partial\left\langle x^2(t)\right\rangle}{\partial t} &= D\int dx x^2 \frac{\partial^2 C(x,t)}{\partial x^2}\\ &= 2D\end{aligned}$$

Assuming without loss of generality that the particle is at the origin at time $t = 0$, we can integrate the above equation to get

$$\left\langle x^2 (t) \right\rangle = 2Dt$$

This is precisely the long time limit of the dynamics of a Brownian particle that obeys a Langevin equation and hence is the "emergent" or macroscopic theory associated with the microdynamics described in the previous section.

IV. BROWNIAN MOTION - BRIDGING THE TWO DESCRIPTIONS

The bridge that enables us to extract the Fokker-Planck equation and finally the diffusion equation is that of non-equilibrium statistical mechanics. In order to do this right, we need the machinery of stochastic calculus. This is beyond the scope of this class. The interested reader is referred to the Van Kampen book for a detailed formulation of these methods and for a quick and dirty introduction to stochastic calculus these lecture notes from a non equilibrium class at UIUC (http://www.ks.uiuc.edu/Services/Class/PHYS498/LectureNotes/chp2.pdf). In the following a simple method to see the answer emerge is outlined.

Let us begin by considering an abstract problem. The case of a brownian particle in a fluid is a special case of the derivation outlined here. Various other named equations you will encounter, such as the Smoluchowski equation and the Vlasov equation are all special cases as well. Let the microstate of the system be given by M variables $(a_1 ... a_M)$. Suppose each variable obeys a Langevin equation of the form

$$\frac{\partial a_i}{\partial t} = V_i (a_1 ... a_M) + F_i (t)$$

where V_i is some function of the microstate $(a_1 ... a_M)$ (for example a potential of interaction like from E and M) and F_i is a stochastic force. Introduce a vector notation that would allow us to give a unified representation to the M dynamical equations above in the form

$$\frac{\partial \mathbf{a}}{\partial t} = \mathbf{V} (\mathbf{a}) + \mathbf{F} (t)$$

The stochastic forces F_i's are assumed to be Markovian with correlations given by

$$\langle F_i (t) F_j (t') \rangle = 2B_{ij} \delta (t - t')$$

with B_{ij} being a matrix of constants. Now, the statistical mechanics associated with this system must be given by the distribution function $\hat{f} (\mathbf{a}, t|\mathbf{F})$ where we use the $\hat{}$ to denote the fact that this is not yet noise averaged. Clearly this distribution function must be normalized at all times, i.e.,

$$\int d\mathbf{a} \hat{f} (\mathbf{a}, t|\mathbf{F}) = 1$$

Further, the distribution function must be locally conserved, i.e., the time derivative must be related to the gradient of a flux. This gives us the analog of the Liouville equation for stochastic microdynamics in the form

$$\frac{\partial \hat{f}}{\partial t} + \frac{\partial}{\partial \mathbf{a}} \cdot \left(\frac{\partial \mathbf{a}}{\partial t} \hat{f} \right) = 0$$

Using the specific form of the dynamics prescribed above, we have,

$$\frac{\partial \hat{f}}{\partial t} = -\frac{\partial}{\partial \mathbf{a}} \cdot \left(\mathbf{V} (\mathbf{a}) \hat{f} \right) - \frac{\partial}{\partial \mathbf{a}} \cdot \left(\mathbf{F} (t) \hat{f} \right) \tag{1}$$

Now, let us introduce some notation as follows. Let us define an operator L such that its action on any function Φ is given by

$$L\Phi = \frac{\partial}{\partial \mathbf{a}} \cdot (\mathbf{V} (\mathbf{a}) \Phi) ,$$

i.e., precisely the deterministic part of our microdynamics. Then, I can formally integrate up the "Liouville equation" above as

$$\hat{f} (\mathbf{a}, t|\mathbf{F}) = e^{-tL} \hat{f} (\mathbf{a}, 0) - \int_0^t ds e^{-(t-s)L} \frac{\partial}{\partial \mathbf{a}} \cdot \left(\mathbf{F} (s) \hat{f} (\mathbf{a}, s|\mathbf{F}) \right)$$

Let us then substitute this formal solution back into the second term of Eq. 1 to get the following equivalent dynamical equation,

$$\frac{\partial \hat{f}}{\partial t} = -\frac{\partial}{\partial \mathbf{a}} \cdot \left(\mathbf{V}(\mathbf{a}) \hat{f} \right) - \frac{\partial}{\partial \mathbf{a}} \cdot \left(\mathbf{F}(t) \hat{f}(\mathbf{a}, 0) \right) + \frac{\partial}{\partial \mathbf{a}} \cdot \mathbf{F}(t) \int_0^t ds e^{-(t-s)L} \frac{\partial}{\partial \mathbf{a}} \cdot \left(\mathbf{F}(s) \hat{f}(\mathbf{a}, s|\mathbf{F}) \right).$$

We are now ready to carry out the noise average. We are interested in the dynamical equation for the noise-averaged distribution function

$$f(\mathbf{a}, t) = \left\langle \hat{f}(\mathbf{a}, t|\mathbf{F}) \right\rangle$$

Clearly $\left\langle \mathbf{F}(t) \hat{f}(\mathbf{a}, 0) \right\rangle = \langle \mathbf{F}(t) \rangle \hat{f}(\mathbf{a}, 0) = 0$. In the other term we have to calculate $\left\langle \mathbf{F}(t) \mathbf{F}(s) \hat{f}(\mathbf{a}, s|\mathbf{F}) \right\rangle$. If we make the naive guess that $\left\langle \mathbf{F}(t) \mathbf{F}(s) \hat{f}(\mathbf{a}, s|\mathbf{F}) \right\rangle = \langle \mathbf{F}(t) \mathbf{F}(s) \rangle \left\langle \hat{f}(\mathbf{a}, s|\mathbf{F}) \right\rangle$ then we would expect that $\left\langle \mathbf{F}(t) \mathbf{F}(s) \hat{f}(\mathbf{a}, s|\mathbf{F}) \right\rangle = \delta(t-s) 2\mathbf{B} f(\mathbf{a}, t)$. The right way to carry out this average is to use Ito calculus. This is a formulation that we have not had the time to develop carefully. So, we just state the result, that $\left\langle \mathbf{F}(t) \mathbf{F}(s) \hat{f}(\mathbf{a}, s|\mathbf{F}) \right\rangle = \delta(t-s) \mathbf{B} f(\mathbf{a}, t)$. Doing it correctly gives an additional factor of 1/2.So, even though in the end we have to cheat a little, it is hoped that the "derivation" above gives you a feeling of how the microdynamics is related to the macrodynamics. In any case at the end of the day the dynamical equation associated with the noise-averaged distribution function is

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \mathbf{a}} \cdot (\mathbf{V}(\mathbf{a}) f) + \frac{\partial}{\partial \mathbf{a}} \cdot \mathbf{B} \cdot \frac{\partial}{\partial \mathbf{a}} f(\mathbf{a}, t)$$

This is the most general Fokker-Planck equation one can write down.

Now let us specialize to the case we studied the microdynamics in detail for, namely the Langevin equation for a Brownian particle in a fluid in one dimension. In this case, each of the quantities above become

$$\mathbf{a} \to \begin{pmatrix} x \\ v \end{pmatrix}; \mathbf{V}(\mathbf{a}) \to \begin{pmatrix} v \\ -\frac{\zeta}{m} v \end{pmatrix};$$
$$\mathbf{F} \to \begin{pmatrix} 0 \\ \frac{\eta}{m} \end{pmatrix}; \mathbf{B} \to \begin{pmatrix} 0 & 0 \\ 0 & \frac{\zeta k_B T}{m^2} \end{pmatrix}$$

So, substituting the various specific forms, we get

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial x} v f + \frac{\zeta}{m} \frac{\partial}{\partial v} v f + \frac{\zeta k_B T}{m} \frac{\partial^2 f}{\partial v^2} \tag{2}$$

This is the Fokker-Planck equation associated with the Brownian motion of a particle in a fluid. Note that this equation has dissipation built into it. It is easy to see that the homogenous stationary solution to the above equation is the Maxwell-Boltzmann distribution,

$$f \sim \exp\left(-\frac{1}{2} \frac{m v^2}{k_B T} \right)$$

So, equilibrium is built into the dynamics prescibed by this equation. It needs a little bit more work, but one can show that the equation does exhibit irreversible approach to equilibrium. Finally, we need to see the relationship between the Fokker-Planck equation above to the phenomenological diffusion equation described in the previous section. For this purpose note that the concentration field C is related to the one particle distribution function by

$$C(x, t) = \int dv f(x, v, t),$$

i.e., it is the zeroth moment with respect to velocity of f. Also define

$$J(x, t) = \int dv v f(x, v, t),$$

a flux J that is the first moment with respect to velocity. Then from the Fokker-Planck equation above we can identify the dynamical equations associated with these two quantities. Taking corresponding moments with respect to the velocity in Eq. 2 we get

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x} J(x, t)$$

and

$$\frac{\partial J}{\partial t} = -\frac{\zeta}{m} J(x,t) - \frac{\partial}{\partial x} \int dv v^2 f(x,v,t)$$

The concentration equation is a conservation law that tells us the concentration is conserved and hence its time derivative must be the gradient of a flux. The equation for the flux is overdamped, i.e., the homogeneous dynamics (no gradients) is characterized by an exponential decay whose time scale is set by ζ/m. Also, this equation couples into the second moment with respect to velocity of the one particle distribution. Note that we expect the diffusion equation to be the relevant description of the system at times long compared to ζ/m. We base this expectation on our study of the microdynamics of the system which showed us that the velocity of the particle decays to its asymptotic value on this time scale. Hence, it is reasonable to assume that $f(x,v,t) \sim f_{eq}(v) C(x,t)$, i.e., the velocity part of the distribution function relaxes to its equilibrium (or long time) value while the concentration remains dynamical. Using this physically motivated guess in the equation for J above and overdamping (i.e., drop $\partial/\partial t$ in comparison to ζ/m) the resulting equation gives us an expression for the flux J in terms of the concentration field,

$$J(x,t) \to -\frac{k_B T}{\zeta} \frac{\partial C(x,t)}{\partial x}$$

Substituting this form in the dynamical equation for the concentration gives

$$\frac{\partial C}{\partial t} = \frac{k_B T}{\zeta} \frac{\partial^2 C(x,t)}{\partial x^2}$$

which is precisely the diffusion equation with the diffusion coefficient identified as $D = k_B T/\zeta$.

Note that the purpose of this long-winded exercise is to identify precisely the physical circumstances under which the diffusion equation is a relevant description for the dynamics of a system. Make sure that you are able to track the various approximations we have made and their physical motivation.

V. WHERE DOES A LANGEVIN EQUATION COME FROM ?

The Langevin equation we have discussed in the first section is a phenomenological description. The fundamental description of a Brownian particle in a fluid should consist of Newton's equations for the Brownian particle and every particle in the fluid. There exists a systematic way of going from the Newton's equations to the Langevin equation that is called the Mori-Zwanzig projection operator method. This is an involved framework in which it is not straightforward to see what is going on and how this might be connected to the Langevin picture above. So, for the intellectual satisfaction of seeing the Langevin equations emerge from a truly microscopic description, we consider below a particular simple case where we can work out all of the details without resorting to any formalism beyond what we already know how to do. So, for the intellectual satisfaction of seeing the Langevin equations emerge from a truely microscopic description, we consider below a particular simple case where we can work out all of the details without resorting to any formalism beyond what we already know how to do.

The particular case we consider here is that of a Brownian particle in $1-D$ harmonically coupled to a bath of non-interacting harmonic oscillators. The Hamiltonian of such a system is given by

$$H = \frac{p_0^2}{2m_0} + \sum_{j=1}^{N} \left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 \left(q_j - \frac{\gamma_j}{\omega_j^2} x_0 \right)^2 \right)$$

where (p_0, x_0) is the microstate of the brownian particle and (p_i, q_i) are the microstates of the bath particles. In the above, the mass of the bath particle is taken to be 1 (i.e., we have chosen it to be the unit of mass). Given the Hamiltonian, we can readily write down the equations of motion for all of the particles. These are

$$\frac{\partial x_0}{\partial t} = \frac{p_0}{m_0}; \frac{\partial p_0}{\partial t} = \sum_j \gamma_j \left(q_j - \frac{\gamma_j}{\omega_j^2} x_0 \right)$$

$$\frac{\partial q_j}{\partial t} = p_j; \frac{\partial p_j}{\partial t} = -\omega_j^2 q_j + \gamma_j x_0$$

Now, we seek to extract from here the effective dynamics of the Brownian particle alone. To this end, let us first rewrite the equations of motion of the bath particles as

$$\frac{\partial^2 q_j}{\partial t^2} = -\omega_j^2 q_j + \gamma_j x_0(t)$$

Then, given initial positions and velocities of all of the bath particles, we can solve for the dynamics implicitly in terms of the the position of the Brownian particle $x_0(t)$. This gives

$$q_j(t) = q_j(0)\cos\omega_j t + p_j(0)\frac{\sin\omega_j t}{\omega_j} + \gamma_j \int_0^t ds x_0(s)\frac{\sin\omega_j(t-s)}{\omega_j}$$

Integrating by parts on the last term and rearranging the resulting expression, this can be written in the following equivalent form,

$$q_j(t) - \frac{\gamma_j}{\omega_j^2}x_0(t) = \left(q_j(0) - \frac{\gamma_j}{\omega_j^2}x_0(0)\right)\cos\omega_j t + p_j(0)\frac{\sin\omega_j t}{\omega_j} - \gamma_j\int_0^t ds\frac{p(s)}{m_0}\frac{\cos\omega_j(t-s)}{\omega_j^2}$$

Note that the left hand side now is precisely $\frac{\partial p_0}{\partial t}$. Therefore the equation of motion of the Brownian particle can now be written as

$$\frac{\partial p_0}{\partial t} = -\int_0^t dsK(s)\frac{p(t-s)}{m_0} + F_p(t) \tag{3}$$

$$K(t) = \sum_j \frac{\gamma_j^2}{\omega_j^2}\cos\omega_j t$$

$$F_p(t) = \sum_j \frac{\gamma_j p_j(0)}{\omega_j}\sin\omega_j t + \sum_j \gamma_j\left(q_j(0) - \frac{\gamma_j}{\omega_j^2}x(0)\right)\cos\omega_j t$$

Up through this point, we have made no approximations. All of the above has just been a formal rewriting of the equations of motion of the system. This formally equivalent equation now has the "Langevin" form in that we have been able to partition the interaction with the bath into a "dissipation" given by the Kernel K and a "fluctuation" given by the force F_p. We now make a physically motivated approximation. We are interested in the dynamics of the Brownian particle. This is slow enough such that many collision events occur with the fluid particles on the relevant time scale. Hence, it is reasonable to assume that the dissipation kernel K and the fluctuating force F_p can be approximated by their ensemble averaged values with the ensemble being the canonical ensemble associated with the fluid at temperature T, $P \sim \exp(-H/k_B T)$. Using this distribution function we can readily see that the average of $p_i(0)$ and $q_i(0)$ vanish, while their mean squared values are given by

$$\left\langle p_j^2(0)\right\rangle = k_B T; \left\langle\left(q_j(0) - \frac{\gamma_j}{\omega_j^2}x(0)\right)^2\right\rangle = \frac{k_B T}{\omega_j^2}$$

Using this result and the fact that terms such as $p_i(0)p_j(0)$ and $q_i(0)p_j(0)$ etc vanish under the average to see that the ensemble averaged value od the fluctuating force at two times t and t' is given by

$$\begin{aligned}\langle F_p(t)F_p(t')\rangle &= \sum_j \gamma_j^2\frac{k_B T}{\omega_j^2}\sin\omega_j t\sin\omega_j t' + \sum_j \gamma_j^2\frac{k_B T}{\omega_j^2}\cos\omega_j t\cos\omega_j t' \\ &= k_B T\sum_j \frac{\gamma_j^2}{\omega_j^2}\cos\omega_j(t-t') \\ &= k_B T K(t-t')\end{aligned}$$

Thus, as long as there is scale separation to the extent that ensemble averaging is justified, the fluctuating force is simply related to the dissipation kernel. The above result is the generalized version of a fluctuation-dissipation theorem.

Finally, to make a mapping to the particular simple form of a Langevin equation we studied in the first section, let us assume that there are a large number of oscillators in the bath and hence give the dissipation kernel a continuous representation as follows:

$$K(t) = \sum_j \frac{\gamma_j^2}{\omega_j^2} \cos \omega_j t$$
$$= \int d\omega g(\omega) \frac{\gamma(\omega)^2}{\omega^2} \cos \omega t$$

where $g(\omega)$ is a "density of states" in that it is the number of oscillators at a given frequency. Now, clearly the kernel is a Fourier transform of potentially arbitrary functions $g(\omega)$ and $\gamma(\omega)^2/\omega^2$ So, in principle we can make the kernel have any form we like by tuning the bath properties through the density of states and the coupling constant. In particular, if $\gamma(\omega)$ is a constant independent of ω and $g(\omega)$ is quadratic in ω then $K(t) = C\delta(t)$. Then, the Langevin equation Eq. 3 reduces to the simple form we postulated in the first section. But generally for real physical system the Markov approximation of making K and $\langle FF \rangle$ proportional to delta functions is just that, an approximation. They are both typically sharply peaked about $t = 0$ but are not true delta functions. This concludes our derivation of a Langevin description from the underlying Newton's equations.