IP326. Lecture 23. Thursday, March 21, 2019

● Diffusion equations of various kinds

In Lecture 19, we saw that the application of the GLE to the dynamics of a large mass (such as a colloid) in a fluid of much smaller masses led to a Langevin equation for the larger mass's velocity. In one dimension, this Langevin equation is given by

$$m\frac{\partial v(t)}{\partial t} = -\zeta v(t) + f(t) \tag{1}$$

where m is the particle's mass, $v(t)$ its velocity at time t, ζ its friction coefficient, and $f(t)$ a random variable that we argued could be assumed to have these properties:

$$\langle f(t)\rangle = 0, \tag{2a}$$

$$\langle f(t) f(t')\rangle = 2\zeta k_B T\delta(t-t') \tag{2b}$$

In arriving at Eqs. (1) and (2), we made the following assumptions: (1) that $f(t)$ decayed from its initial value extremely fast (essentially instantaneously), and (2) that at long times the average energy of the system was dictated by the equipartition theorem.

We'd now like to convert the above Langevin equation into an equation for the probability density, $P(v,t)$, that the particle has a velocity v at the time t. Formally, we can define $P(v,t)$ as follows:

$$P(v,t) = \langle \delta(v - v(t))\rangle \tag{3}$$

where the angular brackets denote an average over the distribution of the random variable $f(t)$. That the RHS of Eq. (3) does indeed correspond to the distribution of values that the particle's velocity can assume at time t can be seen as follows: a particle starting off with some initial velocity eventually ends up – under the influence of the random force – with the velocity $v(t)$ after an interval of time t; that velocity may or may not correspond to some given value v; if it does, the delta function "counts" the occurrence by becoming infinitely large; if it doesn't, the delta function returns the value 0, meaning the mismatch is not counted. At the end of the given time interval, the particle is "reset" to an initial value and then again allowed to evolve (stochastically) for the same interval of time t. Its velocity at that time is again counted if it equals v, but not otherwise. The process is repeated a large number of times, in this way effectively building up a histogram of the number of times $v(t)$ assumes a particular value at time t.

To determine how $P(v,t)$ evolves in time, we first differentiate both sides of Eq. (3) with respect to t, and then use the chain rule to proceed further, as shown below:

$$\frac{\partial P(v,t)}{\partial t} = \frac{\partial}{\partial t}\left\langle \delta(v - v(t)) \right\rangle$$

$$= \left\langle \frac{\partial}{\partial t}\delta(v - v(t)) \right\rangle$$

$$= \left\langle \frac{\partial}{\partial v(t)}\delta(v - v(t))\dot{v}(t) \right\rangle \tag{4}$$

It's easy to show that delta functions have the following property:

$$\frac{\partial}{\partial b}\delta(a-b) = -\frac{\partial}{\partial a}\delta(a-b) \tag{5}$$

The proof is based on the Fourier representation of the delta function; in this representation, the LHS of Eq. (5) is given by

$$\frac{\partial}{\partial b}\delta(a-b) = \frac{\partial}{\partial b}\int d\lambda e^{i\lambda(a-b)}$$

$$= -i\int d\lambda e^{i\lambda(a-b)}\lambda$$

Exactly the same result is obtained when the delta function on the RHS of Eq. (5) is represented as a Fourier integral, establishing that the equality in Eq. (5) does indeed hold. And when this equality is applied to Eq. (4), we get

$$\frac{\partial P(v,t)}{\partial t} = -\left\langle \frac{\partial}{\partial v}\delta(v - v(t))\dot{v}(t) \right\rangle$$

$$= -\frac{\partial}{\partial v}\left\langle \delta(v - v(t))\dot{v}(t) \right\rangle \tag{6}$$

where the second line follows from the fact that v is just a parameter and not a dynamical variable, so it is unaffected by the averaging procedure represented by the angular brackets, and can therefore be taken outside them.

The expression for $\dot{v}(t)$ from Eq. (1) is now substituted into Eq. (6), producing

$$\frac{\partial P(v,t)}{\partial t} = -\frac{\partial}{\partial v}\left\langle \delta(v - v(t))\left\{ -\frac{\zeta}{m}v(t) + \frac{1}{m}f(t) \right\} \right\rangle$$

$$= \frac{\zeta}{m}\frac{\partial}{\partial v}\left\langle \delta(v - v(t))v(t) \right\rangle - \frac{1}{m}\frac{\partial}{\partial v}\left\langle \delta(v - v(t)) f(t) \right\rangle \qquad (7)$$

We can appeal to another property of delta functions at this stage of the calculation: $x\delta(a-x) = a\delta(a-x)$. This allows us treat the average in the first term on the RHS of Eq. (7) as follows:

$$\left\langle \delta(v - v(t))v(t) \right\rangle = \left\langle \delta(v - v(t))v \right\rangle$$

$$= v\left\langle \delta(v - v(t)) \right\rangle$$

$$= vP(v,t) \qquad (8)$$

As for the second term on the RHS of Eq. (7), this is where we invoke Novikov's theorem; this term is exactly of the form $\left\langle \theta(t) F[\theta] \right\rangle$, with $f(t)$ playing the role of $\theta(t)$ and $\delta(v - v(t))$ playing the role of the functional F; $\delta(v - v(t))$ is a functional of f because the velocity $v(t)$ is a functional of f (as becomes evident when Eq. (1) is solved for $v(t)$.) So using Novikov's theorem, we have

$$\left\langle \delta(v - v(t)) f(t) \right\rangle = \int_0^t dt' \left\langle f(t) f(t') \right\rangle \left\langle \frac{\delta}{\delta f(t')} \delta(v - v(t)) \right\rangle$$

$$= \int_0^t dt' \left\langle f(t) f(t') \right\rangle \left\langle \frac{\partial}{\partial v(t)} \delta(v - v(t)) \frac{\delta v(t)}{\delta f(t')} \right\rangle \quad \text{(chain rule)}$$

$$= -\frac{\partial}{\partial v} \int_0^t dt' \left\langle f(t) f(t') \right\rangle \left\langle \delta(v - v(t)) \frac{\delta v(t)}{\delta f(t')} \right\rangle \quad \text{(delta function property)} \qquad (9)$$

To proceed further, we need to derive an expression for the functional derivative $\delta v(t)/\delta f(t')$. This can be done starting from Eq. (1); if we functionally differentiate this equation with respect to $f(t')$ (interchanging the order of the t and $f(t')$ differentiations), we get

$$\frac{\partial}{\partial t}\frac{\delta v(t)}{\delta f(t')} = -\frac{\zeta}{m}\frac{\delta v(t)}{\delta f(t')} + \frac{1}{m}\delta(t - t') \qquad (10)$$

This is a linear first order differential equation for the function $\delta v(t)/\delta f(t')$ that can be solved, as usual, by the method of integrating factors. The solution, under the initial condition $\delta v(0)/\delta f(t') = 0$, is

$$\frac{\delta v(t)}{\delta f(t')} = \frac{1}{m}\int_0^t dt'' e^{-\zeta(t-t'')/m}\delta(t''-t') \tag{11}$$

On the face of it, the integral over t'' in this expression is easy to carry out; the result would appear to be $\exp[-\zeta(t-t')/m]$, and indeed it is, but only if t' happens to lie in the interval between 0 and *t*; if it is larger than *t*, the integral is actually 0 (courtesy the delta function.) So, in fact, Eq. (11) actually reduces to

$$\frac{\delta v(t)}{\delta f(t')} = \frac{1}{m} e^{-\zeta(t-t')/m} H(t-t') \tag{12}$$

where $H(t-t')$ is the Heaviside step function, with the property that $H(x)=1$ for $x>0$ and $H(x)=0$ for $x<0$.

Substituting Eqs. (8), (9) and (12) into Eq. (7), using Eq. (2b) for the correlation of random forces, and recalling that $\langle \delta(v-v(t)) \rangle$ is the definition of $P(v,t)$, we arrive at the following intermediate result

$$\frac{\partial P(v,t)}{\partial t} = \frac{\zeta}{m}\frac{\partial}{\partial v} vP(v,t) + \frac{2\zeta k_B T}{m^2}\frac{\partial^2}{\partial v^2}\int_0^t dt' \delta(t-t') P(v,t) e^{-\zeta(t-t')/m} H(t-t') \tag{13}$$

The final step is to carry out the integration over t', which again, because of the delta function, is easily done, but the process leads to a factor of *H*(0). Strictly speaking, this quantity is undefined, but by common convention it is understood to have the value 1/2. With this understanding, Eq. (13) finally becomes

$$\frac{\partial P(v,t)}{\partial t} = \frac{\zeta}{m}\frac{\partial}{\partial v} vP(v,t) + \frac{\zeta k_B T}{m^2}\frac{\partial^2}{\partial v^2} P(v,t) \tag{14}$$

This is the Ornstein-Uhlenbeck equation for diffusion in velocity space.

● Diffusion in position space

In dense fluids, the velocity of a large mass (such as a colloid) relaxes extremely quickly from an initial non-equilibrium value, so its inertia (as represented by the term $m\dot{v}(t)$) is negligible. In such fluids, then, Eq. (1) reduces to

$$\zeta \frac{dx(t)}{dt} = f(t) \tag{15}$$

which can be described as the *overdamped* limit of Eq. (1). This limiting form of Eq. (1) can be used to derive an expression for the probability density $P(x,t)$ that the particle is at the position *x* at time *t*. The starting point of this derivation is the definition

$$P(x,t) = \left\langle \delta(x - x(t)) \right\rangle \tag{16}$$

where as before the angular brackets denote an average with respect to the distribution of *f*(*t*). Proceeding now as we did in the derivation of Eq. (14), we first differentiate both sides of Eq. (15) with respect to *t*; this leads to

$$\begin{aligned} \frac{\partial P(x,t)}{\partial t} &= -\frac{\partial}{\partial x}\left\langle \delta(x - x(t))\dot{x}(t) \right\rangle \\ &= -\frac{1}{\zeta}\frac{\partial}{\partial x}\left\langle \delta(x - x(t))\, f(t) \right\rangle \end{aligned} \tag{17}$$

Applying Novikov's theorem, we now arrive at

$$\begin{aligned} \frac{\partial P(x,t)}{\partial t} &= -\frac{1}{\zeta}\frac{\partial}{\partial x}\int_0^t dt' \left\langle f(t) f(t') \right\rangle \left\langle \frac{\delta}{\delta f(t')}\delta(x - x(t)) \right\rangle \\ &= 2k_B T \frac{\partial^2}{\partial x^2}\int_0^t dt' \delta(t - t') \left\langle \delta(x - x(t)) \frac{\delta x(t)}{\delta f(t')} \right\rangle \end{aligned} \tag{18}$$

From Eq. (15), we see that

$$\frac{d}{dt}\frac{\delta x(t)}{\delta f(t')} = \frac{1}{\zeta}\delta(t - t')$$

and therefore

$$\begin{aligned} \frac{\delta x(t)}{\delta f(t')} &= \frac{1}{\zeta}\int_0^t dt'' \delta(t'' - t') \\ &= \frac{1}{\zeta} H(t - t') \end{aligned} \tag{19}$$

After substituting Eq. (19) into (18), carrying out the integration over t', and again using the definition $H(0) = 1/2$, we are led to the following position space diffusion equation:

$$\frac{\partial P(x,t)}{\partial t} = \frac{k_B T}{\zeta} \frac{\partial^2}{\partial x^2} P(x,t) \tag{20a}$$

$$\equiv D \frac{\partial^2}{\partial x^2} P(x,t) \tag{20b}$$

● <u>The phase space diffusion equation</u>

The same methods can be used to derive an evolution equation for the probability density, $P(x, v, t)$, that at time t a particle is at the position x and has the velocity v. This probability is defined as

$$P(x,v,t) = \left\langle \delta(x - x(t))\delta(v - v(t)) \right\rangle \tag{21}$$

where the variables $x(t)$ and $v(t)$ evolve according to the equations

$$\dot{x}(t) = v(t) \tag{22a}$$

$$m\dot{v}(t) = -\zeta v(t) + f(t) \tag{22b}$$

After differentiating Eq. (21) with respect to t, we get

$$\frac{\partial P(x,v,t)}{\partial t} = -\frac{\partial}{\partial x}\left\langle \delta(x - x(t))\delta(v - v(t))\dot{x}(t) \right\rangle - \frac{\partial}{\partial v}\left\langle \delta(x - x(t))\delta(v - v(t))\dot{v}(t) \right\rangle \tag{23}$$

The substitution of Eqs. (22a) and (22b) into Eq. (23) leads to

$$\frac{\partial P(x,v,t)}{\partial t} = -\frac{\partial}{\partial x}\left\langle \delta(x - x(t))\delta(v - v(t))v(t) \right\rangle$$

$$- \frac{\partial}{\partial v}\left\langle \delta(x - x(t))\delta(v - v(t))\left\{ -\frac{\zeta}{m} v(t) + \frac{1}{m} f(t) \right\} \right\rangle$$

$$= -v\frac{\partial}{\partial x} P(x,v,t) + \frac{\zeta}{m}\frac{\partial}{\partial v} vP(x,v,t) - \frac{1}{m}\frac{\partial}{\partial v}\left\langle \delta(x - x(t))\delta(v - v(t)) f(t) \right\rangle \tag{24}$$

The last term on the RHS of the above equation is now treated using Novikov's theorem; the result is

$$\left\langle \delta(x-x(t))\delta(v-v(t))\,f(t)\right\rangle = \int_0^t dt' \left\langle f(t)f(t')\right\rangle \left\{ \left\langle \delta(v-v(t))\frac{\delta}{\delta f(t')}\delta(x-x(t))\right\rangle + \right.$$

$$\left. + \left\langle \delta(x-x(t))\frac{\delta}{\delta f(t')}\delta(v-v(t))\right\rangle \right\}$$

$$= -2\zeta k_B T \int_0^t dt' \delta(t-t') \left\{ \frac{\partial}{\partial x}\left\langle \delta(v-v(t))\delta(x-x(t))\frac{\delta x(t)}{\delta f(t')}\right\rangle + \right.$$

$$\left. + \frac{\partial}{\partial v}\left\langle \delta(v-v(t))\delta(x-x(t))\frac{\delta v(t)}{\delta f(t')}\right\rangle \right\} \qquad (25)$$

From Eq. (22b), as we've shown earlier,

$$\frac{\delta v(t)}{\delta f(t')} = \frac{1}{m} e^{-\zeta(t-t')/m} H(t-t') \qquad (26a)$$

and so from Eq. (22a)

$$\frac{\delta x(t)}{\delta f(t')} = \frac{1}{m}\int_0^t dt'' e^{-\zeta(t''-t')/m} H(t''-t') \qquad (26b)$$

When Eq. (26b) is substituted into Eq. (25), the first term on the RHS of the latter contains the contribution

$$\int_0^t dt' \int_0^t dt'' \delta(t-t') \left\langle \delta(v-v(t))\delta(x-x(t))\right\rangle e^{-\zeta(t''-t')/m} H(t''-t')$$

which reduces to

$$\int_0^t dt'' P(x,v,t) e^{-\zeta(t''-t)/m} H(t''-t)$$

after the integration over t' is carried out. But this term vanishes because the argument of the step function is always negative in the interval over which the integration variable t'' is varied. So Eq. (25) simplifies to

$$\left\langle \delta(x-x(t))\delta(v-v(t)\,f(t)\right\rangle = -\frac{2\zeta k_B T}{m}\frac{\partial}{\partial v}\int_0^t dt' \delta(t-t') P(x,vt) e^{-\zeta(t-t')/m} H(t-t')$$

$$= -\frac{\zeta k_B T}{m} \frac{\partial}{\partial v} P(x, vt) \qquad (27)$$

Substituting Eq. (27) into Eq. (24), we finally arrive at the so-called phase space diffusion equation:

$$\frac{\partial P(x,v,t)}{\partial t} = -v \frac{\partial}{\partial x} P(x,v,t) + \frac{\zeta}{m} \frac{\partial}{\partial v} vP(x,v,t) + \frac{\zeta k_B T}{m^2} \frac{\partial^2}{\partial v^2} P(x,v,t) \qquad (28)$$