IP326. Lecture 24. Tuesday, March 26, 2019

● The Ornstein-Uhlenbeck distribution

In the previous lecture we showed that the Langevin equation for the velocity $v(t)$ of a particle in one dimension, viz.,

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

could be used to derive the following equation for the probability density that $v(t)$ has the value v at time t:

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

Here and in Eq. (1), m is the mass of the particle, ζ its friction coefficient, and $f(t)$ a random variable defined by the correlations $\langle f(t)\rangle = 0$ and $\langle f(t) f(t')\rangle = 2\zeta k_B T\delta(t-t')$.

We'd now like to find the solution to this equation as a function of t and the particle's initial velocity v_0. There are several ways to do this, and the approach we'll take is based on the properties of the random variable $f(t)$, which, as we've noted before, is Gaussian. What we mean by this is that the probability that $f(t)$ follows a certain trajectory in a certain interval of time t is given by a *quadratic functional* of f; that is

$$P[f] \propto \exp\left[-\frac{1}{4\zeta k_B T}\int_0^t dt' f^2(t')\right] \tag{3}$$

This particular structure of $P[f]$ guarantees – although we won't show it – that the mean of $f(t)$ is 0 and that its two-time correlation is a delta function. From (1), it's evident that $v(t)$ is a linear functional of f, meaning, effectively, that it is a sum of Gaussian random variables. That makes $v(t)$ a Gaussian random variable too, which means that the values that it can take, at some time t, are Gaussianly distributed. Now a Gaussian distribution of a random variable, say z, is defined completely by its mean, $\overline{z(t)}$ and its variance $\sigma_z^2(t) \equiv \overline{z^2(t)} - \overline{z(t)}^2$. Given these two parameters the distribution of z values, $P(z,t)$, is given by

$$P(z,t) = \frac{1}{\sqrt{2\pi\sigma_z^2(t)}}\exp\left[-\frac{(z-\overline{z(t)})^2}{2\sigma_z^2(t)}\right] \tag{4}$$

So to determine the distribution of velocities, it's enough to calculate $\overline{v(t)}$ and $\sigma_v^2(t) \equiv \overline{v^2(t)} - \overline{v(t)}^2$. For this purpose, we first solve Eq. (1) for *v*(*t*); the solution is

$$v(t) = v(0)e^{-\zeta t/m} + \frac{1}{m}\int_0^t dt' e^{-\zeta(t-t')/m} f(t') \tag{5}$$

This means that

$$v^2(t) = v^2(0)e^{-\zeta t/m} + \frac{2v(0)e^{-\zeta t/m}}{m}\int_0^t dt' e^{-\zeta(t-t')/m} f(t') + \frac{1}{m^2}\int_0^t dt' \int_0^t dt'' e^{-\zeta(t-t')/m - \zeta(t-t'')/m} f(t') f(t'') \tag{6}$$

The average of these two equations over the distribution of *f* leads to

$$\overline{v(t)} = \overline{v(0)} e^{-\zeta t/m} \tag{7}$$

and

$$\begin{aligned} \overline{v^2(t)} &= \overline{v^2(0)} e^{-\zeta t/m} + \frac{2\zeta k_B T}{m^2}\int_0^t dt' \int_0^t dt'' e^{-\zeta(t-t')/m} e^{-\zeta(t-t'')/m} \delta(t'-t'') \\ &= \overline{v^2(0)} e^{-\zeta t/m} + \frac{2\zeta k_B T}{m^2}\int_0^t dt' e^{-2\zeta(t-t')/m} \\ &= \overline{v^2(0)} e^{-\zeta t/m} + \frac{k_B T}{m}\left[1 - e^{-2\zeta t/m}\right] \end{aligned} \tag{8}$$

Thus, if we set the initial value of the velocity, *v*(0), to v_0, we see that the variance of the velocity is given by

$$\sigma_v^2(t) = \frac{k_B T}{m}\left[1 - e^{-2\zeta t/m}\right] \tag{9}$$

and so

$$P(v,t) = \left(\frac{m}{2\pi k_B T(1 - e^{-2\zeta t/m})}\right)^{1/2} \exp\left[-\frac{m(v - v_0 e^{-\zeta t/m})^2}{2k_B T(1 - e^{-2\zeta t/m})}\right] \tag{10}$$

which is known as the Ornstein-Uhlenbeck distribution. It can be verified by direct substitution that Eq. (10) satisfies Eq. (2).

The following points about the Ornstein-Uhlenbeck distribution are worth noting:

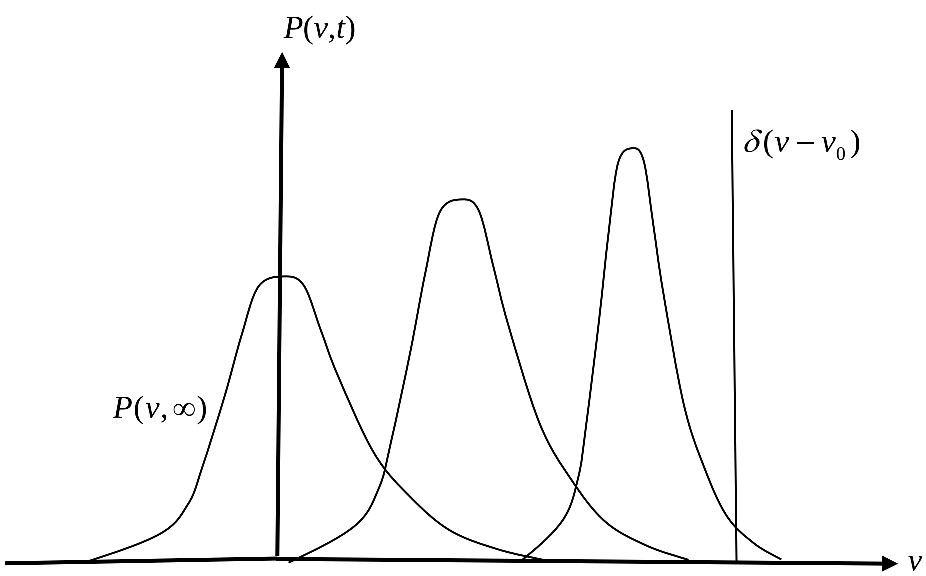
(i) The peak of the distribution is located at $v_0 e^{-\zeta t/m}$, its value at $t=0$ being v_0, which then drifts to 0 as $t \to \infty$.

(ii) The width of the distribution broadens as t increases [see Eq. (9); at $t=0$, $\sigma_v = 0$, while at $t \to \infty$, $\sigma_v = \sqrt{k_B T / m}$.]

(iii) In the $t \to \infty$ limit, the distribution becomes Maxwellian. That is,

$$P(v,\infty) = P_{eq}(v) = \left(\frac{m}{2\pi k_B T} \right)^{1/2} \exp\left[-\frac{mv^2}{2k_B T} \right] \tag{11}$$

Schematically, the evolution of $P(v,t)$ with t looks something like this:



● <u>Solutions of the diffusion equation</u>

In the overdamped limit, when the inertial term in Eq. (1) can be neglected (typically in dense fluids), the particle's position is governed by the equation

$$\zeta \frac{dx(t)}{dt} = f(t) \tag{12}$$

which we've shown can be transformed to the following equation for the probability density that the particle is at *x* at time *t*:

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2}{\partial x^2}P(x,t) \tag{13}$$

where D is the diffusion coefficient, defined as $k_B T/\zeta$. The usual way of solving this equation is through Fourier transforms, the Fourier transform of some function $f(x)$ being defined as $\tilde{f}(k) = \int_{-\infty}^{\infty} dx e^{ikx} f(x)$. If we apply this transform to both sides of Eq. (13), under the assumption that $P(x,t)$ and its derivatives vanish at $x = \pm\infty$, we get

$$\frac{\partial \tilde{P}(k,t)}{\partial t} = -Dk^2 \tilde{P}(k,t)$$

which is solved by

$$\tilde{P}(k,t) = \tilde{P}(k,0)e^{-Dk^2 t} \tag{14}$$

Assuming that the particle starts off at the point x_0, we can express the initial condition on the particle's distribution as $P(x,0) = \delta(x - x_0)$, which means that

$$\tilde{P}(k,0) = e^{ikx_0} \tag{15}$$

When this expression is put back into Eq. (14) and the result inverse Fourier transformed according to the formula

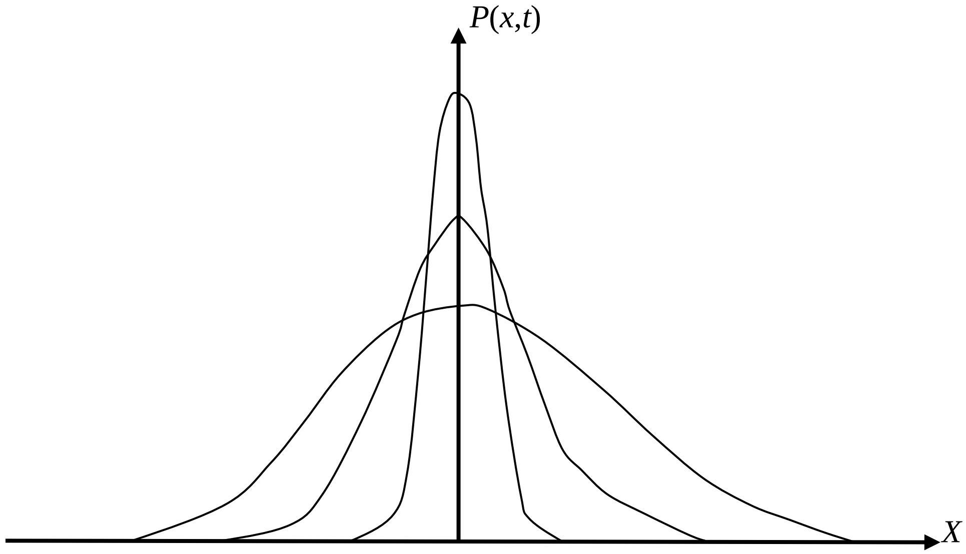
$$f(k) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dk e^{-ikx} \tilde{f}(k)$$

where the factor of 2π is introduced as a matter of convention, we find that

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{(x-x_0)^2}{4Dt}\right] \tag{16}$$

which is the solution to Eq. (13) under the so-called *natural* boundary conditions $P(\pm\infty, t) = 0$ and for the initial condition $P(x,0) = \delta(x - x_0)$. You can also verify that $P(x,t)$, as given by Eq. (16), is normalized to unity.

The evolution of $P(x,t)$ as *t* increases is sketched in the figure below for the case of a particle starting off at $x_0 = 0$.



The widths of the curves in the above figure increase as $t^{1/2}$ (because $\sigma_x = \sqrt{2Dt}$), while their heights decrease as $t^{-1/2}$ (because $P(0,t) = 1/\sqrt{4\pi Dt}$). The area under the curves remains unity for all *t*. There is no non-trivial limiting distribution as $t \to \infty$; instead $P(x, t \to \infty) \to 0$ for all *x*.

● Dynamics of two independent non-interacting particles

If two identical particles labelled 1 and 2, initially located at the origin, move freely in one dimension according to Eq. (12) without mutual interactions (implying that they can even pass through each other), we can use Eq. (16) to say something about the distribution of their center of mass and the distribution of their inter-particle separations. The center of mass of the two particles, x_{cm}, is given by $\frac{1}{2}(x_1 + x_2)$, while their spatial separation, *r*, is given by $x_2 - x_1$. From these definitions, the distribution $P_{cm}(x_{cm}, t)$ of x_{cm} at time *t* can be found from

$$P_{cm}(x_{cm}, t) = \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 P(x_1, t) P(x_2, t) \delta(x_{cm} - (x_1 + x_2)/2)$$

$$= 2\int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 P(x_1, t) P(x_2, t) \delta(2x_{cm} - x_1 - x_2), \quad \text{[using } \delta(ay) = \frac{1}{|a|}\delta(y) \text{]}$$

$$= 2\int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 P(x_1,t)P(x_2,t)\delta(x_2 - (2x_{cm} - x_1)), \quad \text{[using } \delta(y) = \delta(-y)\text{]}$$

$$= 2\int_{-\infty}^{\infty} dx_1 P(x_1,t)P(2x_{cm} - x_1, t)$$

Carrying out the simple Gaussian integration in the last relation, we obtain

$$P_{cm}(x_{cm},t) = \frac{1}{\sqrt{2\pi Dt}} \exp\left[-\frac{x_{cm}^2}{2Dt}\right] \tag{17}$$

The effective diffusion coefficient of the center-of-mass "particle" is therefore $D/2$.

In the same way, the distribution $P_r(r,t)$ of the separation between the two particles can be calculated from

$$P_r(r,t) = \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 P(x_1,t)P(x_2,t)\delta(r - (x_2 - x_1))$$

$$= \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 P(x_1,t)P(x_2,t)\delta(x_2 - x_1 - r)$$

$$= \int_{-\infty}^{\infty} dx_1 P(x_1,t)P(x_1 + r, t)$$

$$= \frac{1}{\sqrt{8\pi Dt}} \exp\left[-\frac{r^2}{8Dt}\right] \tag{18}$$

The effective diffusion coefficient of the inter-particle distance is therefore $2D$.

● Solution of the diffusion equation under reflecting boundary conditions

Up to now, we've been looking at the dynamics of a particle that was free to move anywhere. But in many of the systems to which the model of Brownian motion is applied, there are often restrictions on where the particle can move. One common situation, for instance, is when the particle is confined to a line segment between the points 0 and L, where it may be supposed that there exist impenetrable walls that completely reflect the particle's motion. The probability density $P(x,t)$ in these circumstances is no longer the expression given in Eq. (16), but must be found by solving Eq. (13) subject to the given constraint (and any accompanying initial condition.) This constraint is manifested as a boundary condition on x. In the present case, because of the impenetrable walls at 0 and

L, there is no flow of probability through them. In other words the "probability current" at these points is 0. An expression for this current can be found from the diffusion equation itself [Eq. (13)], which can be written in the form

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x} J(x,t) \tag{19}$$

where $J(x,t) = D\partial P(x,t)/\partial x$. In this form, the equation has the structure of a *continuity* equation, and the function $J(x,t)$ is therefore what we identify as the current. The vanishing of this current at the end points of the line segment then gives rise to the boundary conditions

$$J(x,t)\big|_{x=0,L} = 0\,, \quad \text{for all } t > 0 \tag{20}$$

which must be satisfied by any putative solution of the diffusion equation.

To solve the equation, we can use the method of separation of variables, which proceeds by writing $P(x,t)$ as

$$P(x,t) = T(t)\phi(x) \tag{21}$$

where T and ϕ are as yet unknown functions of their arguments. If this expression is used in Eq. (13), the result is

$$\frac{1}{D}\frac{\dot{T}(t)}{T(t)} = \frac{\phi''(x)}{\phi(x)} \tag{22}$$

where the dot denotes differentiation with respect t and the double prime denotes differentiation with respect to x. Since the LHS of Eq. (22) is solely a function of t, and the RHS solely a function of x, it follows that both sides must actually equal a constant, which we'll assign the arbitrary value $-k^2$, the negative sign being introduced to ensure physically meaningful behavior at long times. So now we have the two equations

$$\frac{dT(t)}{dt} = -k^2 DT(t) \tag{23a}$$

and

$$\frac{d^2\phi(x)}{dx^2} = -k^2\phi(x) \tag{23b}$$

The first of these is easily seen to be solved by

$$T(t) \propto e^{-k^2 Dt} \quad . \tag{24}$$

There is no need at the moment to include a proportionality constant in this relation.

The second of these equations – Eq. (23b) – is a specific instance of an eigenvalue equation, the constant k functioning as the eigenvalue and the function $\phi(x)$ as the eigenfunction. The general solution of Eq. (23b) is also easily derived; it is

$$\phi(x) = A\sin kx + B\cos kx \tag{25}$$

where A and B are constants of integration that will have to be fixed by the boundary and initial conditions. One of these conditions, as noted before, is $J(x=0)=0$, which translates to the condition

$$\phi'(x=0) = (Ak\cos kx - Bk\sin kx)|_{x=0} = 0 \tag{26}$$

The solution of this equation requires that $A=0$. Hence, $\phi(x) = B\cos kx$. The other boundary condition, viz., $\phi'(x=L) = -Bk\sin kx|_{x=L} = 0$, requires that $kL = n\pi$, with n an integer that can take the values 0, 1, 2, etc. So the boundary conditions have fixed the value of the separation constant k as

$$k = \frac{n\pi}{L}, \qquad n = 0,1,2,\ldots \tag{27}$$

in the process identifying the eigenfunction $\phi(x)$ as

$$\phi(x) \propto \cos(n\pi x/L) \tag{28}$$

The proportionality constant in this relation, as well as the one in Eq. (24), will be chosen later to ensure that $\int_0^L dx P(x,t) = 1$.

With Eqs. (24), (27) and (28) in hand, the distribution function $P(x,t)$ can now be written as the linear combination

$$P(x,t) = \sum_{n=0}^{\infty} C_n \cos(n\pi x/L) e^{-n^2\pi^2 Dt/L^2}$$

$$= C_0 + \sum_{n=1}^{\infty} C_n \cos(n\pi x/L) e^{-n^2\pi^2 Dt/L^2} \tag{29}$$

where the expansion coefficients C_n are to be determined. To determine these coefficients, we apply the initial condition $P(x,0) = \delta(x - x_0)$ to Eq. (29), which leads to

$$\delta(x - x_0) = C_0 + \sum_{n=1}^{\infty} C_n \cos(n\pi x / L) \tag{30}$$

We now multiply both sides of this equation by $\cos(m\pi x / L)$, and then integrate the result over *x* from 0 to *L*, obtaining

$$\cos(m\pi x_0 / L) = C_0 \frac{\sin m\pi x / L}{m\pi / L}\bigg|_{x=0}^{x=L} + \frac{1}{2}\sum_{n=1}^{\infty} C_n \int_0^L dx\big[\cos((m+n)\pi x / L) + ((m-n)\pi x / L)\big]$$

$$= LC_0\delta_{m,0} + \frac{L}{2}\sum_{n=1}^{\infty} C_n \delta_{m,n} \tag{31}$$

From this last relation one sees that $C_0 = 1/L$ and $C_m = (2/L)\cos(m\pi x_0 / L)$ for $m \geq 1$. Having thus found C_m (or equivalently C_n, since *m* is a dummy index), the complete expression for $P(x,t)$ is given by

$$P(x,t) = \frac{1}{L} + \frac{2}{L}\sum_{n=0}^{\infty} \cos(n\pi x_0 / L)\cos(n\pi x / L) e^{-n^2\pi^2 Dt / L^2} \tag{32}$$

It is easily verified that $\int_0^L dx P(x,t) = 1$.