IP326. Lecture 25. Thursday, March 28, 2019

● Solution of the diffusion equation under absorbing boundary conditions

In the example discussed in the last lecture of a particle constrained to move along a line segment with end points at 0 and L, the barriers located at these points were assumed to be *reflecting*. This meant that there was no probability current through 0 and L. But if the barriers there are such that a particle encountering them for the first time is immediately annihilated, then they constitute what are referred to as *absorbing* boundaries, and the conditions they impose on the solution of the diffusion equation that governs the particle's motion are different. These conditions are now given by the relations

$$P(0,t) = P(L,t) = 0 \tag{1}$$

The diffusion equation remains the same, viz., $\partial P(x,t)/\partial t = D\partial^2 P(x,t)/\partial x^2$, and it is solved as before by the method of separation of variables, which leads to the equations

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

and

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

whose solutions are

$$T(t) \propto e^{-k^2Dt} \quad . \tag{3a}$$

and

$$\phi(x) = A\sin kx + B\cos kx \tag{3b}$$

But the new boundary conditions now lead to new constraints on $\phi(x)$, specifically the constraint $\phi(0) = \phi(L) = 0$, which requires that $B = 0$ and that $A\sin kL = 0$. The latter is satisfied by $k = n\pi/L$, $n = 1,2,3,\ldots$, which means that $\phi(x)$ is now given by

$$\phi(x) \propto \sin(n\pi x/L) \tag{4}$$

The complete solution to the diffusion equation therefore takes the form

$$P(x,t)=\sum_{n=1}^{\infty}B_n\sin(n\pi x/L)e^{-n^2\pi^2Dt/L^2} \tag{5}$$

where the B_n are expansion coefficients, which are determined, as before, by application of the initial condition $P(x,0)=\delta(x-x_0)$. This leads to

$$\delta(x-x_0)=\sum_{n=1}^{\infty}B_n\sin(n\pi x/L) \tag{6}$$

After multiplying both sides of this equation by $\sin m\pi x/L$, and integrating the result over x between the limits 0 and L, we find that

$$B_m=\frac{2}{L}\sin(m\pi x_0/L) \tag{7}$$

and so finally

$$P(x,t)=\frac{2}{L}\sum_{n=1}^{\infty}\sin(n\pi x_0/L)\sin(n\pi x/L)e^{-n^2\pi^2Dt/L^2} \tag{8}$$

It's evident from this equation that $P(x,t\to\infty)=0$, which was not the case when the boundary conditions were reflecting. Nor is the integral $\int_0^L dxP(x,t)$ a non-zero constant; in fact, it has an interesting interpretation – it can be regarded as the probability density that a particle starting from some point between 0 and L survives up to a time t without being absorbed by either of the end-points. Denoting this probability $S(t)$, we see from Eq. (8) that it is given by

$$S(t)=-2\sum_{n=1}^{\infty}\sin(n\pi x_0/L)\frac{(-1)^n-1}{n\pi}e^{-n^2\pi^2Dt/L^2} \tag{9}$$

It's clear from this relation that as time passes the chances of the particle remaining unabsorbed become smaller and smaller, meaning that sooner or later it *will* be absorbed.

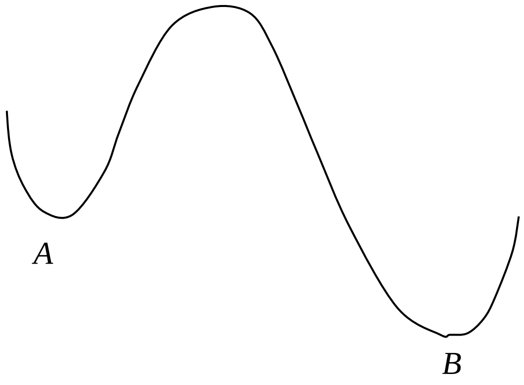
● A model of chemical reaction rates

Density distributions play an important role in the theory of reaction dynamics in the condensed phase, a field that arguably began with the publication of H. A. Kramers' seminal paper, "Brownian motion in a field of force and the diffusion model of chemical reactions", Physica **7**, *284* (1940). Kramers' interest was in chemical transformations of the kind $A\to B$ that occurred in solution at ambient temperatures. Empirically, such transformations are governed by a mass action law of the form

$$\frac{d[A]}{dt} = -k[A] \tag{10}$$

where $[A]$ stands for the concentration of A and k is a rate constant that at this level of description is purely phenomenological, meaning its dependence on details of the system (such as the viscosity of the solvent, temperature, inter-molecular interaction parameters, etc.) is not known à priori but must be determined experimentally. Kramers' objective was to derive an expression for k in which these dependences were explicit.

For this purpose, he began with a model of what a chemical reaction at the molecular level might conceivably look like. He assumed that in a dense fluid at constant temperature, a reactive species like A experiences a constantly fluctuating set of forces from its surroundings. As a result, it occasionally acquires sufficient energy to be transformed to B. The transformation can be assumed to proceed along what is now referred to as a reaction coordinate, a somewhat ill-defined parameter that corresponds to some degree of freedom of A (or a combination of degrees of freedom) that changes continuously during the course of the change $A \to B$. A reaction coordinate could be an angle of rotation, for instance, or a bond length, or even a combination of the two. In any case, Kramers thought of this coordinate as the position of a particle that evolved stochastically along a potential surface with this general form:



Here the left well corresponds to the energy of A and the right well to that of B, the hump in the middle representing the barrier A has to overcome to change to B. Most of the time the particle moves around in the neighborhood of the reactant potential minimum, but every now and then it gets enough energy to surmount the barrier and to cross over into the product potential minimum. When this happens, A is imagined to have been transformed to B.

Accepting this picture of the reaction process, we can assert that the reaction's dynamics are governed by these equations:

$$\dot{x}(t) = v(t) \tag{11a}$$

$$m\dot{v}(t) = -\zeta v(t) - \frac{\partial U(x(t))}{\partial x(t)} + f(t) \tag{11b}$$

where U is the potential energy profile depicted above. All the other terms in these two equations have their usual definitions. The idea now is to use these equations to say something about k.

As a starting point, Eq. (10) can be rearranged to

$$k = -\frac{d[A]/dt}{[A]} \tag{12}$$

The RHS of this relation can be interpreted as the ratio of a flux of A (over the barrier) to the population of A (in the reactant well.) Now, in general, a flux can be thought of as a mean velocity (since velocities are what lead to physical transport of matter from one place to another), so one can write,

$$\text{flux} \sim \int dx \int dv\, v P(x, v, t \to \infty) \tag{13}$$

Along the same lines one can write

$$\text{population} \sim \int dx \int dv\, P(x, v, t \to \infty) \tag{14}$$

where $P(x, v, t)$ is the probability density of finding the particle at position x with a velocity v at time t. In taking the limit $t \to \infty$ in these expressions the assumption is that it is only after the system has had a long enough time to evolve that the rate constant actually attains a steady constant value. But this limit imposes some constraints on how we interpret the details of the reaction mechanism. For instance, it requires that we imagine that whenever a particle crosses the barrier, the potential well from which it left is replenished by another molecule of A so that its distribution is essentially in equilibrium. It also requires the barrier to be relatively high so that barrier crossing events take place relatively infrequently, again allowing time for the system to settle into equilibrium.

To evaluate Eqs. (13) and (14), we need an expression for $P(x, v, t)$, which must be obtained from the solution of the equation that describes its phase space evolution. For a system whose stochastic dynamics takes place on a potential energy surface U, this equation, using the functional calculus methods of the earlier sections, is easily shown to be

$$\frac{\partial P}{\partial t} = -v\frac{\partial P}{\partial x} + \frac{\zeta}{m}\frac{\partial}{\partial v} vP + \frac{1}{m}\frac{\partial U}{\partial x}\frac{\partial P}{\partial v} + \frac{\zeta k_B T}{m^2}\frac{\partial^2 P}{\partial v^2} \tag{15}$$

The only difference between this equation and the earlier phase space diffusion equation is the additional term involving the force from the potential.

In the long time limit of this equation that we're interested in, the system is assumed to have achieved a "steady state", where things don't change with time. In other words in this limit, $\partial P/\partial t = 0$. You can show by direct substitution that the resulting equation, viz.,

$$-v\frac{\partial P}{\partial x}+\frac{\zeta}{m}\frac{\partial}{\partial v}vP+\frac{1}{m}\frac{\partial U}{\partial x}\frac{\partial P}{\partial v}+\frac{\zeta k_B T}{m^2}\frac{\partial^2 P}{\partial v^2}=0 \tag{16}$$

is satisfied by the thermal equilibrium distribution, i.e., the distribution

$$P_0(x,v)=C\exp\left[-\beta m v^2/2-\beta U]\right] \tag{17}$$

where C is a normalization constant, and $\beta = 1/k_B T$.