

Time-Dependent Statistical Mechanics

4. Self-diffusion

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1 Introduction

Self-diffusion is one of the simplest transport processes from a theoretical point of view, and the kinds of theories that are applied to it are also applied to other transport and relaxation processes. Thus, it provides a useful process with which to begin our discussion.

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2 The basic experiment

The basic experiment is one in which we have an equilibrium system containing trace amounts of one component. That component might be a solute dissolved in a solvent (e.g. a dye molecule dissolved in an organic solvent). Or it might be a trace radioactive version of the major component of the system (e.g. a trace of T_2O in H_2O).

The entire system is in thermal equilibrium, with the exception that the concentration of the trace component is not uniform; there are parts of the system where the concentration is higher than others. The typical experiment then starts with some initial inhomogeneous concentration, and measurements are made to observe how the system approaches a final equilibrium state in which the concentration of the trace component is the same everywhere.

3 The diffusion equation

3.1 Derivation of the diffusion equation

During the approach to equilibrium, the temperature, the overall density, the pressures, and the concentrations of the major components do not change. The only thing that changes is the concentration of the trace component.

Suppose $c(\mathbf{r}, t)$ is the position and time dependent concentration of the trace component. For our purposes, let's use molecules per unit volume as the units of c . In analyzing the property of the system, it is usually assumed that c satisfies the following diffusion equation.

$$\frac{\partial c(\mathbf{r}, t)}{\partial t} = D \nabla^2 c(\mathbf{r}, t)$$

This is an example of a hydrodynamic equation. It is a macroscopic equation and contains a parameter D , called the diffusion constant. It is the first example of several such macroscopic equations we shall discuss. Other examples include the Navier-Stokes equations and rate equations for chemical reactions. All such equations contains such parameters. E.g. the Navier-Stokes equations contain the viscosity coefficients, and the chemical rate equations contain rate constants for chemical reactions.

The usual handwaving 'derivation' of the diffusion equation is the following. Let's first consider a situation in which c varies in the x direction only. Then c is a function of x and t , namely $c(x, t)$. Suppose c increases as x increases. Then at any point, there are more trace molecules to the right than to the left. If each of them moves in some random way, with no bias as to whether to move to the left or the right, there should some net flow of the trace component from right to left. There is no reason to think that there would be any flow in the y or z direction. Let $j(x, t)$ be the flux of the trace component. The flux has the meaning of the number of molecules flowing in the x direction per unit area per unit time. That is, we imagine a small area that is oriented perpendicular to the x direction. Molecules cross that area. Those that flow in the $+x$ direction contribute positively to the flux and those that flow in the $-x$ direction contribute negatively to the flux.

We expect the flux to be related to the derivative of the concentration. If the concentration were uniform, there would be no flux. If $\partial c / \partial x$ is positive, we expect j to be

negative. If $\partial c/\partial x$ is negative, we expect j to be positive. The simplest assumption to make is that j is proportional to the concentration gradient.

$$j(x, t) = -D \frac{\partial c(x, t)}{\partial x} \quad (1)$$

We put the minus sign there so that the constant of proportionality, D , will be a positive constant.

Since the molecules are flowing, we expect the concentration to be changing with time. What is the relationship? I.e. suppose we know $j(x, t)$. How does this determine $\partial c/\partial t$?

If $j(x, t)$ were independent of x , the concentration would not change in any region of space. Concentration changes must be related to gradients in j . The *continuity equation* is

$$\frac{\partial c(x, t)}{\partial t} = -\frac{\partial j(x, t)}{\partial x} \quad (2)$$

This equation is exact. (We shall discuss this in detail in a handout and in a future problem set.)

Putting these two equations together, we get the form of the diffusion equation for this one dimensional geometry.¹

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

¹The detailed reasoning is

$$\frac{\partial c(x, t)}{\partial t} = -\frac{\partial j(x, t)}{\partial x} = -\frac{\partial}{\partial x} \left(-D \frac{\partial c(x, t)}{\partial x} \right) = D \frac{\partial^2 c(x, t)}{\partial x^2} + \frac{\partial D}{\partial x} \frac{\partial c(x, t)}{\partial x}$$

We get the result quoted above only if we can neglect the last term.

The self-diffusion coefficient depends on the molecule that is diffusing as well as the intensive thermodynamic state of the system in which it is diffusing. The only thing that is varying with x in the thermodynamic state is c itself. Thus $D(x)$ is a function of $c(x)$. Hence $\partial D/\partial x = (\partial D/\partial c)(\partial c(x, t)/\partial x)$. Hence the second term in the equation above is

$$\frac{\partial D}{\partial c} \left(\frac{\partial c(x, t)}{\partial x} \right)^2$$

For self-diffusion, c has a very small value, and its gradients and second derivatives are also small. A term containing the square of the gradient will be small compared with a term that contains the first power of the gradient. Hence we can neglect this term.

If we were to analyze the more general situation in which the concentration could vary in all three directions, then we would obtain

$$\frac{\partial c(x, t)}{\partial t} = D \left(\frac{\partial^2 c(x, t)}{\partial x^2} + \frac{\partial^2 c(x, t)}{\partial y^2} + \frac{\partial^2 c(x, t)}{\partial z^2} \right)$$

which is the form of the equation that we quoted above.

The diffusion equation is used to analyze experiments involving self-diffusion. There are lots of experimental confirmations of it and lots of theoretical reasons for thinking it is correct. The object of any self-diffusion experiment is to measure the value of D by setting up a particular initial inhomogeneous c , observing how it relaxes, and then using the data to infer the value of D . The implicit or explicit assumption is that we would get the same value of D for any initial c , and so we pick an initial c that is experimentally convenient.

3.2 Comments on the hydrodynamic equation

Note that the diffusion equation is based on a set of assumptions:

- The concentration $c(\mathbf{r}, t)$ is continuous enough that it has both a time derivative as well as two space derivatives.
- The flux $j(\mathbf{r}, t)$ exists and is also differentiable.
- The flux j is linear in the concentration gradient - Eq. (1)
- The continuity equation - Eq. (2).

These are ideas based on continuum fluid mechanics that are not dependent on the atomic and molecular nature of matter. They were developed in the nineteenth century (or maybe before), and they are found to correct for the interpretation of experimental data for systems that are large enough to contain large numbers of molecules, provided the distance scale of interest is large compared with molecular distances and the time scale is large compared with molecular times. These assumptions about distance and time scales are correct for most classical and most modern experiments that measure the self-diffusion process.²

²There are some experiments, however, such as inelastic neutron scattering, that can probe this process on time and length scales that are so short that the diffusion equation is not an accurate description.

4 Elementary solutions of diffusion equation

The diffusion equation is first order in time. Knowing $c(\mathbf{r}, t)$ for all \mathbf{r} for one t is enough to determine it for all \mathbf{r} for all later times. The solutions of the equation are unique.³

We shall be interested in two particular solutions of the equation. We shall in each case focus on the one dimensional version and then generalize the discussion to the three dimensional case.

4.1 Initial sinusoidal variation of the concentration

Suppose that at time 0 we have

$$c(x, 0) = A \sin kx$$

Let's try a trial solution of the form

$$c(x, t) = f(t) \sin kx$$

(This sort of factorization of a function of two variables does not always work, but it does work for this case.) Substitution of this into the one dimensional version of the diffusion equation gives

$$\frac{df(t)}{dt} \sin kx = -k^2 D f(t) \sin kx$$

$$\frac{df(t)}{dt} = -k^2 D f(t)$$

The solution of this is

$$f(t) = A e^{-k^2 D t}$$

The overall solution is

$$c(x, t) = A e^{-k^2 D t} \sin kx$$

The more general three dimensional problem with the initial condition

$$c(\mathbf{r}, 0) = A \sin \mathbf{k} \cdot \mathbf{r}$$

³For systems in a bounded region of space, a precise discussion of uniqueness should include a discussion of boundary conditions. This need not concern us in the present discussion.

has a similar solution

$$c(\mathbf{r}, t) = Ae^{-k^2 Dt} \sin \mathbf{k} \cdot \mathbf{r}$$

as can easily be verified.

Comments on the solution. Thus a sinusoidal variation of the concentration in space decays exponentially with time. The exponential can be written in the following way

$$\exp(-t/(1/Dk^2)) = \exp(-t/\tau)$$

where the relaxation time τ is equal to $1/Dk^2$. The larger the diffusion constant, the shorter the relaxation time. This makes sense. The dependence on k is also interesting. The relaxation time is inversely proportional to the square of k . Note that the wave vector k is related to the wavelength λ of the initial fluctuation by $k = 2\pi/\lambda$. Thus

$$\tau = \frac{\lambda^2}{(2\pi)^2 D}$$

In order to wipe out the initial concentration variation, solute particles must diffuse a distance of the order of the distance between the peaks and valleys of the initial distribution, which is roughly half the wavelength associated with the initial variation. The relaxation time is proportional to the *square* of that distance. The time it takes to move a certain distance is roughly proportional to the square of that distance. This is a fundamental physical characteristic of diffusive motion. The mathematical reason why the relaxation *time* is proportional to the square of a *distance* is the fact that the original differential equation is *first* order in time but *second* order in space. The microscopic physical reason for this behavior is something that we shall be discussing later.

4.2 Initial delta function variation of the concentration

Suppose at time 0 we have

$$c(x, 0) = A\delta(x)$$

I.e. all of the solute is initially at one point at the origin. Here $\delta(x)$ is a Dirac delta function. We shall just write down a trial solution and then verify that it is correct.

Here is the trial solution:

$$c(x, t) = A \left(\frac{a(t)}{\pi} \right)^{1/2} \exp(-a(t)x^2)$$

If $a(0)$ is infinitely large, then gives a delta function behavior for the concentration. We want to verify that a function of this form is indeed a solution of the diffusion equation and find the time dependence of $a(t)$ given that $a(0)$ is infinitely large. This

involves some straightforward calculations.⁴

The final solution is

$$c(x, t) = A \left(\frac{1}{4\pi Dt} \right)^{1/2} \exp(-x^2/4Dt)$$

This has all the desired characteristics.

⁴Do some miscellaneous preparatory calculations.

$$\frac{\partial c}{\partial t} = \frac{1}{2a(t)} \dot{a}(t) c(x, t) - x^2 \dot{a}(t) c(x, t) = \left(\frac{1}{2a(t)} - x^2 \right) \dot{a}(t) c(x, t)$$

$$\frac{\partial c}{\partial x} = -2a(t) x c(x, t)$$

$$\frac{\partial^2 c}{\partial x^2} = -2a(t) c + 4a(t)^2 x^2 c = (-2a(t) + 4a(t)^2 x^2) c$$

Substitute this into the diffusion equation and see what happens.

$$\left(\frac{1}{2a(t)} - x^2 \right) \dot{a}(t) c(x, t) = D (-2a(t) + 4a(t)^2 x^2) c(x, t)$$

Cancel the c on both sides.

$$\left(\frac{1}{2a(t)} - x^2 \right) \dot{a}(t) = D (-2a(t) + 4a(t)^2 x^2)$$

Manipulate to make the common factor apparent.

$$-\frac{1}{4a(t)^2} (-2a(t) + 4a(t)^2 x^2) \dot{a}(t) = D (-2a(t) + 4a(t)^2 x^2)$$

Cancel the common factor.

$$-\frac{1}{4a(t)^2} \dot{a}(t) = D$$

$$\dot{a}(t) = -4Da(t)^2$$

It is reassuring that we get an equation for $a(t)$ that does not depend on x .

It is not obvious, but the next thing to do is try a power law solution: $a(t) = bt^{-n}$. Note that if n and b are both positive, then $a(t)$ goes to infinity as $t \rightarrow 0+$, which is what we want. Substitute this trial solution into the equation for $a(t)$.

$$-nbt^{-n-1} = -4Db^2t^{-2n}$$

$$t^{n-1} = \frac{4Db}{n}$$

Since the right side is independent of t , the left side must be independent of t . Therefore $n-1=0$ or $n=1$. We get $1=4Db$. $b=1/4D$. Thus $a(t)=1/4Dt$.

- For $t = 0$, all the solute material is concentrated at a point at the origin.
- For $t > 0$, this satisfies the diffusion equation.

For a three dimensional situation, the corresponding solution is

$$c(\mathbf{r}, 0) = A\delta(\mathbf{r})$$

$$c(\mathbf{r}, t) = A \left(\frac{1}{4\pi Dt} \right)^{3/2} \exp(-\mathbf{r} \cdot \mathbf{r}/4Dt)$$

Comments on the solution. The solute material is initially concentrated at a point at the origin, but as time goes on the distribution of the solute spreads out. The maximum is always at the origin but it extends farther to the left and right as time goes on.

The average vector distance traveled by the solutes between time 0 and time t is

$$\bar{\mathbf{r}} = \frac{\int d\mathbf{r} c(\mathbf{r}, t) \mathbf{r}}{\int d\mathbf{r} c(\mathbf{r}, t)} = 0$$

This is easily seen by symmetry and can easily be shown by direct calculation.

Of somewhat more interest is the *mean squared displacement*, or the average of the square of the distance traveled by the solute molecules.

$$\overline{\mathbf{r} \cdot \mathbf{r}} = \overline{r^2(t)} = \frac{\int d\mathbf{r} c(\mathbf{r}, t) \mathbf{r} \cdot \mathbf{r}}{\int d\mathbf{r} c(\mathbf{r}, t)} = 6Dt$$

This is worked out in the answer sheet for the first problem set.

This result illustrates a general feature of diffusive processes. If you want a solute to spread out by diffusion over a distance of order L , you must give it an amount of time that is proportional to L^2 . This is consistent with the result we found for a sinusoidal variation of initial concentration.

5 Correlation function expression for the diffusion constant

The description of diffusion in terms of the diffusion equation is valid only on distance scales and time scales that are much larger than typical microscopic or molecular distance and time scales.

A typical molecular distance scale is an Angstrom or 0.1 nm. A typical atom has a diameter of 1-5 Angstroms. A typical microscopic time scale is about a picosecond, which is roughly the time it takes a typical atom to move an Angstrom at room temperature.

A typical laboratory measurement of diffusion might involve a container whose size is measured in cm. Typical experimental measurements of diffusion might take minutes or hours.

We are now ready to use a type of reasoning that we shall be using several times in this course. I want to make explicit the nature of the argument.

Suppose we *assume* that:

- the diffusion equation, which is a hydrodynamic description, is valid on distance scales and length scales that are much longer than microscopic distance and length scales;
- the material of interest is ultimately made up of atoms and molecules that move according to the laws of dynamics and that the laws of dynamics hold for all distance and time scales.

Note that we are not claiming that we can derive the diffusion equation from a molecular theory. We are merely stating that two very different types of descriptions of the same system are both valid.

It follows that on long distance and time scales, the hydrodynamical and mechanical molecular descriptions are *both* valid.

If they are both valid, then they must be consistent with one another, but this holds only (of course) for long distance and time scales.

Now consider the case of an experiment in which all the solute starts out at one point.

Above we defined a quantity, $\bar{\mathbf{r}}$, the average vector distance traveled by a solute between time 0 and time t . What is the molecular meaning of this quantity? It corresponds to the average of $\mathbf{r}_i(t) - \mathbf{r}_i(0)$ over all solute particles in the system.

$$\bar{\mathbf{r}}(t) \leftrightarrow \frac{1}{N_s} \sum_{i=1}^{N_s} (\mathbf{r}_i(t) - \mathbf{r}_i(0))$$

in the sense that a measurement of the quantity on the left is equivalent to a measurement of the microscopic quantity on the right. (Here N_s is the number of solute

particles in the system.) By our ensemble postulate, the measured value of the quantity on the right is equal to its ensemble average. So we have

$$\bar{\mathbf{r}}(t) = \left\langle \frac{1}{N_s} \sum_{i=1}^{N_s} (\mathbf{r}_i(t) - \mathbf{r}_i(0)) \right\rangle$$

The appropriate ensemble for this is an equilibrium ensemble (e.g. a canonical ensemble or grand canonical ensemble), because the system is in equilibrium except for the very small inhomogeneity associated with the solutes. Thus the average on the right is an average over an equilibrium ensemble. To emphasize this, let's write

$$\bar{\mathbf{r}}(t) = \left\langle \frac{1}{N_s} \sum_{i=1}^{N_s} (\mathbf{r}_i(t) - \mathbf{r}_i(0)) \right\rangle_{eq}$$

This is our first example of an equation, applicable to a specific experiment, that relates something calculated from a macroscopic theory and something calculated from a microscopic theory. We calculate the left side by solving the diffusion equation. The result will contain D , which appears in the diffusion equation. We calculate the right side, in principle, from some sort of theory that calculates the dynamical behavior of individual molecules. However, it is important to note that we expect the equality to hold only for long enough times.

Since all the solute molecules have the same properties, each term on the right has the same average. It follows that we can just focus on one solute.

$$\bar{\mathbf{r}}(t) = \langle \mathbf{r}_1(t) - \mathbf{r}_1(0) \rangle_{eq}$$

- We have evaluated the left side of this equation above. The result is zero.
- To evaluate the right side, we write

$$\mathbf{r}_1(t) - \mathbf{r}_1(0) = \int_0^t dt' \mathbf{v}_1(t')$$

Thus, the equation tells us that

$$0 = \left\langle \int_0^t dt' \mathbf{v}_1(t') \right\rangle_{eq}$$

We can bring the averaging process inside the integral.

$$0 = \int_0^t dt' \langle \mathbf{v}_i(t') \rangle_{eq}$$

This is entirely reasonable. In an equilibrium system, the average velocity of a particle at any particular time is zero, so the right side is clearly zero.

So far, we have gotten no blinding insights from statistical mechanics, but the discussion illustrates the general procedure that we use. Let's now apply the same procedure to

$$\overline{r^2(t)} \leftrightarrow \frac{1}{N_s} \sum_{i=1}^{N_s} (\mathbf{r}_i(t) - \mathbf{r}_i(0)) \cdot (\mathbf{r}_i(t) - \mathbf{r}_i(0))$$

The measured value of the microscopic quantity on the right is equal to its ensemble average.

$$\overline{r^2(t)} = \left\langle \frac{1}{N_s} \sum_{i=1}^{N_s} (\mathbf{r}_i(t) - \mathbf{r}_i(0)) \cdot (\mathbf{r}_i(t) - \mathbf{r}_i(0)) \right\rangle_{eq}$$

In an equilibrium ensemble, all of the solute particles have the same statistical properties.

$$\overline{r^2(t)} = \langle (\mathbf{r}_1(t) - \mathbf{r}_1(0)) \cdot (\mathbf{r}_1(t) - \mathbf{r}_1(0)) \rangle_{eq}$$

This is the second of these equalities, for a specific experimental situation, between something that can be calculated from a hydrodynamic theory and something that can be calculated from a microscopic theory. Let's see what this tells us.

- The left side is equal to $6Dt$.
- The right side is equal to

$$\begin{aligned} \langle (\mathbf{r}_1(t) - \mathbf{r}_1(0)) \cdot (\mathbf{r}_1(t) - \mathbf{r}_1(0)) \rangle_{eq} &= \left\langle \int_0^t dt' \mathbf{v}_1(t') \cdot \int_0^t dt'' \mathbf{v}_1(t'') \right\rangle_{eq} \\ &= \int_0^t dt' \int_0^t dt'' \langle \mathbf{v}_1(t') \cdot \mathbf{v}_1(t'') \rangle_{eq} \end{aligned}$$

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$$\overline{r^2(t)} = \int_0^t dt' \int_0^t dt'' \langle \mathbf{v}_1(t') \cdot \mathbf{v}_1(t'') \rangle_{eq}$$

***end of slide Equating the two results, which is a valid thing to do at long times, gives

$$6Dt = \int_0^t dt' \int_0^t dt'' \langle \mathbf{v}_1(t') \cdot \mathbf{v}_1(t'') \rangle_{eq}$$

$$D = \frac{1}{6t} \int_0^t dt' \int_0^t dt'' \langle \mathbf{v}_1(t') \cdot \mathbf{v}_1(t'') \rangle_{eq}$$

This is a very interesting result. On the left we have a quantity that appears in a macroscopic hydrodynamic equation. On the right we have a purely microscopic expression involving the detailed dynamics of molecules and an average over an equilibrium ensemble, which is essentially an equilibrium average. Thus we have a microscopic expression for a transport coefficient. Moreover, this microscopic expression contains a quantity that is often called a time correlation function. It is an average of the product of a dynamical variable at one time and a dynamical variable at another time.

One of the major points of this course is that for very many transport coefficients and rate constants, as well as spectroscopic properties, there is a similar expression. The basic line of reasoning for obtaining these relationships is similar to what we have just done, but the details can be much more complicated for some transport coefficients.

We still have some work to do, however. Note that the left side is a constant, independent of time, but the right side depends on t . How can this be? Recall, however, that we are justified in equating the results of the microscopic and macroscopic descriptions only for long times. So we should apply this formula only at long times. If it works at long times, it works in the limit of infinite time. So we have

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \int_0^t dt' \int_0^t dt'' \langle \mathbf{v}_1(t') \cdot \mathbf{v}_1(t'') \rangle_{eq}$$

However, we still have some work to do. How do we know that this limit exists? A related question is: what are the properties of the correlation function $\langle \mathbf{v}_1(t') \cdot \mathbf{v}_1(t'') \rangle_{eq}$ that insure that this limit exists?

Later in the course, we shall have a systematic discussion of the general properties of such functions. For now, let me just quote the few that we need.

- $\langle \mathbf{v}_1(t') \cdot \mathbf{v}_1(t'') \rangle_{eq}$ depends on the time interval $t' - t''$. Let's call it $C_{\mathbf{v}_1\mathbf{v}_1}(t' - t'')$.

- It is unchanged if the two time arguments are interchanged.

$$\langle \mathbf{v}_1(t') \cdot \mathbf{v}_1(t'') \rangle_{eq} = \langle \mathbf{v}_1(t'') \cdot \mathbf{v}_1(t') \rangle_{eq}$$

Hence $C_{\mathbf{v}_1\mathbf{v}_1}(t' - t'') = C_{\mathbf{v}_1\mathbf{v}_1}(t'' - t')$ or

$$C_{\mathbf{v}_1\mathbf{v}_1}(t) = C_{\mathbf{v}_1\mathbf{v}_1}(-t)$$

- When the two time arguments are equal, we have an equilibrium static average.

$$C_{\mathbf{v}_1\mathbf{v}_1}(t) = \langle \mathbf{v}_1(0) \cdot \mathbf{v}_1(0) \rangle_{eq} = \frac{3kT}{m}$$

This follows because

$$\left\langle \frac{1}{2} m \mathbf{v}_1(0) \cdot \mathbf{v}_1(0) \right\rangle_{eq} = \frac{3kT}{2}$$

which follows from the classical equipartition principle.

- For large values of $|t' - t''|$,

$$\langle \mathbf{v}_1(t') \cdot \mathbf{v}_1(t'') \rangle \approx \langle \mathbf{v}_1(t') \rangle \langle \mathbf{v}_1(t'') \rangle = 0$$

Hence

$$C_{\mathbf{v}_1\mathbf{v}_1}(t) \rightarrow 0 \quad \text{as } |t| \rightarrow \infty$$

Making use of these results, we can carry out the limiting operation indicated above.

$$\begin{aligned} \frac{1}{6t} \int_0^t dt' \int_0^t dt'' C_{\mathbf{v}_1\mathbf{v}_1}(t' - t'') &= \frac{1}{6t} \int_0^t dt'' \int_0^t dt' C_{\mathbf{v}_1\mathbf{v}_1}(t' - t'') \\ &\approx \frac{1}{6t} \int_0^t dt'' \int_{-\infty}^{\infty} dt' C_{\mathbf{v}_1\mathbf{v}_1}(t' - t'') \\ &= \frac{1}{6t} \int_0^t dt'' \int_{-\infty}^{\infty} d\tau C_{\mathbf{v}_1\mathbf{v}_1}(\tau) \\ &= \frac{1}{6} \int_{-\infty}^{\infty} d\tau C_{\mathbf{v}_1\mathbf{v}_1}(\tau) \\ &= \frac{1}{3} \int_0^{\infty} d\tau C_{\mathbf{v}_1\mathbf{v}_1}(\tau) \\ D = \lim_{t \rightarrow \infty} \frac{1}{6t} \int_0^t dt' \int_0^t dt'' C_{\mathbf{v}_1\mathbf{v}_1}(t' - t'') &= \frac{1}{3} \int_0^{\infty} d\tau C_{\mathbf{v}_1\mathbf{v}_1}(\tau) \end{aligned}$$

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$$D = \frac{1}{3} \int_0^\infty d\tau C_{\mathbf{v}_1\mathbf{v}_1}(\tau)$$

***end of slide

In getting the second (approximate) equality, we used the fact that the correlation function is small for large absolute values of its time argument, so that the error made in extending the range of integration is quite small. In particular, the fractional error is negligible in the limit of large t .

An alternative form is

$$D = \int_0^\infty d\tau \langle v_{1x}(\tau) v_{1x}(0) \rangle$$

The quantity on the first is one third of the integral in the previous equation, since each of the three components of velocity make equivalent contributions to the integral.

Qualitative discussion of the result for dilute gas and dense liquid.

End of
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6 Evaluation by molecular dynamics calculations

Lecture
2 starts
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One of the uses of formulas like those we have been deriving is to figure out how to obtain transport coefficients from molecular dynamics simulations.

In molecular dynamics computer simulations, we solve the equations of motion of the atoms or molecules of a fluid and observe how they move about. The system usually studied are rather small (typically hundreds to thousands of atoms). The sizes of the systems are very small in terms of length - typically tens of Angstroms. The time scale of the simulation is small - typically picoseconds to nanoseconds.

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lecture.

For normal liquid situations, it is typically possible to calculate the time correlation function of the velocity, namely $C_{\mathbf{v}_1\mathbf{v}_1}(t)$. If this function decays to zero rapidly enough, then its integral can be calculated, giving a value of the self-diffusion coefficient.

Alternatively, we calculate the mean squared displacement

$$\langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle$$

(To get better statistics, we average the result for all atoms i of the same type.) If this is plotted versus time, then at long times the plot should be linear with a slope

of $6D$. If such a linear region is seen in the data, the slope can be used to calculate D .

Alternatively, if

$$\langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle = 6Dt$$

then

$$\log_{10} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle = \log_{10}(6D) + \log_{10} t$$

A plot of $\log_{10} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle$ vs. $\log_{10} t$ should be linear with a slope of 1. If it is, then the intercept of the straight line (at $\log_{10} t = 0$) should be equal to $\log_{10}(6D)$.

Figure. The mean square displacement for one of the two types of atoms in a two component atomic mixture at various temperatures. Note that at long times the lines are all straight with the same slope of 1.

The very short time behavior is also straight, but the slope is different. At very short times, $\mathbf{r}_i(t) - \mathbf{r}_i(0) = \mathbf{v}_i(0)t + O(t^2)$. Hence

$$\langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle = t^2 \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(0) \rangle = \frac{3k_B T}{m} t^2$$

$$\log_{10} \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle = \log_{10} \frac{3k_B T}{m} + 2 \log_{10} t$$

At short times, the slope on the log-log plot should be 2, not 1, and it is. Moreover, the intercept is $\log_{10}(3k_B T/m)$.

7 Langevin equation

7.1 Introduction

In early and influential experiments, Brown observed that small particles suspended in a fluid are typically moving around continuously, rather than settling down because of friction with the surrounding fluid. This type of motion is now called Brownian motion, in honor of Brown. It was eventually accepted that the perceptible motion of such large particles was a consequence of the molecular nature of matter and the fact that all atoms, molecules, and particles, large and small, are continually moving.

The Langevin equation was developed (presumably by someone whose name was Langevin) as a description of the dynamics of *large* particles suspended in a fluid of

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small molecules. The fluid is regarded as a hydrodynamic continuum. The equation itself is the result of a set of guesses about the statistical features of the dynamics, and it represents a model for how dynamics could take place. As a mathematical model for classical and even quantum mechanics, it has been very influential, and Langevin ideas are routinely applied in new situations even in the most current research. Moreover, the structure of the Langevin equations for Brownian motion have been historically very influential in the subsequent development of modern statistical mechanics. Finally, it has led to remarkably accurate approximate theories for fluids in which all the particles are of the same size. So some knowledge of the Langevin equation is indispensable in understanding physical chemistry.

Here we want to discuss the Langevin approach to dynamics in its simplest context.

7.2 Assumptions of the Langevin theory

⁵ A large heavy particle in a fluid experiences forces due to the effect of the surrounding solvent molecules. These forces vary rapidly in time, because the surrounding molecules move so rapidly. The overall system is in equilibrium, and so we are considering the dynamics of fluctuations in an equilibrium system.⁶ Thus, most of the ensemble averaging we are about to do is for an equilibrium ensemble. Newton's equation of motion for the heavy particle is

$$m\dot{\mathbf{v}}(t) = \mathbf{F}(t)$$

where \mathbf{v} is the velocity of the particle and $\mathbf{F}(t)$ is the total force experienced by the particle. The Langevin description assumes that the total force can be divided into two parts: a systematic frictional force and a random force.

The systematic frictional force arises when the particle is moving. As it plows through the solvent, it experiences a force that slows it down. This force always points in the opposite direction from that of the velocity. The frictional force is equal to $-\zeta\mathbf{v}(t)$.

⁵References: A classic reference for Langevin theory (and other stochastic theories) is: S. Chandrasekhar, *Rev. Mod. Phys.* **15**, 1-89 (1943); [http://prola.aps.org/abstract/RMP/v15/i1/p1_1] It is reprinted in a Dover edition of: Wax, *Noise and Stochastic Processes*. Also see Section 7.3 of: J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed.

⁶We will usually leave out the *eq* subscript on ensemble averages, but the subscript should be understood to be present.

Here ζ is a friction coefficient. We shall come back to the question of how to estimate ζ . The dimensions of ζ are force/velocity = mass/time.

The random force will be denoted $\mathbf{R}(t)$.

So we have

$$m\dot{\mathbf{v}}(t) = -\zeta\mathbf{v}(t) + \mathbf{R}(t)$$

This is called the Langevin equation.

Note that the systematic force is completely determined by the current velocity of the particle. The random force $\mathbf{R}(t)$ is regarded as a random variable. Its particular value is the result of the combined effect of the detailed positions and momenta of the solvent particles at the initial time. To specify Langevin dynamics, we have to make some assumptions about the statistical properties of this random variable.

The first thing we assume is that the average value of $\mathbf{R}(t)$ is zero. $\langle\mathbf{R}(t)\rangle = 0$. This is entirely reasonable, indeed necessary, because if we take the ensemble average of the Langevin equation, we get

$$m\langle\dot{\mathbf{v}}(t)\rangle = -\zeta\langle\mathbf{v}(t)\rangle + \langle\mathbf{R}(t)\rangle$$

The first two averages are clearly zero for an equilibrium system, and so the third term must be zero as well.

Next we assume that the random force is statistically independent of the *initial value* of the velocity itself.

$$\langle\mathbf{R}(t) \cdot \mathbf{v}(0)\rangle = 0$$

Thirdly, we assume that the fluctuating force fluctuates very rapidly and the correlation function of the fluctuating force goes to zero so quickly that the correlation function can be represented as a Dirac delta function.

$$\langle\mathbf{R}(t) \cdot \mathbf{R}(t')\rangle = R_0\delta(t - t')$$

Here R_0 is a positive constant. Thus, there is no statistical correlation between the fluctuating forces at different times. The delta function that appears here is a function that decays to zero instantaneously on the time scale appropriate for the motion of the heavy particle. For example, it might decay to zero in a time of about 1 picosecond or 10 picoseconds. But for a heavy colloidal particle, the momentum relaxation time is much longer than this.

The nontrivial content of this assumption is that the statistical properties of the random force are completely unrelated to the initial velocity of the particle.

For a complete calculation of the dynamics using the Langevin equation, we need to make some additional assumptions about the random force. But we will not need this right now.

Let's explore the consequences of these assumptions about Langevin dynamics. Along the way, we shall have to ask whether the theory is consistent with what we know about equilibrium statistical mechanics.

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Langevin description of the Brownian motion of a single particle

$$m\dot{\mathbf{v}}(t) = -\zeta\mathbf{v}(t) + \mathbf{R}(t)$$

where

$\mathbf{v}(t)$ is the velocity of the particle

m is the mass of the particle

ζ is a friction constant

$\mathbf{R}(t)$ is a random force acting on the particle. It is assumed that

$$\langle \mathbf{R}(t) \rangle = 0 \quad \langle \mathbf{R}(t) \cdot \mathbf{R}(t') \rangle = R_0 \delta(t - t') \quad \langle \mathbf{R}(t) \cdot \mathbf{v}(0) \rangle = 0$$

***(*end of slide*)

7.3 Consequences of the Langevin theory

We have a rather complete description of the dynamics of the particle. Let's assume the description is correct and start calculating properties of interest for the system. Most of the properties we will be concerned with are time correlation functions of various types as well as averages of certain properties.

7.3.1 The free Brownian particle

Let's solve the equation of motion to get the velocity as a function of time. The equation is of a standard form, and we can write the solution as

$$m\mathbf{v}(t) = m\mathbf{v}(0)e^{-(\zeta/m)t} + \int_0^t ds e^{-(\zeta/m)(t-s)} \mathbf{R}(s)$$

It can easily be verified that this satisfies the differential equation as well as the initial condition that the value of the velocity at time zero be $\mathbf{v}(0)$. We can now use this to do a number of interesting calculations.

If we merely take the ensemble average of both sides, we get a trivial but correct result that $0 = 0$.

Let's multiply both sides by $\mathbf{v}(0)$ and then average.

$$m\mathbf{v}(t) \cdot \mathbf{v}(0) = m\mathbf{v}(0) \cdot \mathbf{v}(0)e^{-(\zeta/m)t} + \int_0^t ds e^{-(\zeta/m)(t-s)} \mathbf{R}(s) \cdot \mathbf{v}(0)$$

$$m\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle = m\langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle e^{-(\zeta/m)t} + \int_0^t ds e^{-(\zeta/m)(t-s)} \langle \mathbf{R}(s) \cdot \mathbf{v}(0) \rangle$$

The average in the first term on the right is $3k_B T/m$. The average in the second term on the right is zero. We get

$$\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle = \frac{3k_B T}{m} e^{-(\zeta/m)t}$$

Thus the Langevin equation predicts that the velocity autocorrelation function of the heavy particle decays exponentially.

Let's derive this result in another way. Go back to the original Langevin equation for $\dot{\mathbf{v}}(t)$ and multiply both sides by $\mathbf{v}(0)$.

$$m\dot{\mathbf{v}}(t) \cdot \mathbf{v}(0) = -\zeta \mathbf{v}(t) \cdot \mathbf{v}(0) + \mathbf{R}(t) \cdot \mathbf{v}(0)$$

Now take the ensemble average and divide by m .

$$\langle \dot{\mathbf{v}}(t) \cdot \mathbf{v}(0) \rangle = -\frac{\zeta}{m} \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle + \frac{1}{m} \langle \mathbf{R}(t) \cdot \mathbf{v}(0) \rangle$$

- The average in the first term on the right is just the correlation function for the particle velocity.

$$C_{\mathbf{v}\mathbf{v}}(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$$

- The average in the second term on the right is zero, by the assumptions we made about the random force in the Langevin theory.
- The average on the left is just the time derivative of the velocity autocorrelation function.

$$\dot{C}_{\mathbf{v}\mathbf{v}}(t) = \frac{d}{dt} C_{\mathbf{v}\mathbf{v}}(t) = \frac{d}{dt} \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle = \left\langle \frac{d\mathbf{v}(t)}{dt} \cdot \mathbf{v}(0) \right\rangle = \langle \dot{\mathbf{v}}(t) \cdot \mathbf{v}(0) \rangle$$

Thus the equation above is

$$\dot{C}_{\mathbf{v}\mathbf{v}}(t) = -\frac{\zeta}{m}C_{\mathbf{v}\mathbf{v}}(t)$$

The initial condition is

$$C_{\mathbf{v}\mathbf{v}}(0) = \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle = \frac{3k_B T}{m}$$

This is the equation for simple exponential decay, and we get

$$C_{\mathbf{v}\mathbf{v}}(t) = \frac{3k_B T}{m} e^{-(\zeta/m)t}$$

This is the same result that we got above.

Let's check out the dimensions. Above we showed that the dimensions of ζ were (mass)/(time). Thus ζ/m has dimensions of 1/(time). This makes the exponent dimensionless, as it should be.

There are two rather general characteristics of this result that should be noticed.

- The theory was constructed to include systematic forces and random forces. Both are needed to obtain a consistent theory. We find, nevertheless, that the correlation function for the velocity contains no apparent reference to the random force. The properties of only the systematic force appear explicitly in this particular correlation function.
- The correlation function decays exponentially in time. Many simple theories (but certainly not all theories) give exponential decay, or a simple sum of exponentials, or exponential decay at long times. We shall be interested in understanding the physical and mathematical reasons for these types of behavior. When we have seen several different examples of this and other behavior, we will make some generalizations about the conditions under which exponential decay is or is not to be expected.

Next, let's square the result for $\mathbf{v}(t)$ and take the average over the initial equilibrium

distribution of velocities and over the statistical distribution of random forces.

$$\begin{aligned}
\mathbf{v}(t) &= \mathbf{v}(0)e^{-(\zeta/m)t} + \frac{1}{m} \int_0^t ds e^{-(\zeta/m)(t-s)} \mathbf{R}(s) \\
\mathbf{v}(t) \cdot \mathbf{v}(t) &= \mathbf{v}(0) \cdot \mathbf{v}(0)e^{-2(\zeta/m)t} + \frac{2}{m} e^{-(\zeta/m)t} \int_0^t ds e^{-(\zeta/m)(t-s)} \mathbf{R}(s) \cdot \mathbf{v}(0) \\
&\quad + \frac{1}{m^2} \int_0^t ds e^{-(\zeta/m)(t-s)} \int_0^t ds' e^{-(\zeta/m)(t-s')} \mathbf{R}(s) \cdot \mathbf{R}(s') \\
\langle \mathbf{v}(t) \cdot \mathbf{v}(t) \rangle &= \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle e^{-2(\zeta/m)t} + \frac{2}{m} e^{-(\zeta/m)t} \int_0^t ds e^{-(\zeta/m)(t-s)} \langle \mathbf{R}(s) \cdot \mathbf{v}(0) \rangle \\
&\quad + \frac{1}{m^2} \int_0^t ds e^{-(\zeta/m)(t-s)} \int_0^t ds' e^{-(\zeta/m)(t-s')} \langle \mathbf{R}(s) \cdot \mathbf{R}(s') \rangle \\
\langle \mathbf{v}(t) \cdot \mathbf{v}(t) \rangle &= \frac{3kT}{m} e^{-2(\zeta/m)t} + \frac{1}{m^2} \int_0^t ds e^{-(\zeta/m)(t-s)} \int_0^t ds' e^{-(\zeta/m)(t-s')} R_0 \delta(s-s') \\
&= \frac{3kT}{m} e^{-2(\zeta/m)t} + \frac{R_0}{m^2} \int_0^t ds e^{-2(\zeta/m)(t-s)} \\
&= \frac{3kT}{m} e^{-2(\zeta/m)t} + \frac{R_0}{m^2} \frac{m}{2\zeta} e^{-2(\zeta/m)(t-s)} \Big|_0^t \\
&= \frac{3kT}{m} e^{-2(\zeta/m)t} + \frac{R_0}{m^2} \frac{m}{2\zeta} (1 - e^{-2(\zeta/m)t}) \\
&= e^{-2(\zeta/m)t} \left(\frac{3kT}{m} - \frac{R_0}{2m\zeta} \right) + \frac{R_0}{2m\zeta}
\end{aligned}$$

In fact, the left side of this equation is just the equilibrium average of the square of the velocity of a particle. From the equipartition principle, it follows that the value is $3k_B T/m$ and is independent of time. So the right side must also be independent of time and must have that value. The right side can be independent of time only if

$$\frac{3kT}{m} = \frac{R_0}{2m\zeta}$$

and if this is the case it also has the right value for all times. The result can be expressed as

$$R_0 = 6kT\zeta$$

or

$$\zeta = \frac{R_0}{6kT}$$

The basis of these equations is the assumptions that:

- the Langevin equation assumptions are correct;
- the predictions of the theory are consistent with equilibrium statistical mechanics.

The interesting consequence is that there is a relationship between the strength of the systematic force, represented by ξ , and the strength of the fluctuating force, represented by R_0 . In order for the theory to be consistent with equilibrium statistical mechanics, these two must be proportional to one another and their ratio is

$$\frac{R_0}{\zeta} = 6kT$$

It should not be surprising that the temperature appears in the relationship. The systematic force always tends to slow down the particle and reduce its kinetic energy. The random force sometimes increases and sometimes decreases the kinetic energy of the particle, but on the average it must increase the kinetic energy of the particle, because on the average the kinetic energy of the particle must remain constant at $3k_B T/m$ (but of course it can fluctuate about this average value).

Finally, let's calculate the diffusion constant. From our result above for the velocity autocorrelation function, we have

$$D = \frac{1}{3} \int_0^\infty dt \frac{3kT}{m} e^{-(\zeta/m)t} = \frac{kT}{\zeta}$$

The larger the friction constant, the smaller the self-diffusion coefficient.

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Consequences of the Langevin equation for a single particle

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$$\begin{aligned} \mathbf{v}(t) &= \mathbf{v}(0)e^{-(\zeta/m)t} + \frac{1}{m} \int_0^t ds e^{-(\zeta/m)(t-s)} \mathbf{R}(s) \\ \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle &= \frac{3k_B T}{m} e^{-(\zeta/m)t} \quad \text{hence} \quad D = k_B T / \zeta \\ \langle \mathbf{v}(t) \cdot \mathbf{v}(t) \rangle &= e^{-2(\zeta/m)t} \left(\frac{3k_B T}{m} - \frac{R_0}{2m\zeta} \right) + \frac{R_0}{2m\zeta} \end{aligned}$$

The left side, according to equilibrium statistical mechanics is equal to $3k_B T/m$ for all t . The right side will be consistent with this if $3k_B T/m = R_0/2m\zeta$ or

$$\frac{R_0}{\zeta} = 6k_B T$$

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7.3.2 The Brownian particle in an external field

Now let's consider the problem of a Brownian particle in an external field. We imagine that in addition to the systematic friction and the random force, there is an additional steady external force acting on the system. It could be a gravitational force pulling the particle down. Or if the particle is charged, it could be a force caused by an external field.

We imagine that the system was initially in equilibrium, and then the external force is turned on. The strength of the force is so small that it does not perturb the system greatly. The net result is that the particle will tend to move in the direction of the external force.

The new equation of motion is

$$m\dot{\mathbf{v}}(t) = -\zeta\mathbf{v}(t) + \mathbf{R}(t) + \mathbf{f}(t)$$

where $f(t)$ is the weak external force. It is something that is under our control, so it is not a random variable. We make the same assumptions about \mathbf{R} as we made in the absence of this external force. Let's decide that $\mathbf{f}(0) = 0$ and that it jumps to a value of \mathbf{f}_0 and stays at that value.

Let's solve this equation and use it to calculate the behavior of the particle. The solution can easily be shown to be

$$m\mathbf{v}(t) = m\mathbf{v}(0)e^{-(\zeta/m)t} + \int_0^t ds e^{-(\zeta/m)(t-s)} (\mathbf{R}(s) + \mathbf{f}(s))$$

Now let's take the ensemble average of this over the initial equilibrium ensemble. We get

$$m\langle\mathbf{v}(t)\rangle = m\langle\mathbf{v}(0)\rangle e^{-(\zeta/m)t} + \int_0^t ds e^{-(\zeta/m)(t-s)} (\langle\mathbf{R}(s)\rangle + \mathbf{f}(s))$$

The two averages on the right are both zero.

$$\begin{aligned} m\langle\mathbf{v}(t)\rangle &= \int_0^t ds e^{-(\zeta/m)(t-s)} \mathbf{f}(s) \\ \langle\mathbf{v}(t)\rangle &= \frac{1}{m} \int_0^t ds e^{-(\zeta/m)(t-s)} \mathbf{f}(s) \end{aligned}$$

Notice that the average of the velocity contains some properties of the systematic friction, but the random force does not appear. This is reminiscent of what we found for the velocity correlation function in the absence of an external field.

The right side is zero at $t = 0$ and it then increases with time. Let's calculate the behavior at long times, where $f(t)$ has saturated at the value f_0 . Because of the exponential in the integrand, the behavior of f only near $s = t$, i.e. long times, is important. Thus

$$\langle \mathbf{v}(t) \rangle = \frac{1}{m} \int_0^t ds e^{-(\zeta/m)(t-s)} \mathbf{f}_0 = \frac{\mathbf{f}_0}{m} \int_0^t ds e^{-(\zeta/m)(t-s)} = \frac{\mathbf{f}_0}{\zeta}$$

Not surprisingly, in the limit of long times, under the application of a steady force, the velocity of the particle is proportional to the force applied to it.

A simple way of seeing that this answer is right is to note that as the particle accelerates, the frictional force builds up and tends to counterbalance the applied force. You might expect that the particle adopts a velocity such that on the average the systematic friction is just such as to counterbalance the applied force, leading to no net force and hence no acceleration and hence no change in velocity. In other words we would expect that at large times

$$-\zeta \mathbf{v}(t) + \mathbf{f}_0 \approx 0$$

or

$$\mathbf{v}(t) = \mathbf{f}_0 / \zeta$$

This has the same form as the more correct statement above, which is expressed in terms of statistical averages.

In situations with this type of frictional force, the coefficient of proportionality between the average velocity of something and the force applied to it is usually called the *mobility*. Various symbols (μ , L , H) are used for the mobility in different contexts. Let's use μ . The connotation is obvious. A particle that moves fast when a small force is applied to it is very mobile and a particle that moves slowly when a force is applied to it is not very mobile.

Our result then is that the mobility is the reciprocal of the friction constant.

$$\mu = \frac{1}{\zeta}$$

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Brownian particle subject to an external field. System initially at equilibrium at $t = 0$. A time dependent external force is applied to the particle. The equation of motion is

$$m\dot{\mathbf{v}}(t) = -\zeta\mathbf{v}(t) + \mathbf{R}(t) + \mathbf{f}(t)$$

The solution can easily be shown to be

$$m\mathbf{v}(t) = m\mathbf{v}(0)e^{-(\zeta/m)t} + \int_0^t ds e^{-(\zeta/m)(t-s)} (\mathbf{R}(s) + \mathbf{f}(s))$$

Take the average of this over the initial equilibrium distribution.

$$m\langle\mathbf{v}(t)\rangle = m\langle\mathbf{v}(0)\rangle e^{-(\zeta/m)t} + \int_0^t ds e^{-(\zeta/m)(t-s)} (\langle\mathbf{R}(s)\rangle + \mathbf{f}(s))$$

The two averages on the right are both zero.

$$\langle\mathbf{v}(t)\rangle = \frac{1}{m} \int_0^t ds e^{-(\zeta/m)(t-s)} \mathbf{f}(s)$$

Suppose $\mathbf{f}(0) = \mathbf{0}$ and $\mathbf{f}(t)$ rises to \mathbf{f}_0 and stays at that value.

$$\langle\mathbf{v}(t)\rangle = \frac{1}{m} \int_0^t ds e^{-(\zeta/m)(t-s)} \mathbf{f}_0 \rightarrow \frac{\mathbf{f}_0}{\zeta}$$

Define mobility μ as

$$\langle\mathbf{v}\rangle = \mu\mathbf{f}_0$$

Then

$$\mu = \frac{1}{\zeta}$$

Since $D = k_B T / \zeta$, we have

$$D = \mu k_B T$$

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7.3.3 Comparison of the results for the diffusion constant and for the mobility

The diffusion constant, D , appears in the diffusion equation that is meant to describe one set of experiments, namely how low concentration solute particles move around

in a system that is in equilibrium except for spatial variations of the concentration of the solute.

The mobility, μ , arises in trying to describe an entirely different type of experiment, namely one in which a field is applied and you measure how rapidly the particles move in response to that field.

At first glance, there would seem to be no obvious relationship between two these two experiments.

However, we have found an interesting relationship when we described both using the Langevin equation. We found that $D = k_B T / \zeta$ and $\mu = 1 / \zeta$. Therefore

$$D = \mu k_B T$$

Moreover, we also have the relationship that

$$D = \frac{1}{3} \int_0^\infty dt \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$$

In effect we have found a relationship among the following three things:

- The rate at which solute particles move to eliminate small concentration gradients. (This is for a system with no applied fields.)
- The frictional force on a particle due to the solvent.
- The average rate at which the solute particles move when an external field is applied to them.
- The statistical properties of the fluctuation of the velocity of a solute particle for an equilibrium system with no concentration gradients and no applied fields.

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Various properties of a Brownian particle are related.

Frictional force on a particle due to its velocity $= -\zeta \mathbf{v}$

Correlation function of random force on a particle $= \langle \mathbf{R}(t) \cdot \mathbf{R}(t') \rangle = R_0 \delta(t - t')$

Velocity of a particle subject to a steady external force $= \mu \mathbf{f}$

The diffusion constant D , related to the rate at which concentration fluctuations are dissipated

The velocity autocorrelation function $= \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$

Relationships: $R_0 = 6k_B T \zeta$ $\mu = 1/\zeta$

$$D = \mu k_B T = k_B T / \zeta = \frac{1}{3} \int_0^\infty dt \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$$

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We have derived this relationship using the Langevin equation, which is basically a guess as to how to describe the dynamics, and you might wonder whether these simple results are a consequence of some special assumptions we made. In fact, such relationships are ubiquitous when you use what are physically correct formulations of dynamics. The Langevin dynamics is basically correct for colloidal particles under some conditions. The same types of results are obtained from other dynamical models, such as classical mechanics and quantum mechanics.

What we have found are special cases of two rather general principles:

- The response of a system to weak external fields
is related to
the fluctuations of the system at equilibrium (in the absence of external field)
- The rate at which dissipative processes (e.g. diffusion, viscous momentum flow, chemical reactions) take place in systems close to equilibrium
is related to
the fluctuations of the system at equilibrium (when none of these dissipative processes are taking place).

These are related to a third principle, which we have not illustrated for Brownian particles, but I'll state it anyway.

- The way in which an equilibrium system scatters radiation (e.g. electromagnetic radiation) or particles (e.g. neutrons)
is related to
the fluctuations of the system at equilibrium (when it is not being bombarded with radiation or particles).

As we explore other ways of describing dynamics (e.g. classical mechanics, quantum mechanics), we shall see many examples of these principles.

7.4 Hydrodynamic estimate of the friction coefficient

If the Brownian particle of interest is large and spherical, it is plausible to use a hydrodynamic theory to estimate the friction coefficient. $-\zeta\mathbf{v}$ is supposedly the frictional force on the sphere when it is moving with velocity \mathbf{v} .

A standard problem in hydrodynamics is the following one. Suppose a rigid sphere is moving at constant velocity in a fluid that is stationary. The particle causes the fluid near it to move. It basically pushes the fluid out of the way. It causes a flow pattern to be set up near the particle, but far away the fluid is still stationary. The fluid impedes the motion of the sphere and exerts a force on it. A straightforward calculation that solves the hydrodynamic equations for the fluid leads to the result

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that the force exerted by the fluid on the sphere is

$$-3\pi d\eta\mathbf{v}$$

where η is the shear viscosity coefficient of the fluid and d is the diameter of the sphere. The shear viscosity is related to how momentum flows in the fluid as a result of there being velocity gradients. The flow pattern that is created is inhomogeneous and thus there is momentum flow in the fluid. Some of the momentum flow represents momentum that is ultimately transferred to the sphere itself, and this is the force that the fluid applies to the sphere.

The result above is what is obtained when it is assumed that at the surface of the sphere the velocity of the fluid is equal to that of the sphere itself. This is called the ‘stick’ boundary condition. (This word is used because in effect the fluid at the surface of the sphere sticks to the sphere and moves with the same velocity as the surface of the sphere.)

There are other boundary conditions that could be used. The major alternative to the stick boundary condition is the ‘slip’ boundary condition. The slip boundary condition assumes that at the surface of the sphere the component of the fluid velocity that is perpendicular to the surface of the sphere is equal to the component of the sphere velocity that is perpendicular to the surface. This gives the result that the force exerted on the sphere is somewhat smaller.

$$-3\pi d\eta\mathbf{v}$$

If we assume that this hydrodynamic calculation is at all relevant to the Langevin theory, we conclude that

$$\begin{aligned}\zeta &= 3\pi d\eta \quad (\text{stick}) \\ \zeta &= 2\pi d\eta \quad (\text{slip})\end{aligned}$$

Here d is the diameter of the particle. The friction coefficient is determined by the mass of the particle, its diameter, and the viscosity of the fluid.

If this is correct, then we have

$$\begin{aligned}D &= kT/3\pi d\eta \quad (\text{stick}) \\ D &= kT/2\pi d\eta \quad (\text{slip})\end{aligned}$$

These relationships often go by the name of the Stokes-Einstein equations.

While the use of the solution of hydrodynamic equations to calculate the friction constant is reasonable for a large solute, the result is reasonably accurate even for small molecules in a pure liquid or in a solution. One way of testing this is to rewrite the equations as

$$\begin{aligned}d &= \frac{k_B T}{3\pi\eta D} \quad (\text{stick}) \\d &= \frac{k_B T}{2\pi\eta D} \quad (\text{slip})\end{aligned}$$

Then use experimental data for η and D to calculate values of d and compare with other estimates of the diameter of a molecule. Moreover, the value of d should be roughly independent of temperature if this is to make sense.

For liquids under ordinary conditions, you get reasonable numbers, with the numbers for slip boundary conditions being somewhat more reasonable.

There are analogous relationships for the rotational diffusion constant for a molecule, and this has provided ways of quantitatively interpreting light scattering data that measures rotational relaxation rates.

There is some evidence that as liquids are supercooled to very low temperatures, the quantity $k_B T/\eta D$ is no longer independent of temperature. This ‘breakdown’ of the Stokes-Einstein relationship is the subject of considerable speculation among people trying to understand supercooled liquids.