Chapter 5

Near-equilibrium dynamics

Conventional textbooks on statistical mechanics typically enforce a nearly complete separation between discussions of equilibrium and non-equilibrium phenomena, with the latter often relegated to the end of the course (or beyond). In this course, we focus on simulation techniques as both an important way to visualize ensembles and fluctuations, as well as a central technique for carrying out statistical calculations. Thus we immediately confront non-equilibrium phenomena, if only to have some idea of how and when a simulation reaches equilibrium.

Furthermore, with molecular dynamics simulations, we have direct access to a reasonably realistic “movie” of the dynamics of the system. In particular, we can study near-equilibrium phenomena, by which we mean, the time-dependence of the system when local regions of the system can be regarded as equilibrated, but some properties are inhomogeneous across the system, for example the energy, density, or concentration of some species.

Most degrees of freedom in a system equilibrate quite quickly, on the timescale of a few molecular collisions. But long wavelength variations in conserved quantities such as the energy, density, or species concentrations, relax slowly towards a homogeneous equilibrium state, because such relaxation requires transport of the conserved quantity over the length scale of the variation.

In addition, long-wavelength variations in an “order parameter” associated with a “broken symmetry” will relax slowly, because the restoring force towards the uniform state is quite weak. A simple example is provided by a nematic liquid crystal, which may be thought of as a liquid in which the molecules are rodlike and locally aligned. A nematic can be uniformly aligned in any direction; the rotational symmetry of an isotropic liquid is “broken” by the alignment direction. Now consider a nematic in which the alignment direction wiggles slowly along \( z \), as \( \hat{n}(z) = \hat{x} + \epsilon \hat{y} \cos(qz) \). Locally, the molecules are nearly as well aligned as in the preferred uniformly aligned state; hence, the restoring force is weak, and the relaxation is slow.

Hydrodynamics is the theory of the long-wavelength slow dynamics of the conserved quantities or order parameters of a system, which subject lies beyond the bounds of this course. However, MD simulations have an important role to play in the determination of the transport coefficients that appear in hydrodynamic theories.

In hydrodynamics, transport coefficients give the ratio between a driven “current” and some external driving force. For example, the diffusivity is the ratio between the concentration current and the concentration gradient; the electrical conductivity is the ratio between the electric current and the electric field. It turns out that these transport coefficients can also be obtained by observing the diffusion of whatever it is that carries the current in the absence of an external driving force — for the diffusivity, the molecules themselves; for the electrical conductivity, the mobile charged species.
In fact, a general relation exists between the time-dependent response of some quantity to a weak external field, and the natural fluctuations of that quantity in absence of any external field, called the fluctuation-response theorem. This relation generalizes to time-dependent phenomena the connection we demonstrated in Section ?? between the equilibrium response of some thermodynamic quantity (such as the energy) to an external perturbation (such as a change in temperature), and the natural fluctuations of that quantity.

5.1 Stokes-Einstein relation

Self-diffusion is the simplest example of transport phenomena near equilibrium. Imagine a single component fluid in which a small fraction of the particles have been “labeled” so they may be seen amongst the sea of unlabeled particles (for example, the unlabeled particles are transparent, and the labeled particles are dyed red).

![Figure 5.1: (a) Initially concentrated labeled particles. (b) Equilibrium.](image)

Suppose we prepare such a system in an initial state with a higher concentration of red particles near the origin. As time passes, this local excess of red particles will spread out by diffusion into the surrounding volume, until at long times the concentration of red particles is once again uniform.

This process is called “self-diffusion” because the labeled particles are dilute in the system, and so do not interact with each other. The evolution of the concentration $\rho(r, t)$ of labeled particles is governed by a conservation law with a diffusive current $J_D$:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot J_D = 0$$

$$J_D = -D \nabla \rho$$

(5.1)

Now imagine that we alter the labeled particles so that they respond to an external potential $\phi(r)$ that we apply. We write the interaction Hamiltonian as

$$\delta H = \int dr \rho(r) \phi(r)$$

(5.2)
The concentration $\rho(r, t)$ may be written in terms of the particle positions as

$$\rho(r, t) = \sum_{\alpha} \delta(r - r_{\alpha}(t)) \quad (5.3)$$

Using this, the interaction Hamiltonian can be written

$$\delta H = \sum_{\alpha} \phi(r_{\alpha}(t)) \quad (5.4)$$

The particles individually feel the potential $\phi(r)$ in the usual way, with an additional term in the equation of motion

$$\dot{p}_i = -\frac{\partial U}{\partial r_i} - \frac{\partial \phi}{\partial r_i} \quad (5.5)$$

The particles feel a force $F = -\partial \phi / \partial r$.

If we specify a linear potential $\phi(r) = -F \cdot r$, this results in a constant force $F$ on all the labeled particles. This will result in the particles tending to drift in the direction the force pushes them. If the force $F$ is small, the drift velocity $v$ should be proportional to $F$. (Essentially we are arguing that $v(F)$ ought to be a smooth function of $F$, and can therefore be expanded in a Taylor series for small $F$.)

Thus for small $F$ we write

$$v = \mu F \quad (5.6)$$

in which $\mu$ is the “mobility” of the particle. (The inverse of $\mu$ is the “drag coefficient”, since $F = (1/\mu)v$.) In a fluid, we expect that $\mu$ does not depend on the direction of $F$.

When the labeled particles move with velocity $v$ in response to an applied force, a “drift current” results, which we write as

$$J_v = \rho v \quad (5.7)$$

Figure 5.2: Equilibrium concentration $P(x)$ in an external potential $\phi(x)$; canceling currents $J_v$ (downhill in the potential) and $J_D$ (downhill along the concentration gradient) indicated.
Thus a concentration current can arise either from a concentration gradient (diffusive current $J_D$), or from drift in response to an applied force (drift current $J_v$). Remarkably, these apparently distinct mechanisms are in fact connected by the Stokes-Einstein relation,

$$\beta D = \mu \quad (5.8)$$

The argument first given by Einstein for the connection between $D$ and $\mu$ is as follows. Consider a system of dilute labeled particles in equilibrium, in an external potential $\phi(r)$. No net currents are flowing, because the system is in equilibrium; the concentration $\rho(r)$ of labeled species is proportional to the Boltzmann factor

$$\rho(r) \propto e^{-\beta \phi(r)} \quad (5.9)$$

with the proportionality constant set by normalization (the average concentration $(1/V) \int dt \rho(r)$ equals some specified value $\rho_0$).

But we may regard this equilibrium as the result of canceling drift and diffusive currents: particles drift under the force $F = -\nabla \phi$ towards regions of more favorable potential, where they tend to accumulate (as the Boltzmann factor dictates), which leads to a diffusive current away from the concentrated regions, proportional to the concentration gradient.

One way to see that there are actually canceling drift and diffusive currents, is to imagine suddenly turning off the external field. Then, the diffusive current would no longer be cancelled, and the system would evolve by diffusion towards uniform concentration. Such experiments can in fact be carried out, for example using a dilute concentration of colloidal particles with magnetic cores and observing the particles under a microscope in an inhomogeneous magnetic field, which can be turned on and off.

![Figure 5.3](image.png)

Figure 5.3: With the potential $\phi(x)$ turned off, $J_D$ is revealed, as the particles diffuse away.

We write the cancellation of drift and diffusive currents in equilibrium as

$$0 = J_v + J_D = \rho (-\mu \nabla \phi) + D (-\nabla \rho) = -\mu \rho \nabla \phi + \beta D \rho \nabla \phi \quad (5.10)$$

in which the last line follows from using the Boltzmann factor expression for $\rho$ at equilibrium. Evidently the last line vanishes only if $\mu = \beta D$, which is the Stokes-Einstein relation.
Note that the assumption of dilute particles has been used at several places in this elegant argument: 1) writing the drift force as arising only from the external potential and not from interparticle interactions, 2) writing the diffusive current as proportional to concentration gradients, and 3) writing the equilibrium concentration as proportional to a Boltzmann factor involving only the external potential. None of these assumptions are correct for concentrated suspensions; and yet, the Stokes-Einstein relation Eq. 5.8 still holds. We shall give more general arguments for this and other similar relations later in this chapter.

The “Stokes” in Stokes-Einstein refers to the expression for the drag coefficient for spherical particles of radius $a$ in an incompressible viscous (Stokes) fluid of shear viscosity $\eta$, written $F = 6\pi \eta a v$, which implies
\[ 1/\mu = 6\pi \eta a \]  
Using this, we can determine the diffusion coefficient for such particles as
\[ D = \frac{kT}{6\pi \eta a} \]

We can give an intuitive argument for why the mobility and diffusivity should be proportional: the drift current in response to a weak force ultimately arises from a slight bias in the diffusive motion of particles, which is present even in the equilibrium system with no external force. The more readily particles diffuse, the faster they will drift in response to an external force.

This connection is very reminiscent of the static fluctuation-response theorem, in which the equilibrium response to a static (constant in time) applied potential is proportional to the amplitude of fluctuations. We made the same intuitive argument for the static fluctuation-response theorem, that the weak static potential slightly biases the existing equilibrium fluctuations, thereby resulting in an average response.

The Stokes-Einstein relation applies to the driven or diffusive motion of colloidal particles in fluid, but also to motion of molecules in fluid, including the molecules of which the fluid is made. The relation can be fruitfully employed in either direction. Making use of the Stokes calculation of the hydrodynamic drag on a particle in a fluid, we can compute the diffusivity of colloidal particles, proteins, or even small molecules in solution. Or, we can observe in simulations the diffusive motion of a particle or molecule, and determine the its mobility and corresponding transport coefficient. (Alternatively, we could apply an external force to the particle in the simulation, and determine the mobility by observing the resulting drift velocity.)

As a simple example, the diffusion coefficient for a particle of radius 1000Å in water at room temperature (300K, viscosity $\eta = 1$ centipoise, the cgs unit of viscosity) works out to be
\[ D = \frac{kT}{6\pi \eta a} \approx \frac{(1.38 \times 10^{-16}\text{erg/K})(300\text{K})}{6\pi(10^{-2}\text{Poise})(10^{-5}\text{cm})} \approx 2 \times 10^{-8}\text{cm}^2/\text{s} = 2\mu^2/\text{s} \]

We see that such a submicron colloidal particle will diffuse visibly in a few seconds when seen under a high-power microscope. [In this estimate, we have been aided by the certain knowledge that units factors will work out if we consistently use cgs (or MKS) units, so that we need not remember 1 erg equals $1\text{g cm}^2/\text{sec}^2$, 1 Poise equals $1\text{(g/cm}^3\text{)(cm}^2/\text{s)}$ (density times kinematic viscosity, which is a diffusivity) and so forth.]

The assumptions of the Einstein argument are quite general: the mobility $\mu$ need not be that of strictly isolated particles; they can be concentrated enough to interact hydrodynamically, which imparts concentration dependence to $\mu$ (challenging to compute analytically, using hydrodynamic methods). The potential $\phi(r)$ need not be any particular shape; indeed, the potential was just a device for relating $J_v$ and $J_D$. 

5.1. STOKES-EINSTEIN RELATION
The Einstein argument does assume the particles are sufficiently dilute that they do not interact energetically, so that the driving force for their diffusive current is strictly entropic. Otherwise, the equilibrium concentration $\rho$ would have not been proportional to only $\exp(-\beta \phi)$, but would have been affected by interactions among the particles.

Finally, the Einstein argument assumes "linear response": that is, the potential $\phi(r)$ should be weak enough so that the drift velocity $v$ is proportional to the applied force $F$, and so that concentration gradients are small enough that the diffusive current $J_D$ is proportional to the concentration gradient $\nabla \rho$.

Likewise, the Stokes calculation for the hydrodynamic drag on spherical particle, carried out using macroscopic hydrodynamics, is surprisingly reasonable even for molecular-sized "spheres" (i.e., hydrodynamics works surprisingly well even at the scale of a few molecules). We can boldly apply the Stokes-Einstein relation to make semiquantitative estimates for the diffusive motion of, for example, water molecules in water, as follows.

For a molecular size, we represent a water molecule as a sphere of size sufficient to contain 18g/mole at the density of water (1g/cm$^3$); that is, $(4/3)\pi a^3 N_A$ equals $(1\text{cm}^3/\text{g})(18\text{g})$, which leads to $a = 1.9\text{Å}$, a value rather larger than the customary "space-filling" radius of a water molecule.

We can compute the self-diffusion coefficient of a water molecule in water at room temperature as $D \approx 0.1\text{Å}^2/\text{ps}$. From this, we can compute the time for the molecule to diffuse a mean-square distance equal to its own diameter, from the diffusion relation $\langle \Delta R^2 \rangle = 6Dt$. Taking $R = 2a$, we find $\tau_D = 22\text{ps}$.

It is of interest to compare this to an estimate of the time between collisions of water molecules. We can compute the mean thermal velocity of the molecules using the equipartition relation, $(1/2)mv^2 = (3/2)kT$, which gives a value of thermal velocity $v = 645\text{m/s}$. This is of order the sound velocity in water;

We estimate the time between collisions as $\tau_c = 2a/v$, which equals about 0.6ps. Comparing the time to diffuse one diameter with the collision time, we find a ratio $\tau_D/\tau_c \approx 20$. Thus we may estimate that the water molecule undergoes about 20 collisions with neighboring molecules before it manages to diffuse its own diameter. This is the result of a "caging" effect in a dense fluid; many collisions take place with neighboring molecules before a given molecule manages to slip past one of its neighbors.

![Figure 5.4: A particle repeatedly colliding with the “cage” comprising its near neighbors.](image)

Next, we turn to the question of how large an external force $F$ (applied to some tagged subset of
molecules in a fluid) must be in order to violate the assumption of a linear response. If the induced velocity began to approach the thermal velocity, we have certainly not applied a weak bias to the random molecular motion. This would correspond to a force large enough to increase the kinetic energy of the molecule by of order $kT$ between collisions with neighbors, which implies $F$ of order $kT/a$ in a dense fluid. Hence one reasonable limit for linear response is $F << kT/a$.

We may develop an alternative view of the limits to linear response by observing that diffusion is efficient at displacing particles at early times (because the displacement grows as $\sqrt{Dt}$), while drift takes over as more efficient at longer times (since the drift displacement grows as $\mu F t$). There is a time scale $T^*$ at which the two displacements are comparable, $\sqrt{Dt^*} \sim \mu Ft^*$. Thus we have $t^* \sim D/((\mu F)^2)$, during which time the particle is displaced by $a^* \sim D/((\mu F)$. If the displacement $a^*$ is as small as the molecular size $a$, then the force is so large that the molecule “never had a chance to diffuse”, and that force is too large to be considered weak. This again leads to a limit for linear response of $F << kT/a$.

This limiting force is in fact quite large, compared to the forces we can easily apply externally on molecules. For example, consider a molecule carrying a charge of one electron $e$, and a force on that molecule arising from an externally applied electric field $E$. We would need an electric field of order $kT/(ea)$ to exceed linear response. Now $kT$ at room temperature is about $(1/40)eV$, and $a$ is a molecular size of order several Angstroms, so the required field would be perhaps $10^{-3}V/\AA$, or $10^5V/cm$.

Indeed, such strong electric fields are of order the dielectric breakdown field for common insulating materials: if we apply fields this large (by applying large voltages across thin films), charges within the film will be accelerated enough between collisions to accumulate kinetic energy, sufficient to create free electrons in subsequent collisions, leading ultimately to a cascade of electrons and a spark of current across the film.
CHAPTER 5. NEAR-EQUILIBRIUM DYNAMICS

5.2 Fluctuation-response theorem

[Frenkel & Smit App. A]

The Stokes-Einstein relation connects a steady-state nonequilibrium response (drift current in response to a steady force) to the fluctuating dynamics of the equilibrium system (the self-diffusion). It turns out there is a much more general relation, called the “fluctuation-dissipation” or “fluctuation-response” theorem, between the time-dependent nonequilibrium response to applied field, and time-dependent fluctuations in absence of the field.

Here we discuss the fluctuation-response theorem in a manner similar to the intuitive description we gave of the Stokes-Einstein relation, in which we contemplated suddenly turning off an applied field. Consider a potential field \( a(r) \) that couples linearly to some degree of freedom \( A(r) \), in a term in the Hamiltonian of the form

\[
\delta H = - \int dr' A(r') a(r') \tag{5.14}
\]

(We have chosen the sign in such a way that positive values of \( a \) lead to a lower energy for positive \( A \), and hence “encourage” a positive response.)

The field \( A(r) \) can be any local property of interest, such as the density, species concentrations, momentum density (average momentum of particles near \( r \)), energy density, pressure, or other such quantities. All of these can be defined in terms of the instantaneous microscopic degrees of freedom, so that they are inherently fluctuating, non-averaged quantities. Such quantities are called “densities”.

In contrast, the quantities to which these densities linearly couple in a Hamiltonian are externally imposed, and cannot be naturally expressed in terms of microscopic degrees of freedom; these quantities are called “potentials.” Concentrations couple to the chemical potential, the charge density couples to the electrostatic potential, the energy density couples to the temperature, and so forth.

Suppose we impose a steady external potential \( a(r) \), starting from a time far in the past \( t = -\infty \), to the present \( t = 0 \). At \( t = 0 \), a “biased equilibrium” has been established by the field. At \( t = 0 \), we suddenly turn off the field, and observe the subsequent evolution of the average \( \langle A(r, t) \rangle \). (For convenience, we define the degrees of freedom \( A(r) \) to have zero average in equilibrium.)

This process may be described in two equivalent ways. First, we can think of \( \langle A(r, t) \rangle \) as the time-dependent linear response to a particular time-dependent applied field \( a(r, t) = a(r)\theta(-t) \).

5.2.1 Linear response

We can write a general linear response relation for a dynamical field \( A(r, t) \) linearly coupled to a space- and time-varying external potential \( a(r, t) \) as

\[
\langle A(r, t) \rangle = \int_{-\infty}^{t} dt' \int dr' R(r - r', t - t') a(r', t') \tag{5.15}
\]

in which \( R(r, t) \) is the response function.

We can express linear response equivalently by writing the integral over previous times in terms of the delay \( \tau = t - t' \):

\[
\langle A(r, t) \rangle = \int_{0}^{\infty} d\tau \int dr' R(r - r', \tau) a(r', t - \tau) \tag{5.16}
\]

We call Eqn. (5.15) linear response, because we have assumed \( a(r, t) \) is weak enough that we need only retain terms to first order in \( a(r, t) \). Because the response is linear, we have “superposition” — the linear response to the sum of two perturbations is the sum of the response to each separately.
The linear response expression allows for the possibility that an external field applied at \( r' \) leads to a response at some other nearby location \( r \). Likewise, the integral over previous times (from \( t' = -\infty \) up to \( t' = t \)) allows for a field applied at \( t' \) to generate a response at a later time \( t \). Thus Eqn. (5.15) is “causal” — \( A(r, t) \) only responds to fields applied at earlier times \( t' \).

In a system in which \( A \) is equilibrated, we expect \( R(r, t) \) to have “fading memory”; that is, for \( R(r, t) \) decays to zero as the delay time \( t \) increases, so that perturbing fields \( a(r, t) \) applied in the distant past are forgotten.

### 5.2.2 Example of response function

Computing the response function \( R(r, t) \) in general is a big job, because it contains information about the detailed dynamics of the system. But if \( A \) is a conserved quantity (like the density, concentration, momentum or energy density), the behavior of \( R(r, t) \) at times long compared to microscopic collision times and distances large compared to molecular dimensions, is essentially determined by the form of the corresponding hydrodynamic equations.

For the simplest example of a response function for a conserved quantity, we take \( A \) to be the dilute concentration \( \rho(r, t) \) of tagged molecules in a liquid. We have already discussed the conservation law that applies in this case, which leads to a transport equation of the form

\[
0 = \frac{\partial \rho}{\partial t} + \nabla \cdot (J_D + J_v)
\]

in which the drift velocity \( J_v \) is in response to the perturbing potential \( \phi \).

Suppose we take the perturbing potential \( \phi(r, t) \) to be briefly applied, at the origin \( r = 0 \) at time \( t = 0 \); that is, \( \phi(r, t) = \delta(r) \delta(t) \). Then we can write (linearizing the equation, replacing \( \rho \) by the average concentration \( \rho_0 \) where needed)

\[
\frac{\partial \rho}{\partial t} - D \nabla^2 \rho = -\rho_0 \mu \nabla \phi
\]

(5.17)

This equation looks very much like what we would write to describe the diffusive spreading away from a point injection of particles at the origin at time zero, namely

\[
\frac{\partial \rho}{\partial t} - D \nabla^2 \rho = \delta(r) \delta(t)
\]

(5.19)

We are familiar with the solution to this equation, as the normalized Gaussian spreading cloud:

\[
G(r, t) = (4\pi Dt)^{-3/2} e^{-r^2/(4Dt)}
\]

(5.20)

The solution Eqn. (5.20) is called the Green function for the inhomogeneous, “driven” transport equation

\[
\frac{\partial \rho}{\partial t} - D \nabla^2 \rho = s(r, t)
\]

(5.21)

with a space- and time-dependent source \( s(r, t) \) of injected particles. The solution of Eqn. (5.21) can be written in terms of \( G(r, t) \) as

\[
\rho(r, t) = \int_{-\infty}^{t} dt' \int dr' G(r - r', t - t') s(r', t')
\]

(5.22)
To see this, observe that the source \( s(r, t) \) can be thought of as the superposition of a large number of point injections of particles at different locations and times, each of which leads to a Gaussian spreading cloud contribution to \( \rho(r, t) \). Mathematically, we apply the operator \( \partial / \partial t - D \nabla^2 \) to both sides of the equation; on the right side, the operator applied to \( G(r - r', t - t') \) gives \( \delta(r - r', t - t') \), which integrates against \( s(r', t') \) to give \( s(r, t) \), reproducing Eqn. (5.21).

Now we observe that we can get the solution to Eqn. (5.18) by applying the operator \( r^2 \) to the Green function Eqn. (5.20), with the result that the solution to Eqn. (5.18) is the response function,

\[
R(r, t) = \frac{3\rho_0 \mu}{2Dt} \left( 1 - \frac{r^2}{6Dt} \right) \frac{e^{-r^2/(4Dt)}}{(4\pi Dt)^{3/2}} \tag{5.23}
\]

The shape of this function is positive near \( r = 0 \), but negative out around the rim \( r^2 > 6Dt \), as particles diffuse in towards the favorable potential and slightly deplete the surroundings. The integral over all space of \( R(r, t) \) vanishes, as a consequence of conservation — the particles accumulating near \( r = 0 \) are depleted from somewhere else.

![Figure 5.6: Plot of Green function \( R(r, t) \) for response of the particle concentration to application of an attractive potential at the origin at time zero.](image)

(Mathematically, the integral of \( R(r, t) \) must vanish, as \( R \) was obtained by applying the operator \( \nabla^2 \) to \( G \), and the integral over space \( \int dr \nabla^2 G \) by the divergence theorem equals a surface integral \( \int dS \cdot \nabla G \) over a “surface at infinity”, where \( G \) and its derivatives vanish at any finite time.)

### 5.2.3 Biased fluctuations

Alternatively, we can think of \( \langle A(r, t) \rangle \) after the turning off of the field \( a(r) \), as the time evolution of unforced average values from an equilibrium initial state at \( t = 0 \) that is biased by the field \( a(r') \), which we denote \( \langle A(r, t) \rangle_a \).

In calculating such quantities as \( \langle A(r, t) \rangle_a \), the brackets signify averaging both over both the initial state biased by the application of the potential \( a \), and the subsequent fluctuating dynamical history. The biased initial state can be described as an initial equilibrium ensemble weighted by an additional Boltzmann factor \( \exp(-\beta \delta H) = \exp(\beta \int dr' A(r', 0) a(r')) \).
5.2. FLUCTUATION-RESPONSE THEOREM

We can account for this additional Boltzmann factor in the biased initial state by including the factor explicitly inside the brackets \(\langle \rangle\), which denote an average over both the unbiased equilibrium state at \(t = 0\) and the subsequent fluctuating history. If the field is weak, we can expand the Boltzmann factor to first order, to obtain

\[
\langle A(r, t) \rangle_{a(r)} \approx \langle A(r, t) (1 + \int dr' \beta A(r', 0) a(r')) \rangle = \beta \int dr' a(r') \langle A(r, t) A(r', 0) \rangle \equiv \beta \int dr' a(r') S(r - r', t)
\]

(5.24)
in which \(S(r, t)\) is the space- and time-dependent autocorrelation function \(\langle A(r, t) A(0, 0) \rangle\).

The autocorrelation function \(\langle A(r, t) A(r', t') \rangle\) in a system at equilibrium depends only on the time difference \(t - t'\) (there is no distinguished “origin of time” for a system in equilibrium). Likewise, for a translationally invariant system \(\langle A(r, t) A(r', t') \rangle\) depends only on the displacement \(r - r'\) between “observation points” (there is no distinguished “origin of space” for a translationally invariant system). Thus we write \(S(r - r', t)\) above as a function of \(r - r'\) and \(t\) only.

Physically, \(S(r, t)\) reports the tendency for a fluctuation in \(A\) at some location and moment (which we take for convenience to the \(r = 0\) and \(t = 0\)), to be accompanied by a fluctuation in \(A(r, t)\) at some nearby location \(r\) and time \(t\). Evidently, \(S\) tends to vanish for long separations in time \(t\) or distance \(r\) between the two observations of \(A\), for a system in which \(A\) is equilibrated.

5.2.4 Deriving the theorem

We can represent the same process — applying a potential \(a(r')\) for a very long time, and then turning it off at \(t = 0\) — either as the linear response of \(A\) to a time-dependent applied potential \(a\), described by a response function \(R\), or as the unforced evolution of \(A\) from a biased initial state, described by a correlation function \(S\). Hence, we can derive a relation between the response and correlation functions.

To derive the relation, we proceed as follows. We can isolate \(R(r, t)\) by applying \(\partial / \partial t\) to both expressions for \(\langle A(r, t) \rangle\) (i.e., to the response function and biased average expressions). We have after a bit of algebra

\[
\frac{\partial}{\partial t} \langle A(r, t) \rangle = \int_{-\infty}^{0} dt' \int dr' \frac{\partial R(r - r', t - t')}{\partial t} a(r')
\]

\[
= -\int_{-\infty}^{0} dt' \int dr' \frac{\partial R(r - r', t - t')}{\partial t} a(r')
\]

\[
= -\int dr' R(r - r', t) a(r')
\]

(5.25)

(In the above, we have used the fact that \(R(r, t)\) goes to zero for long times, i.e., the response to perturbations in the distant past is vanishingly small.)

Equating this to the time derivative of the biased average expression, we have

\[
-\int dr' R(r - r', t) a(r') = \beta \int dr' \frac{\partial S(r - r', t)}{\partial t} a(r')
\]

(5.26)

This relation is true for any \(a(r')\), and in particular for a delta-function at the origin, so we have finally

\[
-\beta \frac{\partial S(r, t)}{\partial t} = R(r, t)
\]

(5.27)

which is the celebrated fluctuation-response theorem.
5.2.5 Static limit

We can apply the fluctuation-response theorem to the particular case of a perturbing field held constant from the distant past to the present. The constant linear response to such a constant field \( a(r) \) is easily shown to be

\[
\langle A(r) \rangle = \int dr' R(r-r')a(r')
\]

\[
R(r) = \int_0^\infty d\tau R(r, \tau)
\]  

(5.28)

Here \( R(r) \) is the static response function, which gives the equilibrium linear response to the applied field.

Applying \( \int_0^\infty \) to both sides of the fluctuation-response theorem gives

\[
R(r-r') = \beta S(r-r', 0) = \beta \langle A(r)A(r') \rangle
\]  

(5.29)

This is the general form of the static fluctuation-response relations discussed in Section ??, which relates the static response \( R(r-r') \) to the fluctuations.

For our simple example in Section 5.2.2 above, we can explicitly compute the static limit by computing the time integral stipulated in Eqn. (5.28) above. This is made easier by noticing that we applied \(-\nabla^2\) to obtain \( R(r, t) \), which is equivalent to applying \(-(1/D)\partial/\partial t\) (because the operator \(\partial/\partial t - D\nabla^2\) annihilates the Gaussian cloud). So the integral \( \int_0^\infty dt \) “undoes” the time derivative, leaving us with the static response function \( R(r) \) given by the Gaussian cloud at \( t = 0 \), i.e., a localized delta-function response.

Carrying out this procedure gives

\[
R(r) = \beta \rho_0 \delta(r)
\]  

(5.30)

Using Eqn. (5.28), this leads to a static response

\[
\langle \rho(r) \rangle = \beta \rho_0 \phi(r)
\]  

(5.31)

This is precisely what we expect for the perturbative static response to a weak potential; the concentration \( \rho(r) \) is locally enhanced by a Boltzmann factor \( \exp(\beta \phi(r)) \), which for weak potentials can be expanded as \( 1 + \beta \phi(r) \), leading to a perturbation in the local concentration of \( \delta \rho(r) \) equal to \( \beta \rho_0 \phi(r) \). (Recall that for convenience we define the density \( A \) to have zero average, i.e., we make sure to subtract the mean density when defining \( A \).)
5.3 Kubo relations

[Frenkel & Smit p. 78ff] The fluctuation-response theorem provides a general connection between the linear response of some microscopically defined observable quantity to a weak applied external conjugate force, and the natural fluctuations of that same observable in a system in equilibrium with no external forces applied.

In hydrodynamic theories, transport coefficients are the proportionality constants connecting some nonequilibrium steady-state “flow”, with some externally applied force. We already encountered the simplest example of such a transport coefficient, the mobility \( \mu \) relating the drift velocity \( v \) of a particle in a fluid to a weak external force \( F \) acting on the particle, as \( v = \mu F \). Another simple example of a transport coefficient is the electrical conductivity \( \lambda \) of an electrolyte solution, which relates the current density \( j \) to the applied electric field \( E \) as \( j = \lambda E \). The thermal conductivity and shear viscosity of a fluid are two additional examples.

In this section, we use the fluctuation-response theorem to connect transport coefficients to equilibrium fluctuations; these connections are called Kubo relations. Using Kubo relations, we can perform equilibrium MD simulations with no external forces, and determine transport coefficients just by watching how the system fluctuates. In the next section, we derive the Kubo relation for a tagged particle, and show how the resulting expression for \( \mu \) is consistent with the Stokes-Einstein relation. Then in following sections, we show how essentially the same recipe can be applied to transport coefficients for which it is not evident how to generalize the Einstein argument, namely, the electrical conductivity of electrolytes, and the viscosity of simple fluids.

5.3.1 Self-diffusion

Consider a system in which a small number of particles are labeled, and couple to an externally applied time-dependent force \( F(t) \). The perturbation Hamiltonian takes the simple form

\[
\delta H = -r \cdot F(t)
\]

for the position of each labeled particle.

Linear response for the position of a single labeled particle reads

\[
\langle r_i(t) \rangle = \int_{-\infty}^{t} dt' R_{ij}(t-t')F_j(t')
\]

(5.33)

(In contrast to previous lectures, the Roman letter subscripts in this section denote Cartesian coordinate indices.) In writing the above equation, we are assuming the particles are sufficiently dilute that the force acting on other labeled particles has no influence on a given labeled particle, through the flow induced by the drift of the other particles.

Our aim is to relate the drift velocity of the tagged particle in response to an applied force, to fluctuating quantities in a system without external forces. We begin by taking a time derivative \( \partial / \partial t \) of the above, to obtain

\[
\langle v_i(t) \rangle = \int_{-\infty}^{t} dt' \frac{\partial R_{ij}(t-t')}{\partial t} F_j(t')
\]

(5.34)

The term that results from applying the time derivative \( \partial / \partial t \) to the upper limit of the integral \( \int_{-\infty}^{t} dt' \) must vanish, because the response function \( R_{ij}(t-t') \) vanishes at \( t' = t \). This is a general feature of response functions: the response at the very instant a force is applied is zero, as the response always takes some (possibly very short) time to occur.
Next we use the fluctuation-response theorem, to write \( h_r(t) \) as

\[
\begin{align*}
\langle v_i(t) \rangle &= -\beta \int_{-\infty}^{t} dt' \frac{\partial^2 S_{ij}(t-t')}{\partial t^2} F_j(t') \\
&= \beta \int_{-\infty}^{t} dt' \frac{\partial^2 \langle r_i(t) r_j(t') \rangle}{\partial t \partial t'} F_j(t') \\
&= \beta \int_{-\infty}^{t} dt' \langle v_i(t) v_j(t') \rangle F_j(t') 
\end{align*}
\]

(5.35)

For a constant force \( F \) applied from the distant past, we expect a constant response, which we can conveniently evaluate at \( t = 0 \). Then, using the fact that the correlation function actually depends only on the time difference \( t - t' \), we can write

\[
\langle v_i \rangle = \beta \int_{0}^{\infty} dt' \langle v_i(t') v_j(0) \rangle F_j 
\]

(5.36)

By symmetry, in equilibrium in an isotropic liquid \( v_i \) is only correlated with \( v_j \) if \( i = j \). For example, \( \langle v_x v_y \rangle \) must vanish, because the system is invariant under reflection \( x \rightarrow -x \) or \( y \rightarrow -y \). Likewise, the correlations \( \langle v_x v_x \rangle, \langle v_y v_y \rangle \) and \( \langle v_z v_z \rangle \) all must be equal, because there is no “distinguished direction” in an isotropic liquid; the system looks the same when viewed along the \( x, y, z \), or indeed any axis.

Thus the correlation function \( \langle v_i v_j \rangle \) for an isotropic system must be proportional to the Kronecker delta \( \delta_{ij} \), that is \( \langle v_i v_j \rangle \) equals \( C \delta_{ij} \). We may therefore write

\[
\langle v_i(t') v_j(0) \rangle = (1/3) \langle v(t') \cdot v(0) \rangle \delta_{ij} 
\]

(5.37)

in which we verify that we have the correct value of \( C \) by taking the trace of both sides of the above.

We expect that \( v \) should respond to a constant force \( F \) as \( v = \mu F \), which we use to define the mobility \( \mu \). Comparing to the above, we have

\[
\mu = (1/3) \beta \int_{0}^{\infty} dt' \langle v(t') \cdot v(0) \rangle 
\]

(5.38)

This is a Kubo relation: a transport coefficient given in terms of a time integral of a correlation function. Such relations relate the result of a simulation under steady-state nonequilibrium conditions — a fixed force applied to drifting particles, in this case — to the equilibrium velocity fluctuations of those particles in the absence of an applied force.

As derived, Eqn. (5.38) pertains to the velocity autocorrelation function of a single tagged particle in a system. This raises the question of how difficult it might be to obtain good statistics for the velocity fluctuations of a single particle. But in fact, we can average \( \langle v(t') \cdot v(0) \rangle \) over all particles, since the behavior of the velocity autocorrelation function is statistically the same for all identical particles in the system, whether or not they are “tagged”.

Since the right-hand side has to do with velocity fluctuations, and we already have the Stokes-Einstein relation between \( \mu \) and the diffusion coefficient \( D \) (which depends on velocity fluctuations), we may expect that the Stokes-Einstein relation can be obtained from Eqn. (5.38) above.
To see this, we compute the mean-square displacement of a particle from time $t = 0$ to $t$, as

$$
\langle \Delta r^2(t) \rangle = \int_0^t dt_1 \int_0^t dt_2 \langle v(t_1) \cdot v(t_2) \rangle
= 2 \int_0^t dt_1 \int_0^{t_1} dt_2 \langle v(t_1) \cdot v(t_2) \rangle
= 2 \int_0^t dt_1 \int_0^{t_1} d\tau \langle v(t_1) \cdot v(t_1 - \tau) \rangle
\approx 2t \int_0^\infty d\tau \langle v(\tau) \cdot v(0) \rangle
= 6(\mu/\beta)t \quad (5.39)
$$

A few notes as to the above derivation. In the first line, we divide the domain of integration into the portion $t_1 < t_2$ and $t_1 > t_2$, and notice that these contributions are equal, because the integrand is a symmetric function under exchange of $t_1$ and $t_2$. In the next line, we change variables in the inner integral to $\tau = t_1 - t_2$.

Recall that although the notation $\langle v(t_1) \cdot v(t_2) \rangle$ looks as if the correlation function depends on $t_1$ and $t_2$ separately, because the average is performed in an equilibrium system for which there is no distinguished origin of time, only the time difference $t_2 - t_1$ matters.

To reach the penultimate line, we make an approximation valid for large $t$, by observing that the correlation function $\langle v(t_1) \cdot v(t_1 - \tau) \rangle$ has a finite correlation time $\tau^*$, well beyond which the correlation function decays to zero. For $t$ much larger than $\tau^*$, almost all of the integral over $t_1$ involves values $t_1$ much larger than $\tau^*$, so that we can take the upper limit of the inner integral with $\infty$. Then the outer integral $\int_0^t dt_1$ simply gives a factor of $t$. Comparing the result to Eqn. (5.38), we reach the last line.

Recall that we define the diffusion coefficient for a particle (in three dimensions) as

$$
\langle \Delta r^2(t) \rangle = 6Dt \quad (5.40)
$$

(The reason for the factor of six is as follows. We write the diffusion equation in any number of space dimensions as $\partial P/\partial t - D\nabla^2 P = 0$; the spreading Gaussian solution from a point initial condition is $P(r, t) \propto t^{-3/2}e^{-r^2/(4Dt)}$, as can be verified by direct substitution. The function $P(r, t)$ can be thought of as the probability distribution for random walkers starting at the origin at time zero; the variance of each component $r_i$ of the displacement is $2Dt$, for a total $\langle \Delta r^2(t) \rangle$ of $6Dt$ in three dimensions.)

Comparing the results Eqns. (5.39) and (5.40), we must have $\mu = \beta D$, the Stokes-Einstein relation. Of course, we already had a simple argument for the Stokes-Einstein relation, and therefore a route to determining the drag coefficient $\mu$ by observing the mean-square displacement of diffusing tagged particles.

However, an essential ingredient in the argument for the Stokes-Einstein relation was that the tagged particles were dilute and therefore did not interact appreciably with each other, so that their equilibrium concentration in the applied field was proportional to $e^{-\beta\phi(r)}$. For more general situations, involving transport phenomena for degrees of freedom that interact with each other (such as charges in an ionic conductor), we cannot so easily construct an analogous argument.

However, we shall see in the next section that the same route we have used to derive a Kubo relation for the mobility $\mu$ can be used to obtain useful relations for other transport coefficients, including the electrical conductivity $\lambda$ and the shear viscosity $\eta$.  

5.3. KUBO RELATIONS
CHAPTER 5. NEAR-EQUILIBRIUM DYNAMICS

5.3.2 Conductivity

Electrical conductivity provides another important example of a Kubo relation. In this case, the perturbation Hamiltonian can be taken as a coupling of the charge density $\rho$ to an applied external potential $\phi$:

$$\delta H = \int dr' \rho(r')\phi(r')$$  \hbox{(5.41)}

(Here we have taken the sign convention to correspond to electrostatics.)

The microscopic expression for the charge density is

$$\rho(r, t) = \sum_\alpha e z_\alpha \delta(r - r_\alpha(t))$$  \hbox{(5.42)}

and $e z_\alpha$ is the charge of particle $\alpha$.

We write a linear response relation for the charge density as

$$\langle \rho(r, t) \rangle = -\int_{-\infty}^t dt' \int dr' R(r - r', t - t')\phi(r', t')$$  \hbox{(5.43)}

The charge density satisfies a conservation law

$$\frac{\partial \rho}{\partial t} + \nabla \cdot j = 0$$  \hbox{(5.44)}

in which $j(r, t)$ is the electrical current density.

The corresponding microscopic expression for the current density is

$$j(r, t) = \sum_\alpha e z_\alpha v_\alpha(t)\delta(r - r_\alpha(t))$$  \hbox{(5.45)}

which is physically evident, and can be verified directly by substituting the microscopic expressions for $\rho(r, t)$ and $j(r, t)$ into Eqn. (5.44).

In contrast to the simple case of the previous section, the variable of interest here is a density, a function of position $r$, and not simply the position of a single particle. However, the recipe to derive a Kubo relation for the conductivity is strikingly similar to the approach of the previous section:

- take a time derivative on both sides;
- use the fluctuation-response theorem to replace $R$ in terms of $S$;
- use the conservation law to replace $\dot{\rho}$ with $j$ wherever it appears.

This leads to

$$\langle \nabla \cdot j(r, t) \rangle = -\beta \int_{-\infty}^t dt' \int dr' \langle \nabla \cdot j(r, t) \nabla \cdot j(r', t') \rangle \phi(r', t')$$  \hbox{(5.46)}

Now we make the following additional rearrangements:

- integrate by parts in $r'$ to move the divergence operator onto $\phi$;
- assume an isotropic fluid, so the correlation function $\langle j_i j_k \rangle$ takes the form $(1/3)\langle j \cdot j \rangle \delta_{ik}$;
- “remove the divergence operator $\nabla \cdot$ from both sides” (which is valid if the applied field is curl-free, as for example a sinusoidal applied field)
5.3. KUBO RELATIONS

This gives

\[ \langle j_k(r,t) \rangle = \frac{\beta}{3} \int_{-\infty}^{t} dt' \int dr' \langle j(r,t) \cdot j(r',t') \rangle E_k(r',t') \]  \hspace{1cm} (5.47)

in which \( E = -\nabla \phi \) is the electric field.

In the limit of a spatially uniform field \( E \) applied with very slow time variation, we expect that the current density is proportional to the applied field,

\[ \langle j \rangle = \lambda E \]  \hspace{1cm} (5.48)

in which \( \lambda \) is the electrical conductivity.

Thus we have a Kubo relation for the conductivity in terms of current fluctuations. By averaging the current response over the volume of the system (applying \((1/V) \int dr\) to both sides), we obtain finally

\[ \lambda = \frac{\beta}{3V} \int_{0}^{\infty} dt' \langle J(0) \cdot J(t') \rangle \]  \hspace{1cm} (5.49)

in which \( J(t) \) is the total current, i.e., the integral over space of the current density, for which the microscopic expression is

\[ J(t) = \sum_{\alpha} e z_{\alpha} v_{\alpha} \]  \hspace{1cm} (5.50)

Thus by gathering a long time series of the fluctuating total current in a system at equilibrium, we can obtain from its autocorrelation function the conductivity \( \lambda \).

5.3.3 Thermal conductivity

Thermal conductivity describes the transport of internal kinetic and potential energy, by the conserved energy current. The kinetic energy density \( K(r) \) is given by

\[ K(r) = \sum_{\alpha} \frac{p_{\alpha}^{2}}{2m_{\alpha}} \delta(r - r_{\alpha}) \]  \hspace{1cm} (5.51)

The potential energy density \( U(r) \) for a system with pairwise interactions between particles is given by

\[ U(r) = (1/2) \sum_{\alpha \beta} U(r_{\alpha \beta}) \delta(r - r_{\alpha}) \]  \hspace{1cm} (5.52)

in which the factor of \( 1/2 \) takes care of double counting the interactions between particles \( \alpha \) and \( \beta \).

The total internal energy density \( E(r) \) is the sum \( K(r) + U(r) \). Because energy is conserved, there must be a corresponding current \( J_E(r) \), for which a conservation law is satisfied:

\[ \frac{\partial E}{\partial t} + \nabla \cdot J_E = 0 \]  \hspace{1cm} (5.53)

To find the energy current, we compute the time derivatives of \( K(r) \) and \( U(r) \) using the microscopic expressions Eqs. 5.51 and 5.52, and write the result as the divergence of something. We have

\[ \frac{\partial K}{\partial t} = \sum_{\alpha} v_{\alpha} \cdot F_{\alpha} \delta(r - r_{\alpha}) - \nabla \cdot \sum_{\alpha} \frac{p_{\alpha}^{2}}{2m_{\alpha}} v_{\alpha} \delta(r - r_{\alpha}) \]  \hspace{1cm} (5.54)
The first term comes from the time derivative of \( p_{\alpha}^2/2m_{\alpha} \), and the second from the time derivative of \( r_{\alpha} \) inside the delta function. Likewise, we have

\[
\frac{\partial U}{\partial t} = -\text{sum}_{\alpha\beta}(1/2)(F_{\alpha\beta} \cdot v_\alpha + F_{\beta\alpha} \cdot v_\beta)\delta(r - r_\alpha) + \nabla \cdot \sum_{\alpha\beta}(1/2)U(r_{\alpha\beta})v_\alpha\delta(r - r_\alpha) \tag{5.55}
\]

The first term comes from the time derivative of \( U(r_{\alpha\beta}) \), and the second from the time derivative of \( r_\alpha \) inside the delta function.

Combining these, we obtain

\[
\frac{\partial E}{\partial t} = (1/2)\sum_{\alpha\beta}(F_{\alpha\beta} \cdot v_\alpha - F_{\beta\alpha} \cdot v_\beta)\delta(r - r_\alpha) - \nabla \cdot J_1(r) \tag{5.56}
\]

in which we have defined

\[
J_1(r) = \sum_{\alpha} \left( \frac{p_{\alpha}^2}{2m_{\alpha}} + (1/2)U(r_{\alpha\beta}) \right) v_\alpha\delta(r - r_\alpha) \tag{5.57}
\]

In Eq. 5.56, the second term is already the divergence of a current, but the first term is not evidently of that form.

The first term in Eq. 5.56 can be read as the sum of exchanges of potential energy between pairs of interacting particles as they move. The forces \( F_{\alpha\beta} \) and \( F_{\beta\alpha} \) are equal and opposite: \( F_{\alpha\beta} = -F_{\beta\alpha} \).

We can get a hint as to how to write \( \partial E/\partial t \) as the divergence of a current, if we integrate it over space. If we integrate over all space, the terms that are already the divergence of something vanish. The delta function in the first term no longer constrains the sum, and all particles contribute. Then exchanging the labels \( \alpha \) and \( \beta \) in the term \(-F_{\beta\alpha}v_\beta\), the summands all vanish, and the energy is constant.

If we integrate only over some finite volume \( V \) bounded by some surface \( S \), only particles inside \( V \) contribute to the sum. If we again exchange the labels \( \alpha \) and \( \beta \) in the second term, we have after some rearrangement

\[
\int_V dr \frac{\partial E}{\partial t} = (1/2)\sum_{\alpha\beta}F_{\alpha\beta}v_\alpha - F_{\beta\alpha}v_\beta - \int_S dS \cdot J_1 \tag{5.58}
\]

where \( J_1 \) is the current defined in Eq. 5.57.

The first term is a sum of exchanges of potential energy between particles inside and outside the volume \( V \), which do work on each other as they move with their velocities \( v_\alpha \) and \( v_\beta \) while the forces \( F_{\alpha\beta} \) and \( F_{\beta\alpha} \) are active. We can think of these exchanges as occurring by an energy current that flows along “threads” connecting the interacting particles inside and outside \( V \). This motivates the following inspired guess for the corresponding current:

\[
J_2(r) = \sum_{\alpha\beta}(1/2)(F_{\alpha\beta} \cdot v_\alpha - F_{\beta\alpha} \cdot v_\beta)r_{\alpha\beta}g_{\alpha\beta}(r) = \sum_{\alpha\beta}F_{\alpha\beta} \cdot v_\alpha r_{\alpha\beta}g_{\alpha\beta}(r) \tag{5.59}
\]

in which we have defined

\[
g_{\alpha\beta}(r) = \int_0^1 d\lambda r_\alpha + (1 - \lambda)r_\beta - r \tag{5.60}
\]

The function \( g_{\alpha\beta}(r) \) is a straight line of delta functions connecting \( r_\alpha \) and \( r_\beta \), normalized to a total integral of unity. Any surface separating particles \( \alpha \) and \( \beta \) is pierced by this line. Consider a surface \( S \) pierced by the line, with normal \( n \) at the point of intersection. Then the integral \( \int dS \cdot J_2 \)
will give a contribution \((1/2)(F_α \cdot v_α - F_β \cdot v_β)\), times the quantity \(\int dS \cdot r_αβg_αβ(r)\), which is in fact equal to unity. (To see this, regard the integral as the result of translating the surface \(S\) by the vector \(r_αβ\), which causes the intersection point to trace over the entire line.)

Thus we have a microscopic expression for the total energy current, as \(J_E(r) = J_1(r) + J_2(r)\). To obtain a Kubo relation for the thermal conductivity, we start with an “external field” that couples linearly to the energy density in the exponent of a Boltzmann factor — which can be interpreted as \(δβ(r,t)/β\), a local shift in the inverse temperature. This makes physical sense; in a simulation we could induce an energy current by increasing the temperature slightly in one region to inject energy there, and decreasing it slightly elsewhere to take the energy out again. In short, \(δβ(r,t)/β\) plays the same role for energy density as \(φ(r,t)\) does for the charge density biasing the system towards slightly larger or smaller \(E(r,t)\).

The form of the equations describing the response, fluctuations, and transport of energy are then identical to those for charge density, so the derivation of a Kubo relation for thermal conductivity follows exactly, if we define a heat current and corresponding transport coefficient from

\[
J_E = \lambda_E \nabla(δβ)/β
\]  

(5.61)

Then we have

\[
λ_E = \frac{β}{3V} \int_0^∞ dt' \left\langle J_E(0) \cdot J_E(t') \right\rangle
\]  

(5.62)

To translate this transport coefficient into more conventional definitions, we must relate the energy current to temperature changes via the heat capacity \(P\), and connect the gradient of \(δβ/β\) to the temperature gradient. Since \(β = 1/(kT)\), we have \(δβ/β = -δT/T\). Changes in temperature are related to changes in internal energy via the heat capacity, \(CδT = δE\). So the thermal conductivity equation reads

\[
C\partial T/∂t + \nabla \cdot J_E = 0
\]  

(5.63)

and we define the thermal conductivity \(κ_T\) by

\[
J_E = -κ_T \nabla T
\]  

(5.64)

from which we see that \(κ_T = λ_E/T\).

### 5.3.4 Viscosity

[Allen & Tildesley p. 243ff; Frenkel & Smit, p. 81; Allen & Tildesley, p. 60]

Shear viscosity can also be cast in the same general linear response form as self-diffusion, electrical conductivity, and thermal conductivity. In this case, the perturbation Hamiltonian couples to the momentum density \(g(r)\),

\[
δH = -\int dr' g(r') \cdot v(r')
\]  

(5.65)

The microscopic expression for \(g(r)\) is

\[
g(r,t) = \sum_α p_α δ(r - r_α(t))
\]  

(5.66)

The external field \(v(r)\) has dimensions of velocity, and biases the local momenta of particles to move in the direction of \(v(r)\). Thus by imposing an external field \(v(r)\) we can induce the system to flow.
Linear response for \( g \) to the applied field \( v \) takes the form

\[
\langle g(r, t) \rangle = \int_{-\infty}^{t} dt' \int dr' R(r - r', t - t') v(r', t')
\]

(5.67)

Because the equations of motion conserve total momentum, the momentum density satisfies a conservation law,

\[
\frac{\partial g}{\partial t} + \nabla \cdot \Pi = 0
\]

(5.68)
in which the second-rank tensor \( \Pi(r, t) \) is the momentum current. Particles in a region only lose momentum overall, by giving up momentum to particles outside the region; \( \Pi \) measures the momentum flux out of a given region. (The stress tensor \( \sigma \) is \(-\Pi\).)

The microscopic expression for the momentum current \( \Pi(r, t) \) makes use of the same trick we used to write the energy current:

\[
\Pi_{jk}(r, t) = \frac{1}{m} \sum_{\alpha} p_{\alpha,j} p_{\alpha,k} \delta(r - r_{\alpha}(t)) + \frac{1}{2} \sum_{\alpha,\beta} r_{\alpha\beta,j} f_{\alpha\beta,k} g_{\alpha\beta}(r)
\]

(5.69)

Here \( g_{\alpha\beta}(r) \) is the same “line of delta functions” we defined in Eq. 5.60, \( r_{\alpha} - r_{\beta} \) is the separation vector, and \( f_{\alpha\beta} \) is the force on particle \( \alpha \) from particle \( \beta \). (Note that this expression is actually symmetric for central forces, leading to a symmetric stress tensor.)

Following a very similar sequence of manipulations as for the case of electrical conductivity, we arrive at

\[
\langle \Pi_{jk}(r, t) \rangle = -\beta \int_{-\infty}^{t} dt' \int dr' \langle \Pi_{jk}(r, t) \Pi_{lm}(r', t') \rangle \nabla_l v_m(r', t')
\]

(5.70)

Whereas, what we expect for the stress tensor in the limit of a spatially uniform shear flow, with very slow time variation of the deformation rate, is that the shear stress should be proportional to the shear strain rate,

\[
\langle \sigma_{xy} \rangle = \frac{1}{2} (\nabla_x v_y + \nabla_y v_x) \eta \equiv \eta \dot{\epsilon}_{xy}
\]

(5.71)
in which \( \dot{\epsilon}_{jk} \) is the rate of strain tensor, and \( \eta \) is the shear viscosity.

Comparing the two previous equations leads to the Kubo relation for the shear viscosity,

\[
\eta = \frac{\beta}{V} \int_0^\infty dt' \langle \Sigma_{xy}(0) \Sigma_{xy}(t') \rangle
\]

(5.72)
in which \( \Sigma_{jk} \) is the spatial integral of the momentum flux tensor, the microscopic expression for which is

\[
\Sigma_{jk} = \frac{1}{m} \sum_{\alpha} p_{\alpha,j} p_{\alpha,k} + \frac{1}{2} \sum_{\alpha,\beta} r_{\alpha\beta,j} f_{\alpha\beta,k}
\]

(5.73)

The derivation of the microscopic expression for the momentum current follows the same pattern as for the energy current, only with more vector indices to keep track of. Start with the microscopic expression for momentum density,

\[
g(r, t) = \sum_{\alpha} p_{\alpha}(t) \delta(r - r_{\alpha}(t))
\]

(5.74)

Take the time derivative, and use the microscopic equations of motion:

\[
\frac{\partial g_j(r, t)}{\partial t} = \sum_{\alpha\beta} F_{\alpha\beta,j} \delta(r - r_{\alpha}(t)) - \nabla_k \sum_{\alpha} p_{\alpha,j}(t) v_{\alpha,k}(t) \delta(r - r_{\alpha}(t))
\]

(5.75)
in which $F_{\alpha\beta}$ is the total force on particle $\alpha$ from particle $\beta$.

We want to write the right-hand side as the divergence of something; the second term is already in this form. The first term is similar to what we encountered for the energy current. When we integrate over all space the sum clearly vanishes, because the sum is then unrestricted by the delta function, and the forces between particles $\alpha$ and $\beta$ are equal and opposite. That is, the total momentum is indeed conserved.

Just as for the energy current, we can think of the first term as describing how the force $F_{\alpha\beta}$ transfer momentum from particle $\alpha$ to particle $\beta$. If we integrate $\partial g_j/\partial t$ over some finite volume $V$ bounded by a surface $S$, we obtain

$$
\int_V dr \frac{\partial g_j(r,t)}{\partial t} = \sum_{\alpha \in V} \sum_{\beta \notin V} F_{\alpha\beta j} - \int_S dn_k \Pi_{1jk} \tag{5.76}
$$

where we have defined

$$
\Pi_{1jk} = \sum_\alpha p_{\alpha,j}(t)v_{\alpha,k}(t)\delta(r - r_{\alpha}(t)) \tag{5.77}
$$

Forces between particles $\alpha$ inside $V$ and particles $\beta$ outside $V$, transfer momentum between the particles and hence out of the volume $V$. Just as for the energy current, we can think of this momentum as flowing along straight paths from particle $\alpha$ to particle $\beta$. This gives rise to the second part of the momentum current density $\Pi_{2jk}(r,t)$, defined as

$$
\Pi_{2jk} = \frac{1}{2} \sum_{\alpha,\beta} r_{\alpha,\beta,j} F_{\alpha\beta,k} g_{\alpha\beta}(r) \tag{5.78}
$$

The factor of two prevents double-counting of the momentum flux between a given pair of particles.

### 5.3.5 Onsager symmetry

Thus far in our discussion of transport coefficients and Kubo relations we have considered only one concentration field at a time, responding to the corresponding conjugate potential: concentration and chemical potential, charge density and electric potential, energy density and inverse temperature. But in most systems, more than one such field is present. For example, in an electrolyte solution we have three: the concentration of ions, the charge density, and the internal energy density.

It can happen that a potential of one kind applied to a system, can lead to a current of another kind. For example, consider a NaCl solution with an electric field applied. Ions of opposite signs drift in opposite directions in the field. However, the effective radius of the sodium cation (1 Å) is smaller than the chloride anion (1.8 Å) so the drift velocities of the ions in the field are different. We can estimate the drift velocities using Stokes drag, from

$$
F = qE = 6\pi\eta R v \tag{5.79}
$$

So the sodium ions move faster than the chloride ions; but they carry less mass (23 g/mol versus 35.5 g/mol). The momentum density for each ion species is

$$
p = mcv = \frac{mcq}{6\pi\eta R} E \tag{5.80}
$$

The ratio $m/R$ is slightly higher for Na+ than for Cl-. The ions have equal and opposite charges and equal concentrations, so the net momentum density for the ions is nonzero, in the direction of the sodium ions.
However, the electric field exerts no net force on the fluid, since it exerts equal and opposite forces on the positive and negative ions. So the net momentum density for the fluid must remain zero, assuming it was at rest to start with. This means the water molecules must drift slightly, in the direction opposite to the sodium ions. Thus we have a concentration current of the water, in response to an electric field acting on the ions.

We can reverse the situation by considering an osmotic current of water, flowing in a salt solution in response to a chemical potential gradient (resulting from a spatially varying ion concentration). Water diffuses into the region of concentrated ions, and ions diffuse out; locally we have counterflowing diffusive currents of water and ions. But the smaller sodium ions drift faster than the larger chloride ions in response to a chemical potential gradient. Both species move in the same direction, but the cations move faster, so that a net current results. Thus we have an electric current of drifting ions, in response to a chemical potential gradient.

Remarkably, the transport coefficients associated with these “off-diagonal” processes are related; in fact, they are equal. This symmetry is called Onsager reciprocity (named for theorist Lars Onsager, who received the 1968 Nobel Prize in Chemistry for his discovery of these relations). The Onsager relations are a consequence of time-reversal symmetry in the microscopic trajectories of the system, as we shall now show.

We introduce two concentration fields $\rho_A(r, t)$ and $\rho_B(r, t)$, each with a corresponding conjugate potential $\phi_A(r, t)$ and $\phi_B(r, t)$, coupled in a perturbation Hamiltonian as

$$\delta H = \int dr \rho_A \phi_A + \int dr \rho_B \phi_B$$

(5.81)

We can then define a matrix of response functions $R_{\alpha\beta}(r, t)$, i.e., response functions $R_{AA}$, $R_{AB}$, $R_{BA}$, and $R_{BB}$, which describe the time-dependent response of the concentration field $\rho_\alpha$ to the potential $\phi_\beta$. In particular for the cross-response of $\rho_B$ to $\phi_A$, we write

$$\langle \rho_B(r, t) \rangle = \int_{-\infty}^{t} dt' \int dr' R_{BA}(r - r', t - t') \phi_A(r', t')$$

(5.82)

as an obvious generalization of Eq. ??.

The fluctuation-response theorem also generalizes in the obvious way, as

$$\beta \frac{\partial S_{\alpha\beta}}{\partial t} = R_{\alpha\beta}$$

(5.83)

where $S_{\alpha\beta}(r, t)$ is a matrix of time-dependent correlation functions between the different concentration fields.

The derivation of the Kubo relation also goes through as before, leading to

$$\langle J_\beta(r, t) \rangle = -\beta/3 \int_{-\infty}^{t} dt' \int dr' \langle J_\beta(r, t) \cdot J_\alpha(r', t') \rangle \nabla \phi_\alpha(r', t')$$

(5.84)

This leads in the same way as before to a relation

$$\langle J_\beta \rangle = -\lambda_{\beta\alpha} \nabla \phi_\alpha$$

(5.85)

in which $J_\beta(r, t)$ is the spatial integral of the current, and we have defined

$$\lambda_{\beta\alpha} = \frac{\beta}{3V} \int_{0}^{\infty} dt' \langle J_\beta(0) \cdot J_\alpha(t') \rangle$$

(5.86)
We see that the off-diagonal transport coefficient is related to the strength of correlated fluctuations in the two corresponding currents. For example, in a salt solution, if fluctuations in the electric current carried by the ions tend to be correlated with fluctuations in the osmotic current of water molecules, then the off-diagonal transport coefficient will be nonvanishing, with a sign that depends on whether the electric and water currents tend to run in the same or opposite directions.

To prove Onsager symmetry, we exploit the consequences of time-reversal of the microscopic equations of motion: for every trajectory of all the particles in the system, there is another equally valid trajectory, in which “the movie runs backwards”. If we swap every trajectory with its time-reversed partner, particle positions \( r_i(t) \) are replaced by \( r_i(-t) \), and velocities \( v_i(t) \) by \( -v_i(-t) \). Fluctuating currents like \( J_\alpha(r,t) \), which are sums of terms proportional to particle velocities, are replaced under time reversal by \( -J_\alpha(r,-t) \).

Because trajectories can be paired with their time-reversed partners, the averages denoted by \( \langle \ldots \rangle \) are invariant under time reversal. Hence in Eq. 5.86, we can replace \( \langle J_\beta(0) \cdot J_\alpha(t') \rangle \) by \( \langle J_\beta(0) \cdot J_\alpha(-t') \rangle \). This average is also invariant with respect to translation in time, i.e., the choice of what instant corresponds to \( t = 0 \). So we can add \( t' \) to both time arguments and reverse the order in the dot product, to obtain \( \langle J_\alpha(0) \cdot J_\beta(t') \rangle \). But this sequence of operations transforms the right-hand side of Eq. 5.86 to what we would write for \( \lambda_{\alpha\beta} \); hence we must have

\[
\lambda_{\alpha\beta} = \lambda_{\beta\alpha}
\]  

\hspace{1cm} (5.87)

which is Onsager reciprocity.
5.4 Practical considerations

There are many ways to measure near-equilibrium response and transport coefficients. First, we may either use response functions directly, or measure equilibrium fluctuations. A natural question to ask is: which works better? Which gives more accurate results with a given amount of simulation time? Standard textbook sources are remarkably silent on this issue.

There are difficulties that may arise from applying external forces to a simulation, in an effort to achieve a steady-state response of some current. First, the simulation must run long enough that steady-state is reached, the displacement of the moving particles observed to be linear in time, and large enough to be measured.

We may be tempted to apply a larger external force in order to get a bigger and thus more visible response, but in so doing we run the risk of going beyond the regime of linear response, for example in heating the system by the work we do in driving the motion of particles. If we are not too aggressive, this can be dealt with by “thermostatting” the simulation, as described in Section 4.2.1.

Likewise, if for example we force tagged particles with a constant force, we will over time impart momentum to the entire system, causing the entire system to accelerate; we can avoid this by applying a weak opposing force to all the untagged particles, so that the momentum of the system as a whole is undisturbed.

Sometimes, we are interested in the time-dependence of response functions themselves; for this purpose, we may apply different forms of time-dependent perturbation to induce a nonequilibrium response. For example, we can apply a delta-function pulse at $t = 0$ of the external field, in which case the average response will have the same time-dependence as the response function $R(t)$ itself.

Or, we can switch on the perturbing field at $t = 0$, which leads to an average response with time-dependence given by the time integral of the response function $\int_0^t dt'R(t')$. (Or, we can apply an oscillatory external field at some frequency $\omega$; then, the average response will also be at frequency $\omega$, with an amplitude and phase shift related to the Fourier transform of the response function.)

Whichever of these approaches we take, the simulation needs to run long enough that we observe enough of the time-dependent response to predict the steady state of the system under conditions that lead to a steady current or flow. For systems with long relaxation times, this can be challenging.

5.4.1 How best to use the Kubo relation?

We do not escape this requirement by using the Kubo approach, of observing the time-dependent correlation function of equilibrium fluctuations. In order to make use of the Kubo relation Eqn. (5.38), we must obtain the velocity autocorrelation function for sufficiently long times that we can reasonably approximate its integral over all times.

There are several ways to accomplish this, which are equivalent in principle but not in practice. We showed in our discussion of self-diffusion in Section 5.3.1 that the mean-square displacement of particles $\langle \Delta r^2(t) \rangle$ was related to the integral of the velocity autocorrelation function in the long-time limit:

$$\langle \Delta r^2(t) \rangle \approx 2t \int_0^\infty d\tau \langle v(\tau) \cdot v(0) \rangle$$

(5.88)
This allows us to rewrite the Kubo relation for the mobility $\mu$ as

$$\mu = \frac{3}{\beta} \int_0^\infty dt' \langle v(t') \cdot v(0) \rangle$$

$$= \lim_{t \to \infty} \frac{\beta}{6t} \langle \Delta r^2(t) \rangle$$

(5.89)

Of course, simulation runs are never infinitely long. As a result, there are three ways to evaluate $\mu$ from simulation data, which are equivalent in principle but not in practice:

- evaluate the integral of the correlation function;

- follow the average mean-square displacement of particles, and compute the ratio $\beta\langle \Delta r^2(t) \rangle/(6t)$ as in Eqn. (5.89) above, which corresponds to the “chord” in a plot of $(\beta/6)\langle \Delta r^2(t) \rangle$ versus $t$;

- estimate $\mu$ as the long-time limiting “slope” of $(\beta/6)\langle \Delta r^2(t) \rangle$ versus $t$.

The integral method is difficult if the correlation function is slowly relaxing, because we must accurately represent its time-dependence over a wide dynamic range. The chord and slope methods have the advantage that we use the MD equations of motion to “do the integral”, by keeping track of the displacements of particles.

For finite-length simulation data sets (which is to say, all simulation data sets), the “slope” method is preferred to the “chord” method, because it is less sensitive to non-diffusive motion of the particles on shorter timescales (which may in practical situations contaminate much of the simulation run). However, the quality of the data deteriorates for mean-square displacement at late times, so one must be careful in choosing the data range over which to evaluate the slope.

![Figure 5.7: Sketch of $\langle \Delta R^2(t) \rangle$, showing crossover to diffusive behavior.](image)

As an aside, we may ask based on Eqn. (5.89) how long a data series we should expect to have in order to reach the diffusive regime, in which $\langle \Delta r^2(t) \rangle$ is growing linearly with time. For times shorter than the time between collisions, the motion of a molecule in a fluid will be approximately ballistic; that is, it will travel roughly at constant velocity, in a straight line. So its displacement will grow linearly in time, and the average $\langle \Delta r^2(t) \rangle$ will correspondingly grow as $t^2$. This is the “ballistic regime”, which persists up to a collision time or so.
Then, in a dense fluid, there may be a time regime in which a particle undergoes multiple collisions without managing to escape the “cage” formed by its immediate neighbors. (We discussed this phenomenon briefly at the end of Section 5.1.) While a molecule is caged, its mean-square displacement $\langle \Delta r^2(t) \rangle$ will tend to saturate, reaching something like a plateau, at a displacement of about the intermolecular near-neighbor distance. For dense liquids approaching a glass transition, in which molecular motion becomes arrested without accompanying crystalline order, this caging regime can persist for several decades in time.

For a liquid, in which molecules can ultimately move throughout the system volume, molecules must ultimately escape their cages by slipping between neighbors—whereupon they find themselves in another such cage, which they ultimately escape, and so forth. The escapes happen in random directions, and the sequence of random steps upon each escape give rise to molecular diffusion. From the above discussion it is evident that the timescale on which $\langle \Delta r^2(t) \rangle$ becomes diffusive (grows linearly as $t$) may be many molecular collision times, depending on how dense the liquid is. From our simple estimates in Section 5.1 we should not be surprised if this time is at least 20 collision times even for ordinary liquids.

5.4.2 Error analysis for $\langle \Delta R^2(t) \rangle$.

Assuming that we manage to take data for sufficiently long that $\langle \Delta R^2(t) \rangle$ becomes diffusive, we expect there to be errors in the average that result from the finite number of independent contributions to the average (one from each random particle trajectory). An example of this behavior is shown in Fig. 5.8, in which $\langle \Delta R^2(t) \rangle$ is displayed for simulations of 25, 100, and 400 particles (with vertical offsets of the different time series for easier viewing).

![Figure 5.8: $\langle \Delta R^2(t) \rangle$ for averages performed over 25, 100, and 400 particles.](image)

We can analyze the random errors evident in the results of Fig. 5.8 as follows. The quantity plotted is a sum over $N$ independent random walks, which can be written

$$\langle \Delta R^2(t) \rangle = \frac{1}{N} \sum \Delta R^2_i(t)$$  \hspace{1cm} (5.90)

The different fluctuating paths $\Delta R_i(t)$ contributing to the sum are all independent Gaussian random variables, which allows us to compute the variance $\Sigma^2$ of the quantity $\langle 1/N \sum \Delta R^2(t) \rangle$. 

5.4. PRACTICAL CONSIDERATIONS

Each of the random walks is statistically identical and independent of the others, which allows us to write
\[
\Sigma^2 = (1/N) \left( \langle \Delta R_i^2(t) \rangle - \langle \Delta R_i^2(t) \rangle^2 \right)
\]  
(5.91)

Each component of the vector \( \Delta R(t) \) is Gaussian with variance \( 2Dt \), which allows us to compute the above averages after a short calculation as
\[
\Sigma^2 = (1/N)24(Dt)^2
\]  
(5.92)

Comparing this to the diffusive behavior of the average \( \langle \Delta R^2(t) \rangle = 6Dt \), we see that the scale of the random variations in the traces of Fig. 5.8 is set by the standard deviation \( \Sigma \), scales as \( Dt/\sqrt{N} \). The fluctuations in the traces become small proportional to \( N^{-1/2} \) as the number of particles contributing to the average \( N \) increases. Similar considerations apply to the determination of the velocity autocorrelation function, displayed in Fig. 5.9 for averages performed over the velocity time series for 25, 100, and 400 particles.

![Figure 5.9: Velocity autocorrelation function \( \langle v(0) \cdot v(t) \rangle \) obtained from averaging over the velocity time series for 25, 100, and 400 particles, vertically offset for clarity.](image)

5.4.3 Displacement variables for \( \lambda \) and \( \eta \).

Our discussion above has been for self-diffusion, but it turns out that these same methods for extracting a transport coefficient can be applied more generally, to the electrical conductivity \( \lambda \) and the shear viscosity \( \eta \) for example.

What we need for each case is a microscopic expression for the time integral of the thing being correlated, as the displacement \( \Delta r(t) \) is the time integral of the particle velocity \( v(t) \) for the case of self-diffusion. Remarkably, the spatial integral of the current density \( J(t) \) is actually the time derivative of a quantity with a simple microscopic expression, namely
\[
\Delta J \equiv \int_0^t dt' J(t') = \sum_\alpha e z_\alpha r_\alpha
\]  
(5.93)

Following the same logic of Eqn. (5.39), we can derive the relation
\[
\langle \Delta J(t)^2 \rangle \approx 2t \int_0^\infty d\tau \langle J(0) \cdot J(\tau) \rangle
\]  
(5.94)
in which $\Delta \int J(t)$ and $J(t)$ play roles analogous to the displacement $\Delta r(t)$ and velocity $v(t)$ for the case of a single tagged particle.

This allows us to write the conductivity finally as

$$\lambda = \lim_{t \to \infty} \frac{\beta}{6Vt} \langle \Delta \int J(t)^2 \rangle$$  \hspace{1cm} (5.95)

to which the slope method can be applied.

The above expression can be written in a revealing way by substituting the microscopic expression for $\int J$, to obtain

$$\lambda = \lim_{t \to \infty} \frac{e^2 \beta}{6Vt} \sum_{\alpha,\beta} z_\alpha z_\beta \langle \Delta r_\alpha(t) \cdot \Delta r_\beta(t) \rangle$$  \hspace{1cm} (5.96)

This form for the conductivity $\lambda$ is similar to Eqn. (5.89) for the mobility $\mu$, except that instead of self-diffusion, we potentially have contributions from the correlated motion of different particles. We notice for example that if a pair of particles of opposite signs diffuse together, the net contribution from the four terms in the double sum will be zero. Hence the conductivity depends on independently diffusing charges, which can be biased to drift in opposite directions by an applied field.

![Figure 5.10: Charges that remain paired as dipoles may diffuse together a considerable distance, without contributing much to the conductivity as given by Eqn. (5.96).](image)

Finally, the spatial integral of the momentum flux tensor $\Sigma_{jk}$ is actually the time derivative of something as well, namely

$$\int \Sigma_{jk} = \sum_{\alpha} p_{\alpha,j} r_{\alpha,k}$$  \hspace{1cm} (5.97)

as can be shown directly from the equations of motion, and the manipulations used to transform the pressure estimator into a sum over pairs of particles.

Therefore, we can write the shear viscosity as

$$\eta = \lim_{t \to \infty} \frac{\beta}{Vt} \langle \Delta \int \Sigma_{xy}(t)^2 \rangle$$

$$= \lim_{t \to \infty} \frac{\beta}{Vt} \sum_{\alpha,\beta} \langle \Delta(p_{\alpha,x} r_{\alpha,y})(t) \Delta(p_{\beta,x} r_{\beta,y})(t) \rangle$$  \hspace{1cm} (5.98)
5.4. PRACTICAL CONSIDERATIONS

Having cast the Kubo relations for the conductivity $\lambda$ and the viscosity $\eta$ in the same form as for the single-particle mobility $\mu$, we recognize that the arguments of the previous section for the expected scale of fluctuations apply to the corresponding averages $\langle \Delta \int J(t)^2 \rangle$ and $\langle \Delta \int \Sigma_{xy}(t)^2 \rangle$. That is, we expect the noise in these time-dependent averages to scale inversely with the square root of the number of independent contributions to the average.