

2. Kinetic Theory

The purpose of this section is to lay down the foundations of kinetic theory, starting from the Hamiltonian description of 10^{23} particles, and ending with the Navier-Stokes equation of fluid dynamics. Our main tool in this task will be the Boltzmann equation. This will allow us to provide derivations of the transport properties that we sketched in the previous section, but without the more egregious inconsistencies that crept into our previous attempt. But, perhaps more importantly, the Boltzmann equation will also shed light on the deep issue of how irreversibility arises from time-reversible classical mechanics.

2.1 From Liouville to BBGKY

Our starting point is simply the Hamiltonian dynamics for N identical point particles. Of course, as usual in statistical mechanics, here is N ridiculously large: $N \sim \mathcal{O}(10^{23})$ or something similar. We will take the Hamiltonian to be of the form

$$H = \frac{1}{2m} \sum_{i=1}^N \vec{p}_i^2 + \sum_{i=1}^N V(\vec{r}_i) + \sum_{i<j} U(\vec{r}_i - \vec{r}_j) \quad (2.1)$$

The Hamiltonian contains an external force $\vec{F} = -\nabla V$ that acts equally on all particles. There are also two-body interactions between particles, captured by the potential energy $U(\vec{r}_i - \vec{r}_j)$. At some point in our analysis (around Section 2.2.3) we will need to assume that this potential is short-ranged, meaning that $U(r) \approx 0$ for $r \gg d$ where, as in the last Section, d is the atomic distance scale.

Hamilton's equations are

$$\frac{\partial \vec{p}_i}{\partial t} = -\frac{\partial H}{\partial \vec{r}_i} \quad , \quad \frac{\partial \vec{r}_i}{\partial t} = \frac{\partial H}{\partial \vec{p}_i} \quad (2.2)$$

Our interest in this section will be in the evolution of a probability distribution, $f(\vec{r}_i, \vec{p}_i; t)$ over the $6N$ dimensional phase space. This function tells us the probability that the system will be found in the vicinity of the point (\vec{r}_i, \vec{p}_i) . As with all probabilities, the function is normalized as

$$\int dV f(\vec{r}_i, \vec{p}_i; t) = 1 \quad \text{with} \quad dV = \prod_{i=1}^N d^3 r_i d^3 p_i$$

Furthermore, because probability is locally conserved, it must obey a continuity equation: any change of probability in one part of phase space must be compensated by

a flow into neighbouring regions. But now we're thinking in terms of phase space, the “ ∇ ” term in the continuity equation includes both $\partial/\partial\vec{r}_i$ and $\partial/\partial\vec{p}_i$ and, correspondingly, the velocity vector in phase space is $(\dot{\vec{r}}_i, \dot{\vec{p}}_i)$. The continuity equation of the probability distribution is then

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial\vec{r}_i} \cdot (\dot{\vec{r}}_i f) + \frac{\partial}{\partial\vec{p}_i} \cdot (\dot{\vec{p}}_i f) = 0$$

where we're using the convention that we sum over the repeated index $i = 1, \dots, N$. But, using Hamilton's equations (2.2), this becomes

$$\begin{aligned} \frac{\partial f}{\partial t} + \frac{\partial}{\partial\vec{r}_i} \cdot \left(\frac{\partial H}{\partial\vec{p}_i} f \right) - \frac{\partial}{\partial\vec{p}_i} \cdot \left(\frac{\partial H}{\partial\vec{r}_i} f \right) &= 0 \\ \Rightarrow \frac{\partial f}{\partial t} + \frac{\partial f}{\partial\vec{r}_i} \cdot \frac{\partial H}{\partial\vec{p}_i} - \frac{\partial f}{\partial\vec{p}_i} \cdot \frac{\partial H}{\partial\vec{r}_i} &= 0 \end{aligned}$$

This final equation is the *Liouville's equation*. It is the statement that probability doesn't change as you follow it along any trajectory in phase space, as is seen by writing the Liouville equation as a total derivative,

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial\vec{r}_i} \cdot \dot{\vec{r}}_i + \frac{\partial f}{\partial\vec{p}_i} \cdot \dot{\vec{p}}_i = 0$$

To get a feel for how probability distributions evolve, one often evokes the closely related *Liouville's theorem*². This is the statement that if you follow some region of phase space under Hamiltonian evolution, then its shape can change but its volume remains the same. This means that the probability distribution on phase space acts like an incompressible fluid. Suppose, for example, that it's a constant, f , over some region of phase space and zero everywhere else. Then the distribution can't spread out over a larger volume, lowering its value. Instead, it must always be f over some region of phase space. The shape and position of this region can change, but not its volume.

The Liouville equation is often written using the *Poisson bracket*,

$$\{A, B\} \equiv \frac{\partial A}{\partial\vec{r}_i} \cdot \frac{\partial B}{\partial\vec{p}_i} - \frac{\partial A}{\partial\vec{p}_i} \cdot \frac{\partial B}{\partial\vec{r}_i}$$

With this notation, Liouville's equation becomes simply

$$\frac{\partial f}{\partial t} = \{H, f\}$$

²A fuller discussion of Hamiltonian mechanics and Liouville's theorem can be found in the lectures on [Classical Dynamics](#).

It's worth making a few simple comments about these probability distributions. Firstly, an *equilibrium distribution* is one which has no explicit time dependence:

$$\frac{\partial f}{\partial t} = 0$$

which holds if $\{H, f\} = 0$. One way to satisfy this is if f is a function of H and the most famous example is the Boltzmann distribution, $f \sim e^{-\beta H}$. However, notice that there is nothing (so-far!) within the Hamiltonian framework that requires the equilibrium distribution to be Boltzmann: any function that Poisson commutes with H will do the job. We'll come back to this point in Section 2.2.2.

Suppose that we have some function, $A(\vec{r}_i, \vec{p}_i)$, on phase space. The expectation value of this function is given by

$$\langle A \rangle = \int dV A(\vec{r}_i, \vec{p}_i) f(\vec{r}_i, \vec{p}_i; t) \quad (2.3)$$

This expectation value changes with time only if there is explicit time dependence in the distribution. (For example, this means that in equilibrium $\langle A \rangle$ is constant). We have

$$\begin{aligned} \frac{d\langle A \rangle}{dt} &= \int dV A \frac{\partial f}{\partial t} \\ &= \int dV A \left(\frac{\partial f}{\partial \vec{p}_i} \frac{\partial H}{\partial \vec{r}_i} - \frac{\partial f}{\partial \vec{r}_i} \frac{\partial H}{\partial \vec{p}_i} \right) \\ &= \int dV \left(-\frac{\partial A}{\partial \vec{p}_i} \frac{\partial H}{\partial \vec{r}_i} + \frac{\partial A}{\partial \vec{r}_i} \frac{\partial H}{\partial \vec{p}_i} \right) f \end{aligned} \quad (2.4)$$

where we have integrated by parts to get to the last line, throwing away boundary terms which is justified in this context because f is normalized which ensures that we must have $f \rightarrow 0$ in asymptotic parts of phase space. Finally, we learn that

$$\frac{d\langle A \rangle}{dt} = \int dV \{A, H\} f = \langle \{A, H\} \rangle \quad (2.5)$$

This should be ringing some bells. The Poisson bracket notation makes these expressions for classical expectation values look very similar to quantum expectation values.

2.1.1 The BBGKY Hierarchy

Although we're admitting some ignorance in our description of the system by considering a probability distribution over N -particle phase space, this hasn't really made our life any easier: we still have a function of $\sim 10^{23}$ variables. To proceed, the plan is

to limit our ambition. We'll focus not on the probability distribution for all N particles but instead on the *one-particle distribution function*. This captures the expected number of particles lying at some point (\vec{r}, \vec{p}) . It is defined by

$$f_1(\vec{r}, \vec{p}; t) = N \int \prod_{i=2}^N d^3 r_i d^3 p_i f(\vec{r}, \vec{r}_2, \dots, \vec{r}_N, \vec{p}, \vec{p}_2, \dots, \vec{p}_N; t)$$

Although we seem to have singled out the first particle for special treatment in the above expression, this isn't really the case since all N of our particles are identical. This is also reflected in the factor N which sits out front which ensures that f_1 is normalized as

$$\int d^3 r d^3 p f_1(\vec{r}, \vec{p}; t) = N \quad (2.6)$$

For many purposes, the function f_1 is all we really need to know about a system. In particular, it captures many of the properties that we met in the previous chapter. For example, the average density of particles in real space is simply

$$n(\vec{r}; t) = \int d^3 p f_1(\vec{r}, \vec{p}; t) \quad (2.7)$$

The average velocity of particles is

$$\vec{u}(\vec{r}; t) = \int d^3 p \frac{\vec{p}}{m} f_1(\vec{r}, \vec{p}; t) \quad (2.8)$$

and the energy flux is

$$\vec{\mathcal{E}}(\vec{r}; t) = \int d^3 p \frac{\vec{p}}{m} E(\vec{p}) f_1(\vec{r}, \vec{p}; t) \quad (2.9)$$

where we usually take $E(\vec{p}) = p^2/2m$. All of these quantities (or at least close relations) will be discussed in some detail in Section 2.4.

Ideally we'd like to derive an equation governing f_1 . To see how it changes with time, we can simply calculate:

$$\frac{\partial f_1}{\partial t} = N \int \prod_{i=2}^N d^3 r_i d^3 p_i \frac{\partial f}{\partial t} = N \int \prod_{i=2}^N d^3 r_i d^3 p_i \{H, f\}$$

Using the Hamiltonian given in (2.1), this becomes

$$\frac{\partial f_1}{\partial t} = N \int \prod_{i=2}^N d^3 r_i d^3 p_i \left[- \sum_{j=1}^N \frac{\vec{p}_j}{m} \cdot \frac{\partial f}{\partial \vec{r}_j} + \sum_{j=1}^N \frac{\partial V}{\partial \vec{r}_j} \cdot \frac{\partial f}{\partial \vec{p}_j} + \sum_{j=1}^N \sum_{k < l} \frac{\partial U(\vec{r}_k - \vec{r}_l)}{\partial \vec{r}_j} \cdot \frac{\partial f}{\partial \vec{p}_j} \right]$$

Now, whenever $j = 2, \dots, N$, we can always integrate by parts to move the derivatives away from f and onto the other terms. And, in each case, the result is simply zero because when the derivative is with respect to \vec{r}_j , the other terms depend only on \vec{p}_i and vice-versa. We're left only with the terms that involve derivatives with respect to \vec{r}_1 and \vec{p}_1 because we can't integrate these by parts. Let's revert to our previous notation and call $\vec{r}_1 \equiv \vec{r}$ and $\vec{p}_1 \equiv \vec{p}$. We have

$$\begin{aligned} \frac{\partial f_1}{\partial t} &= N \int \prod_{i=2}^N d^3 r_i d^3 p_i \left[-\frac{\vec{p}}{m} \cdot \frac{\partial f}{\partial \vec{r}} + \frac{\partial V(\vec{r})}{\partial \vec{r}} \cdot \frac{\partial f}{\partial \vec{p}} + \sum_{k=2}^N \frac{\partial U(\vec{r} - \vec{r}_k)}{\partial \vec{r}} \cdot \frac{\partial f}{\partial \vec{p}} \right] \\ &= \{H_1, f_1\} + N \int \prod_{i=2}^N d^3 r_i d^3 p_i \sum_{k=2}^N \frac{\partial U(\vec{r} - \vec{r}_k)}{\partial \vec{r}} \cdot \frac{\partial f}{\partial \vec{p}} \end{aligned} \quad (2.10)$$

where we have defined the one-particle Hamiltonian

$$H_1 = \frac{p^2}{2m} + V(\vec{r}) \quad (2.11)$$

Notice that H_1 includes the external force V acting on the particle, but it knows nothing about the interaction with the other particles. All of that information is included in the last term with $U(\vec{r} - \vec{r}_k)$. We see that the evolution of the one-particle distribution function is described by a Liouville-like equation, together with an extra term. We write

$$\frac{\partial f_1}{\partial t} = \{H_1, f_1\} + \left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} \quad (2.12)$$

The first term is sometimes referred to as the *streaming term*. It tells you how the particles move in the absence of collisions. The second term, known as the *collision integral*, is given by the second term in (2.10). In fact, because all particles are the same, each of the $(N - 1)$ terms in $\sum_{k=2}^N$ in (2.10) are identical and we can write

$$\left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} = N(N - 1) \int d^3 r_2 d^3 p_2 \frac{\partial U(\vec{r} - \vec{r}_2)}{\partial \vec{r}} \cdot \frac{\partial}{\partial \vec{p}} \int \prod_{i=3}^N d^3 r_i d^3 p_i f(\vec{r}, \vec{r}_2, \dots, \vec{p}, \vec{p}_2, \dots; t)$$

But now we've got something of a problem. The collision integral can't be expressed in terms of the one-particle distribution function. And that's not really surprising. As the name suggests, the collision integral captures the interactions – or collisions – of one particle with another. Yet f_1 contains no information about where any of the other particles are in relation to the first. However some of that information is contained in the *two-particle distribution function*,

$$f_2(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2; t) \equiv N(N - 1) \int \prod_{i=3}^N d^3 r_i d^3 p_i f(\vec{r}_1, \vec{r}_2, \dots, \vec{p}_1, \vec{p}_2, \dots; t)$$

With this definition, the collision integral is written simply as

$$\left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}} = \int d^3r_2 d^3p_2 \frac{\partial U(\vec{r} - \vec{r}_2)}{\partial \vec{r}} \cdot \frac{\partial f_2}{\partial \vec{p}} \quad (2.13)$$

The collision term doesn't change the distribution of particles in space. This is captured by the particle density (2.7) which we get by simply integrating $n = \int d^3p f_1$. But, after integrating over $\int d^3p$, we can perform an integrating by parts in the collision integral to see that it vanishes. In contrast, if we're interested in the distribution of velocities – such as the current (2.8) or energy flux (2.9) – then the collision integral is important.

The upshot of all of this is that if we want to know how the one-particle distribution function evolves, we also need to know something about the two-particle distribution function. But we can always figure out how f_2 evolves by repeating the same calculation that we did above for f_1 . It's not hard to show that f_2 evolves by a Liouville-like equation, but with a corrected term that depends on the three-particle distribution function f_3 . And f_3 evolves in a Liouville manner, but with a correction term that depends on f_4 , and so on. In general, the n -particle distribution function

$$f_n(\vec{r}_1, \dots, \vec{r}_n, \vec{p}_1, \dots, \vec{p}_n; t) = \frac{N!}{(N-n)!} \int \prod_{i=n+1}^N d^3r_i d^3p_i f(\vec{r}_1, \dots, \vec{r}_N, \vec{p}_1, \dots, \vec{p}_N; t)$$

obeys the equation

$$\frac{\partial f_n}{\partial t} = \{H_n, f_n\} + \sum_{i=1}^n \int d^3r_{n+1} d^3p_{n+1} \frac{\partial U(\vec{r}_i - \vec{r}_{n+1})}{\partial \vec{r}_i} \cdot \frac{\partial f_{n+1}}{\partial \vec{p}_i} \quad (2.14)$$

where the effective n -body Hamiltonian includes the external force and any interactions between the n particles but neglects interactions with any particles outside of this set,

$$H_n = \sum_{i=1}^n \left(\frac{\vec{p}_i^2}{2m} + V(\vec{r}_i) \right) + \sum_{i < j \leq n} U(\vec{r}_i - \vec{r}_j)$$

The equations (2.14) are known as the *BBGKY hierarchy*. (The initials stand for Bogoliubov, Born, Green, Kirkwood and Yvon). They are telling us that any group of n particles evolves in a Hamiltonian fashion, corrected by interactions with one of the particles outside that group. At first glance, it means that there's no free lunch; if we want to understand everything in detail, then we're going to have to calculate everything. We started with the Liouville equation governing a complicated function f of $N \sim \mathcal{O}(10^{23})$ variables and it looks like all we've done is replace it with $\mathcal{O}(10^{23})$ coupled equations.

However, there is an advantage in working with the hierarchy of equations (2.14) because they isolate the interesting, simple variables, namely f_1 and other lower f_n . This means that the equations are in a form that is ripe to start implementing various approximations. Given a particular problem, we can decide which terms are important and, ideally, which terms are so small that they can be ignored, truncating the hierarchy to something manageable. Exactly how you do this depends on the problem at hand. Here we explain the simplest, and most useful, of these truncations: the Boltzmann equation.

2.2 The Boltzmann Equation

“Elegance is for tailors”
Ludwig Boltzmann

In this section, we explain how to write down a closed equation for f_1 alone. This will be the famous Boltzmann equation. The main idea that we will use is that there are two time scales in the problem. One is the time between collisions, τ , known as the scattering time or relaxation time. The second is the collision time, τ_{coll} , which is roughly the time it takes for the process of collision between particles to occur. In situations where

$$\tau \gg \tau_{\text{coll}} \tag{2.15}$$

we should expect that, for much of the time, f_1 simply follows its Hamiltonian evolution with occasional perturbations by the collisions. This, for example, is what happens for the dilute gas. And this is the regime we will work in from now on.

At this stage, there is a right way and a less-right way to proceed. The right way is to derive the Boltzmann equation starting from the BBGKY hierarchy. And we will do this in Section 2.2.3. However, as we shall see, it’s a little fiddly. So instead we’ll start by taking the less-right option which has the advantage of getting the same answer but in a much easier fashion. This option is to simply guess what form the Boltzmann equation has to take.

2.2.1 Motivating the Boltzmann Equation

We’ve already caught our first glimpse of the Boltzmann equation in (2.12),

$$\frac{\partial f_1}{\partial t} = \{H_1, f_1\} + \left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} \tag{2.16}$$

But, of course, we don’t yet have an expression for the collision integral in terms of f_1 . It’s clear from the definition (2.13) that the second term represents the change in

momenta due to two-particle scattering. When $\tau \gg \tau_{\text{coll}}$, the collisions occur occasionally, but abruptly. The collision integral should reflect the rate at which these collisions occur.

Suppose that our particle sits at (\vec{r}, \vec{p}) in phase space and collides with another particle at (\vec{r}, \vec{p}_2) . Note that we're assuming here that collisions are local in space so that the two particles sit at the same point. These particles can collide and emerge with momenta \vec{p}'_1 and \vec{p}'_2 . We'll define the rate for this process to occur to be

$$\text{Rate} = \omega(\vec{p}, \vec{p}_2 | \vec{p}'_1, \vec{p}'_2) f_2(\vec{r}, \vec{r}, \vec{p}, \vec{p}_2) d^3 p_2 d^3 p'_1 d^3 p'_2 \quad (2.17)$$

(Here we've dropped the explicit t dependence of f_2 only to keep the notation down). The scattering function ω contains the information about the dynamics of the process. It looks as if this is a new quantity which we've introduced into the game. But, using standard classical mechanics techniques, one can compute ω for a given inter-atomic potential $U(\vec{r})$. (It is related to the differential cross-section; we will explain how to do this when we do things better in Section 2.2.3). For now, note that the rate is proportional to the two-body distribution function f_2 since this tells us the chance that two particles originally sit in (\vec{r}, \vec{p}) and (\vec{r}, \vec{p}_2) .

We'd like to focus on the distribution of particles with some specified momentum \vec{p} . Two particles with momenta \vec{p} and \vec{p}_2 can be transformed in two particles with momenta \vec{p}'_1 and \vec{p}'_2 . Since both momenta and energy are conserved in the collision, we have

$$\vec{p} + \vec{p}_2 = \vec{p}'_1 + \vec{p}'_2 \quad (2.18)$$

$$p^2 + p_2^2 = p_1'^2 + p_2'^2 \quad (2.19)$$

There is actually an assumption that is hiding in these equations. In general, we're considering particles in an external potential V . This provides a force on the particles which, in principle, could mean that the momentum and kinetic energy of the particles is not the same before and after the collision. To eliminate this possibility, we will assume that the potential only varies appreciably over macroscopic distance scales, so that it can be neglected on the scale of atomic collisions. This, of course, is entirely reasonable for most external potentials such as gravity or electric fields. Then (2.18) and (2.19) continue to hold.

While collisions can deflect particles out of a state with momentum \vec{p} and into a different momentum, they can also deflect particles into a state with momentum \vec{p} .

This suggests that the collision integral should contain two terms,

$$\left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}} = \int d^3p_2 d^3p'_1 d^3p'_2 \left[\omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}, \vec{p}_2) f_2(\vec{r}, \vec{r}, \vec{p}'_1, \vec{p}'_2) - \omega(\vec{p}, \vec{p}_2 | \vec{p}'_1, \vec{p}'_2) f_2(\vec{r}, \vec{r}, \vec{p}, \vec{p}_2) \right]$$

The first term captures scattering into the state \vec{p} , the second scattering out of the state \vec{p} .

The scattering function obeys a few simple requirements. Firstly, it is only non-vanishing for scattering events that obey the conservation of momentum (2.18) and energy (2.19). Moreover, the discrete symmetries of spacetime also give us some important information. Under time reversal, $\vec{p} \rightarrow -\vec{p}$ and, of course, what was coming in is now going out. This means that any scattering which is invariant under time reversal (which is more or less anything of interest) must obey

$$\omega(\vec{p}, \vec{p}_2 | \vec{p}'_1, \vec{p}'_2) = \omega(-\vec{p}'_1, -\vec{p}'_2 | -\vec{p}, -\vec{p}_2)$$

Furthermore, under parity $(\vec{r}, \vec{p}) \rightarrow (-\vec{r}, -\vec{p})$. So any scattering process which is parity invariant further obeys

$$\omega(\vec{p}, \vec{p}_2 | \vec{p}'_1, \vec{p}'_2) = \omega(-\vec{p}, -\vec{p}_2 | -\vec{p}'_1, -\vec{p}'_2)$$

The combination of these two means that the scattering rate is invariant under exchange of ingoing and outgoing momenta,

$$\omega(\vec{p}, \vec{p}_2 | \vec{p}'_1, \vec{p}'_2) = \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}, \vec{p}_2) \quad (2.20)$$

(There is actually a further assumption of translational invariance here, since the scattering rate at position $-\vec{r}$ should be equivalent to the scattering rate at position $+\vec{r}$).

The symmetry property (2.20) allows us to simplify the collision integral to

$$\left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}} = \int d^3p_2 d^3p'_1 d^3p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}, \vec{p}_2) \left[f_2(\vec{r}, \vec{r}, \vec{p}'_1, \vec{p}'_2) - f_2(\vec{r}, \vec{r}, \vec{p}, \vec{p}_2) \right] \quad (2.21)$$

To finish the derivation, we need to face up to our main goal of expressing the collision integral in terms of f_1 rather than f_2 . We make the assumption that the velocities of two particles are uncorrelated, so that we can write

$$f_2(\vec{r}, \vec{r}, \vec{p}, \vec{p}_2) = f_1(\vec{r}, \vec{p}) f_1(\vec{r}, \vec{p}_2) \quad (2.22)$$

This assumption, which sometimes goes by the name of *molecular chaos*, seems innocuous enough. But actually it is far from innocent! To see why, let's look more closely

at what we've actually assumed. Looking at (2.21), we can see that we have taken the rate of collisions to be proportional to $f_2(\vec{r}, \vec{r}, \vec{p}_1, \vec{p}_2)$ where p_1 and p_2 are the momenta of the particles before the collision. That means that if we substitute (2.22) into (2.21), we are really assuming that the velocities are uncorrelated before the collision. And that sounds quite reasonable: you could imagine that during the collision process, the velocities between two particles become correlated. But there is then a long time, τ , before one of these particles undergoes another collision. Moreover, this next collision is typically with a completely different particle and it seems entirely plausible that the velocity of this new particle has nothing to do with the velocity of the first. Nonetheless, the fact that we've assumed that velocities are uncorrelated *before* the collision rather than after has, rather slyly, introduced an arrow of time into the game. And this has dramatic implications which we will see in Section 2.3 where we derive the H-theorem.

Finally, we may write down a closed expression for the evolution of the one-particle distribution function given by

$$\frac{\partial f_1}{\partial t} = \{H_1, f_1\} + \left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} \quad (2.23)$$

with the collision integral

$$\left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} = \int d^3 p_2 d^3 p'_1 d^3 p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}, \vec{p}_2) \left[f_1(\vec{r}, \vec{p}'_1) f_1(\vec{r}, \vec{p}'_2) - f_1(\vec{r}, \vec{p}) f_1(\vec{r}, \vec{p}_2) \right] \quad (2.24)$$

This is the *Boltzmann equation*. It's not an easy equation to solve! It's a differential equation on the left, an integral on the right, and non-linear. You may not be surprised to hear that exact solutions are not that easy to come by. We'll see what we can do.

2.2.2 Equilibrium and Detailed Balance

Let's start our exploration of the Boltzmann equation by revisiting the question of the equilibrium distribution obeying $\partial f^{\text{eq}}/\partial t = 0$. We already know that $\{f, H_1\} = 0$ if f is given by any function of the energy or, indeed any function that Poisson commutes with H . For clarity, let's restrict to the case with vanishing external force, so $V(r) = 0$. Then, if we look at the Liouville equation alone, any function of momentum is an equilibrium distribution. But what about the contribution from the collision integral?

One obvious way to make the collision integral vanish is to find a distribution which obeys the *detailed balance* condition,

$$f_1^{\text{eq}}(\vec{r}, \vec{p}'_1) f_1^{\text{eq}}(\vec{r}, \vec{p}'_2) = f_1^{\text{eq}}(\vec{r}, \vec{p}) f_1^{\text{eq}}(\vec{r}, \vec{p}_2) \quad (2.25)$$

In fact, it's more useful to write this as

$$\log(f_1^{\text{eq}}(\vec{r}, \vec{p}'_1)) + \log(f_1^{\text{eq}}(\vec{r}, \vec{p}'_2)) = \log(f_1^{\text{eq}}(\vec{r}, \vec{p})) + \log(f_1^{\text{eq}}(\vec{r}, \vec{p}_2)) \quad (2.26)$$

How can we ensure that this is true for all momenta? The momenta on the right are those before the collision; on the left they are those after the collision. From the form of (2.26), it's clear that the sum of $\log f_1^{\text{eq}}$ must be the same before and after the collision: in other words, this sum must be conserved during the collision. But we know what things are conserved during collisions: momentum and energy as shown in (2.18) and (2.19) respectively. This means that we should take

$$\log(f_1^{\text{eq}}(\vec{r}, \vec{p})) = \beta (\mu - E(\vec{p}) + \vec{u} \cdot \vec{p}) \quad (2.27)$$

where $E(p) = p^2/2m$ for non-relativistic particles and μ , β and \vec{u} are all constants. We'll adjust the constant μ to ensure that the overall normalization of f_1 obeys (2.6). Then, writing $\vec{p} = m\vec{v}$, we have

$$f_1^{\text{eq}}(\vec{r}, \vec{p}) = \frac{N}{V} \left(\frac{\beta}{2\pi m} \right)^{3/2} e^{-\beta m(\vec{v} - \vec{u})^2/2} \quad (2.28)$$

which reproduces the Maxwell-Boltzmann distribution if we identify β with the inverse temperature. Here \vec{u} allows for the possibility of an overall drift velocity. We learn that the addition of the collision term to the Liouville equation forces us to sit in the Boltzmann distribution at equilibrium.

There is a comment to make here that will play an important role in Section 2.4. If we forget about the streaming term $\{H_1, f_1\}$ then there is a much larger class of solutions to the requirement of detailed balance (2.25). These solutions are again of the form (2.27), but now with the constants μ , β and \vec{u} promoted to functions of space and time. In other words, we can have

$$f_1^{\text{local}}(\vec{r}, \vec{p}; t) = n(\vec{r}, t) \left(\frac{\beta(\vec{r}, t)}{2\pi m} \right)^{3/2} \exp \left(-\beta(\vec{r}, t) \frac{m}{2} [(\vec{v} - \vec{u}(\vec{r}, t))]^2 \right) \quad (2.29)$$

Such a distribution is not quite an equilibrium distribution, for while the collision integral in (2.23) vanishes, the streaming term does not. Nonetheless, distributions of this kind will prove to be important in what follows. They are said to be in *local equilibrium*, with the particle density, temperature and drift velocity varying over space.

The Quantum Boltzmann Equation

Our discussion above was entirely for classical particles and this will continue to be our focus for the remainder of this section. However, as a small aside let's look at how

things change for quantum particles. We'll keep the assumption of molecular chaos, so $f_2 \sim f_1 f_1$ as in (2.22). The main difference occurs in the scattering rate (2.17) for scattering $\vec{p}_1 + \vec{p}_2 \rightarrow \vec{p}'_1 + \vec{p}'_2$ which now becomes

$$\text{Rate} = \omega(\vec{p}, \vec{p}_2 | \vec{p}'_1, \vec{p}'_2) f_1(\vec{p}_1) f_1(\vec{p}_2) \{1 \pm f_1(\vec{p}'_1)\} \{1 \pm f_1(\vec{p}'_2)\} d^3 p_2 d^3 p'_1 d^3 p'_2$$

The extra terms are in curly brackets. We pick the + sign for bosons and the – sign for fermions. The interpretation is particularly clear for fermions, where the number of particles in a given state can't exceed one. Now it's not enough to know the probability that initial state is filled. We also need to know that probability that the final state is free for the particle to scatter into: and that's what the $\{1 - f_1\}$ factors are telling us.

The remaining arguments go forward as before, resulting in the quantum Boltzmann equation

$$\left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}} = \int d^3 p_2 d^3 p'_1 d^3 p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}, \vec{p}_2) \left[f_1(\vec{p}'_1) f_1(\vec{p}'_2) \{1 \pm f_1(\vec{p})\} \{1 \pm f_1(\vec{p}_2)\} \right. \\ \left. - f_1(\vec{p}) f_1(\vec{p}_2) \{1 \pm f_1(\vec{p}'_1)\} \{1 \pm f_1(\vec{p}'_2)\} \right]$$

To make contact with what we know, we can look again at the requirement for equilibrium. The condition of detailed balance now becomes

$$\log\left(\frac{f_1^{\text{eq}}(\vec{p}'_1)}{1 \pm f_1^{\text{eq}}(\vec{p}'_1)}\right) + \log\left(\frac{f_1^{\text{eq}}(\vec{p}'_2)}{1 \pm f_1^{\text{eq}}(\vec{p}'_2)}\right) = \log\left(\frac{f_1^{\text{eq}}(\vec{p})}{1 \pm f_1^{\text{eq}}(\vec{p})}\right) + \log\left(\frac{f_1^{\text{eq}}(\vec{p}_2)}{1 \pm f_1^{\text{eq}}(\vec{p}_2)}\right)$$

Which is again solved by relating each log to a linear combination of the energy and momentum. We find

$$f_1^{\text{eq}}(\vec{p}) = \frac{1}{e^{-\beta(\mu - E(\vec{p}) + \vec{u} \cdot \vec{p})} \mp 1}$$

which reproduces the Bose-Einstein and Fermi-Dirac distributions.

2.2.3 A Better Derivation

In Section (2.2.1), we derived an expression for the collision integral (2.24) using intuition for the scattering processes at play. But, of course, we have a mathematical expression for the collision integral in (2.13) involving the two-particle distribution function f_2 . In this section we will sketch how one can derive (2.24) from (2.13). This will help clarify some of the approximations that we need to use. At the same time, we will also review some basic classical mechanics that connects the scattering rate ω to the inter-particle potential $U(r)$.

We start by returning to the BBGKY hierarchy of equations. For simplicity, we'll turn off the external potential $V(\vec{r}) = 0$. We don't lose very much in doing this because most of the interesting physics is concerned with the scattering of atoms off each other. The first two equations in the hierarchy are

$$\left(\frac{\partial}{\partial t} + \frac{\vec{p}_1}{m} \cdot \frac{\partial}{\partial \vec{r}_1} \right) f_1 = \int d^3 r_2 d^3 p_2 \frac{\partial U(\vec{r}_1 - \vec{r}_2)}{\partial \vec{r}_1} \cdot \frac{\partial f_2}{\partial \vec{p}_1} \quad (2.30)$$

and

$$\left(\frac{\partial}{\partial t} + \frac{\vec{p}_1}{m} \cdot \frac{\partial}{\partial \vec{r}_1} + \frac{\vec{p}_2}{m} \cdot \frac{\partial}{\partial \vec{r}_2} - \frac{1}{2} \frac{\partial U(\vec{r}_1 - \vec{r}_2)}{\partial \vec{r}_1} \cdot \left[\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2} \right] \right) f_2 = \int d^3 r_3 d^3 p_3 \left(\frac{\partial U(\vec{r}_1 - \vec{r}_3)}{\partial \vec{r}_1} \cdot \frac{\partial}{\partial \vec{p}_1} + \frac{\partial U(\vec{r}_2 - \vec{r}_3)}{\partial \vec{r}_2} \cdot \frac{\partial}{\partial \vec{p}_2} \right) f_3 \quad (2.31)$$

In both of these equations, we've gathered the streaming terms on the left, leaving only the higher distribution function on the right. To keep things clean, we've suppressed the arguments of the distribution functions: they are $f_1 = f_1(\vec{r}_1, \vec{p}_1; t)$ and $f_2 = f_2(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2; t)$ and you can guess the arguments for f_3 .

Our goal is to better understand the collision integral on the right-hand-side of (2.30). It seems reasonable to assume that when particles are far-separated, their distribution functions are uncorrelated. Here, "far separated" means that the distance between them is much farther than the atomic distance scale d over which the potential $U(r)$ extends. We expect

$$f_2(\vec{r}_1, \vec{r}_2, \vec{p}_1, \vec{p}_2; t) \rightarrow f_1(\vec{r}_1, \vec{p}_1; t) f_1(\vec{r}_2, \vec{p}_2; t) \quad \text{when } |\vec{r}_1 - \vec{r}_2| \gg d$$

But, a glance at the right-hand-side of (2.30) tells us that this isn't the regime of interest. Instead, f_2 is integrated $\partial U(r)/\partial r$ which varies significantly only over a region $r \leq d$. This means that we need to understand f_2 when two particles get close to each other.

We'll start by getting a feel for the order of magnitude of various terms in the hierarchy of equations. Dimensionally, each term in brackets in (2.30) and (2.31) is an inverse time scale. The terms involving the inter-atomic potential $U(r)$ are associated to the collision time τ_{coll} .

$$\frac{1}{\tau_{\text{coll}}} \sim \frac{\partial U}{\partial \vec{r}} \cdot \frac{\partial}{\partial \vec{p}}$$

This is the time taken for a particle to cross the distance over which the potential $U(r)$ varies which, for short range potentials, is comparable to the atomic distance scale, d ,

itself and

$$\tau_{\text{coll}} \sim \frac{d}{\bar{v}_{\text{rel}}}$$

where \bar{v}_{rel} is the average relative speed between atoms. Our first approximation will be that this is the shortest time scale in the problem. This means that the terms involving $\partial U/\partial r$ are typically the largest terms in the equations above and determine how fast the distribution functions change.

With this in mind, we note that the equation for f_1 is special because it is the only one which does not include any collision terms on the left of the equation (i.e. in the Hamiltonian H_n). This means that the collision integral on the right-hand side of (2.30) will usually dominate the rate of change of f_1 . (Note, however, we'll meet some important exceptions to this statement in Section 2.4). In contrast, the equation that governs f_2 has collision terms on the both the left and the right-hand sides. But, importantly, for dilute gases, the term on the right is much smaller than the term on the left. To see why this is, we need to compare the f_3 term to the f_2 term. If we were to integrate f_3 over all space, we get

$$\int d^3r_2 d^3p_3 f_3 = N f_2$$

(where we've replaced $(N - 2) \approx N$ in the above expression). However, the right-hand side of (2.31) is not integrated over all of space. Instead, it picks up a non-zero contribution over an atomic scale $\sim d^3$. This means that the collision term on the right-hand-side of (2.31) is suppressed compared to the one on the left by a factor of Nd^3/V where V is the volume of space. For gases that we live and breath every day, $Nd^3/V \sim 10^{-3} - 10^{-4}$. We make use of this small number to truncate the hierarchy of equations and replace (2.31) with

$$\left(\frac{\partial}{\partial t} + \frac{\vec{p}_1}{m} \cdot \frac{\partial}{\partial \vec{r}_1} + \frac{\vec{p}_2}{m} \cdot \frac{\partial}{\partial \vec{r}_2} - \frac{1}{2} \frac{\partial U(\vec{r}_1 - \vec{r}_2)}{\partial \vec{r}_1} \cdot \left[\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2} \right] \right) f_2 \approx 0 \quad (2.32)$$

This tells us that f_2 typically varies on a time scale of τ_{coll} and a length scale of d . Meanwhile, the variations of f_1 is governed by the right-hand-side of (2.30) which, by the same arguments that we just made, are smaller than the variations of f_2 by a factor of Nd^3/V . In other words, f_1 varies on the larger time scale τ .

In fact, we can be a little more careful when we say that f_2 varies on a time scale τ_{coll} . We see that – as we would expect – only the relative position is affected by the

collision term. For this reason, it's useful to change coordinate to the centre of mass and the relative positions of the two particles. We write

$$\vec{R} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2) \quad , \quad \vec{r} = \vec{r}_1 - \vec{r}_2$$

and similar for the momentum

$$\vec{P} = \vec{p}_1 + \vec{p}_2 \quad , \quad \vec{p} = \frac{1}{2}(\vec{p}_1 - \vec{p}_2)$$

And we can think of $f_2 = f_2(\vec{R}, \vec{r}, \vec{P}, \vec{p}; t)$. The distribution function will depend on the centre of mass variables \vec{R} and \vec{P} in some slow fashion, much as f_1 depends on position and momentum. In contrast, the dependence of f_2 on the relative coordinates \vec{r} and \vec{p} is much faster – these vary over the short distance scale and can change on a time scale of order τ_{coll} .

Since the relative distributions in f_2 vary much more quickly than f_1 , we'll assume that f_2 reaches equilibrium and then feeds into the dynamics of f_1 . This means that, ignoring the slow variations in \vec{R} and \vec{P} , we will assume that $\partial f_2 / \partial t = 0$ and replace (2.32) with the equilibrium condition

$$\left(\frac{\vec{p}}{m} \cdot \frac{\partial}{\partial \vec{r}} - \frac{\partial U(\vec{r})}{\partial \vec{r}} \cdot \frac{\partial}{\partial \vec{p}} \right) f_2 \approx 0 \quad (2.33)$$

This is now in a form that allows us to start manipulating the collision integral on the right-hand-side of (2.30). We have

$$\begin{aligned} \left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} &= \int d^3 r_2 d^3 p_2 \frac{\partial U(\vec{r}_1 - \vec{r}_2)}{\partial \vec{r}_1} \cdot \frac{\partial f_2}{\partial \vec{p}_1} \\ &= \int d^3 r_2 d^3 p_2 \frac{\partial U(\vec{r})}{\partial \vec{r}} \cdot \left[\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2} \right] f_2 \\ &= \frac{1}{m} \int_{|\vec{r}_1 - \vec{r}_2| \leq d} d^3 r_2 d^3 p_2 (\vec{p}_1 - \vec{p}_2) \cdot \frac{\partial f_2}{\partial \vec{r}} \end{aligned} \quad (2.34)$$

where in the second line the extra term $\partial / \partial \vec{p}_2$ vanishes if we integrate by parts and, in the third line, we've used our equilibrium condition (2.33), with the limits on the integral in place to remind us that only the region $r \leq d$ contributes to the collision integral.

A Review of Scattering Cross Sections

To complete the story, we still need to turn (2.34) into the collision integral (2.24). But most of the work simply involves clarifying how the scattering rate $\omega(\vec{p}, \vec{p}_2 | \vec{p}'_1, \vec{p}'_2)$ is defined for a given inter-atomic potential $U(\vec{r}_1 - \vec{r}_2)$. And, for this, we need to review the concept of the *differential cross section*.

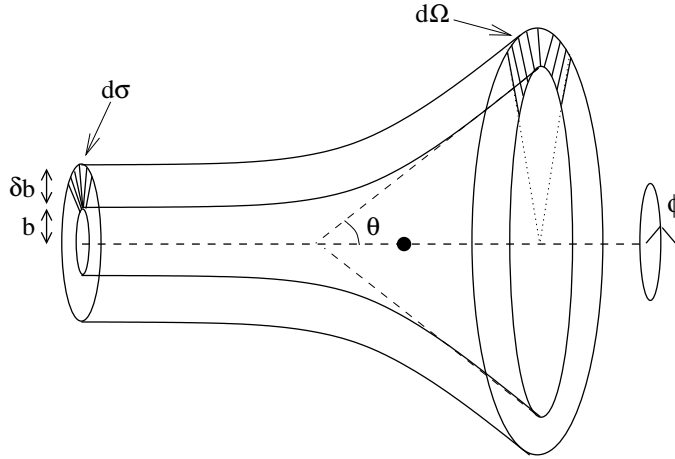


Figure 4: The differential cross section.

Let's think about the collision between two particles. They start with momenta $\vec{p}_i = m\vec{v}_i$ and end with momenta $\vec{p}'_i = m\vec{v}'_i$ with $i = 1, 2$. Now let's pick a favourite, say particle 1. We'll sit in its rest frame and consider an onslaught of bombarding particles, each with velocity $\vec{v}_2 - \vec{v}_1$. This beam of incoming particles do not all hit our favourite boy at the same point. Instead, they come in randomly distributed over the plane perpendicular to $\vec{v}_2 - \vec{v}_1$. The flux, I , of these incoming particles is the number hitting this plane per area per second,

$$I = \frac{N}{V} |\vec{v}_2 - \vec{v}_1|$$

Now spend some time staring at Figure 4. There are a number of quantities defined in this picture. First, the *impact parameter*, b , is the distance from the asymptotic trajectory to the dotted, centre line. We will use b and ϕ as polar coordinates to parameterize the plane perpendicular to the incoming particle. Next, the scattering angle, θ , is the angle by which the incoming particle is deflected. Finally, there are two solid angles, $d\sigma$ and $d\Omega$, depicted in the figure. Geometrically, we see that they are given by

$$d\sigma = b db d\phi \quad \text{and} \quad d\Omega = \sin \theta d\theta d\phi$$

The number of particles scattered into $d\Omega$ in unit time is $I d\sigma$. We usually write this as

$$I \frac{d\sigma}{d\Omega} = I b db d\phi \tag{2.35}$$

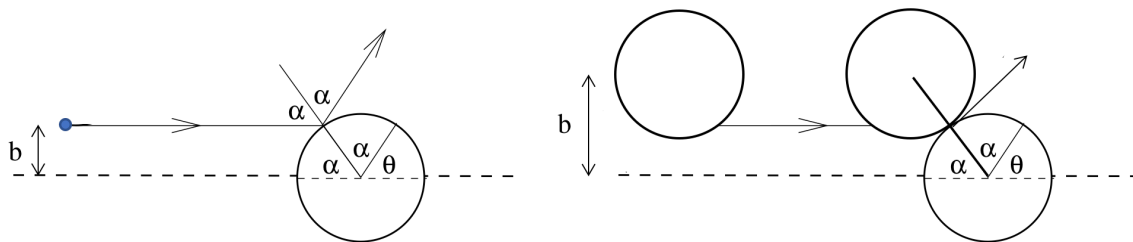


Figure 5: On the left: a point particle scattering off a hard sphere. On the right: a hard sphere scattering off a hard sphere.

where the *differential cross section* is defined as

$$\left| \frac{d\sigma}{d\Omega} \right| = \frac{b}{\sin \theta} \left| \frac{db}{d\theta} \right| = \frac{1}{2} \left| \frac{d(b^2)}{d \cos \theta} \right| \quad (2.36)$$

You should think of this in the following way: for a fixed $(\vec{v}_2 - \vec{v}_1)$, there is a unique relationship between the impact parameter b and the scattering angle θ and, for a given potential $U(r)$, you need to figure this out to get $|d\sigma/d\Omega|$ as a function of θ .

Now we can compare this to the notation that we used earlier in (2.17). There we talked about the rate of scattering into a small area $d^3p'_1 d^3p'_2$ in momentum space. But this is the same thing as the differential cross-section.

$$\omega(\vec{p}, \vec{p}_2; \vec{p}'_1, \vec{p}'_2) d^3p'_1 d^3p'_2 = |\vec{v} - \vec{v}_2| \left| \frac{d\sigma}{d\Omega} \right| d\Omega \quad (2.37)$$

(Note, if you're worried about the fact that $d^3p'_1 d^3p'_2$ is a six-dimensional area while $d\Omega$ is a two dimensional area, recall that conservation of energy and momenta provide four restrictions on the ability of particles to scatter. These are implicit on the left, but explicit on the right).

An Example: Hard Spheres

In Section 1.2, we modelled atoms as hard spheres of diameter d . It's instructive to figure out the cross-section for such a hard sphere.

In fact, there are two different calculations that we can do. First, suppose that we throw point-like particles at a sphere of diameter d with an impact parameter $b \leq d/2$. From the left-hand diagram in Figure 5, we see that the scattering angle is $\theta = \pi - 2\alpha$, where

$$b = \frac{d}{2} \sin \alpha = \frac{d}{2} \sin \left(\frac{\pi}{2} - \frac{\theta}{2} \right) = \frac{d}{2} \cos \frac{\theta}{2}$$

or

$$b^2 = \frac{d^2}{4} \cos^2 \frac{\theta}{2} = \frac{d^2}{8} (1 + \cos \theta)$$

From (2.36), we then find the differential cross-section

$$\left| \frac{d\sigma}{d\Omega} \right| = \frac{d^2}{16}$$

The total cross-section is defined as

$$\sigma_T = 2\pi \int_0^\pi d\theta \sin \theta \frac{d\sigma}{d\Omega} = \pi \left(\frac{d}{2} \right)^2$$

This provides a nice justification for the name because this is indeed the cross-sectional area of a sphere of radius $d/2$.

Alternatively, we could consider two identical hard spheres, each of diameter d , one scattering off the other. Now the geometry changes a little, as shown in the right-hand diagram in Figure 5. The impact parameter is now the distance between the centres of the spheres, and given by

$$b = 2 \times \frac{d}{2} \sin \alpha$$

Clearly we now need $b \leq d$. The same calculation as above now gives

$$\sigma_T = \pi d^2$$

This is the same effective cross-sectional area that we previously used back in Section 1.2 when discussing basic aspects of collisions.

Almost Done

With this refresher course on classical scattering, we can return to the collision integral (2.34) in the Boltzmann equation.

$$\left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} = \int_{|\vec{r}_1 - \vec{r}_2| \leq d} d^3 r_2 d^3 p_2 (\vec{v}_1 - \vec{v}_2) \cdot \frac{\partial f_2}{\partial \vec{r}}$$

We'll work in cylindrical polar coordinates shown in Figure 6. The direction parallel to $\vec{v}_2 - \vec{v}_1$ is parameterized by x ; the plane perpendicular is parameterised by ϕ and

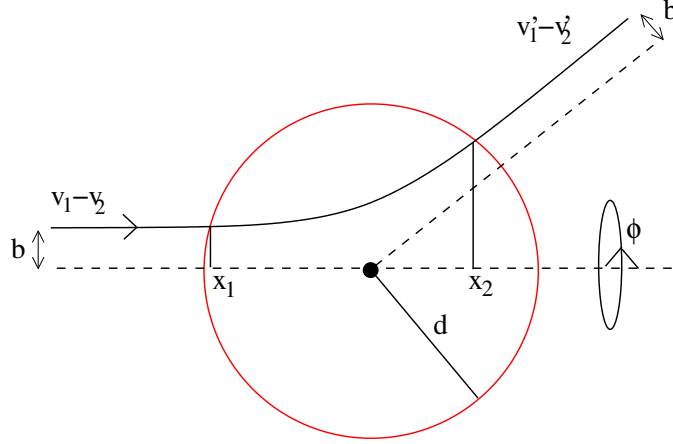


Figure 6: Two particle scattering

the impact parameter b . We've also shown the collision zone in this figure. Using the definitions (2.35) and (2.37), we have

$$\begin{aligned} \left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} &= \int d^3 p_2 |\vec{v}_1 - \vec{v}_2| \int d\phi db b \int_{x_1}^{x_2} \frac{\partial f_2}{\partial x} \\ &= \int d^3 p_2 d^3 p'_1 d^3 p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}, \vec{p}_2) [f_2(x_2) - f_2(x_1)] \end{aligned}$$

It remains only to decide what form the two-particle distribution function f_2 takes just before the collision at $x = x_1$ and just after the collision at $x = x_2$. At this point we invoke the assumption of molecular chaos. Just before we enter the collision, we assume that the two particles are uncorrelated. Moreover, we assume that the two particles are once again uncorrelated by the time they leave the collision, albeit now with their new momenta

$$f_2(x_1) = f_1(\vec{r}, \vec{p}_1; t) f_1(\vec{r}, \vec{p}_2; t) \quad \text{and} \quad f_2(x_2) = f_1(\vec{r}, \vec{p}'_1; t) f_1(\vec{r}, \vec{p}'_2; t)$$

Notice that all functions f_1 are evaluated at the same point \vec{r} in space since we've assumed that the single particle distribution function is suitably coarse grained that it doesn't vary on scales of order d . With this final assumption, we get what we wanted: the collision integral is given by

$$\left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} = \int d^3 p_2 d^3 p'_1 d^3 p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}, \vec{p}_2) \left[f_1(\vec{r}, \vec{p}'_1) f_1(\vec{r}, \vec{p}'_2) - f_1(\vec{r}, \vec{p}) f_1(\vec{r}, \vec{p}_2) \right]$$

in agreement with (2.24).

2.3 The H-Theorem

The topics of thermodynamics and statistical mechanics are all to do with the equilibrium properties of systems. One of the key intuitive ideas that underpins their importance is that if you wait long enough, any system will eventually settle down to equilibrium. But how do we know this? Moreover, it seems that it would be rather tricky to prove: settling down to equilibrium clearly involves an arrow of time that distinguishes the future from the past. Yet the underlying classical mechanics is invariant under time reversal.

The purpose of this section is to demonstrate that, within the framework of the Boltzmann equation, systems do indeed settle down to equilibrium. As we described above, we have introduced an arrow of time into the Boltzmann equation. We didn't do this in any crude way like adding friction to the system. Instead, we merely assumed that particle velocities were uncorrelated before collisions. That would seem to be a rather minor input but, as we will now show, it's enough to demonstrate the approach to equilibrium.

Specifically, we will prove the “H-theorem”, named after a quantity H introduced by Boltzmann. (H is not to be confused with the Hamiltonian. Boltzmann originally called this quantity something like a German \mathcal{E} , but the letter was somehow lost in translation and the name H stuck). This quantity is

$$H(t) = \int d^3r d^3p f_1(\vec{r}, \vec{p}; t) \log(f_1(\vec{r}, \vec{p}; t))$$

This kind of expression is familiar from our first [Statistical Mechanics](#) course where we saw that the entropy S for a probability distribution p is $S = -k_B p \log p$. In other words, this quantity H is simply

$$S = -k_B H$$

The H-theorem, first proven by Boltzmann in 1872, is the statement that H always decreases with time. The entropy always increases. We will now prove this.

As in the derivation (2.4), when you're looking at the variation of expectation values you only care about the explicit time dependence, meaning

$$\frac{dH}{dt} = \int d^3r d^3p (\log f_1 + 1) \frac{\partial f_1}{\partial t} = \int d^3r d^3p \log f_1 \frac{\partial f_1}{\partial t}$$

where we can drop the +1 because $\int f_1 = N$ is unchanging, ensuring that $\int \partial f_1 / \partial t = 0$. Using the Boltzmann equation (2.23), we have

$$\frac{dH}{dt} = \int d^3r d^3p \log f_1 \left(\frac{\partial V}{\partial \vec{r}} \cdot \frac{\partial f_1}{\partial \vec{p}} - \frac{\vec{p}}{m} \cdot \frac{\partial f_1}{\partial \vec{r}} + \left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} \right)$$

But the first two terms in this expression both vanish. You can see this by integrating by parts twice, first moving the derivative away from f_1 and onto $\log f_1$, and then moving it back. We learn that the change in H is governed entirely by the collision terms

$$\begin{aligned} \frac{dH}{dt} &= \int d^3r d^3p \log f_1 \left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} \\ &= \int d^3r d^3p_1 d^3p_2 d^3p'_1 d^3p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}_1, \vec{p}_2) \log f_1(\vec{p}_1) \\ &\quad \times \left[f_1(\vec{p}'_1) f_1(\vec{p}'_2) - f_1(\vec{p}_1) f_1(\vec{p}_2) \right] \end{aligned} \quad (2.38)$$

where I've suppressed \vec{r} and t arguments of f_1 to keep things looking vaguely reasonable. I've also relabelled the integration variable $\vec{p} \rightarrow \vec{p}_1$. At this stage, all momenta are integrated over so they are really nothing but dummy variables. Let's relabel $1 \leftrightarrow 2$ on the momenta. All the terms remain unchanged except the log. So we can also write

$$\begin{aligned} \frac{dH}{dt} &= \int d^3r d^3p_1 d^3p_2 d^3p'_1 d^3p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}_1, \vec{p}_2) \log f_1(\vec{p}_2) \\ &\quad \times \left[f_1(\vec{p}'_1) f_1(\vec{p}'_2) - f_1(\vec{p}_1) f_1(\vec{p}_2) \right] \end{aligned} \quad (2.39)$$

Adding (2.38) and (2.39), we have the more symmetric looking expression

$$\begin{aligned} \frac{dH}{dt} &= \frac{1}{2} \int d^3r d^3p_1 d^3p_2 d^3p'_1 d^3p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}_1, \vec{p}_2) \log [f_1(\vec{p}_1) f_1(\vec{p}_2)] \\ &\quad \times \left[f_1(\vec{p}'_1) f_1(\vec{p}'_2) - f_1(\vec{p}_1) f_1(\vec{p}_2) \right] \end{aligned} \quad (2.40)$$

Since all momenta are integrated over, we're allowed to just flip the dummy indices again. This time we swap $\vec{p} \leftrightarrow \vec{p}'$ in the above expression. But, using the symmetry property (2.20), the scattering function remains unchanged³. We get

$$\frac{dH}{dt} = -\frac{1}{2} \int d^3r d^3p_1 d^3p_2 d^3p'_1 d^3p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}_1, \vec{p}_2) \log [f_1(\vec{p}'_1) f_1(\vec{p}'_2)]$$

³An aside: it's not actually necessary to assume (2.20) to make this step. We can get away with the weaker result

$$\int d^3p'_1 d^3p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}_1, \vec{p}_2) = \int d^3p'_1 d^3p'_2 \omega(\vec{p}_1, \vec{p}_2 | \vec{p}'_1, \vec{p}'_2)$$

which follows from unitarity of the scattering matrix.

$$\times \left[f_1(\vec{p}'_1) f_1(\vec{p}'_2) - f_1(\vec{p}_1) f_1(\vec{p}_2) \right] \quad (2.41)$$

Finally, we add (2.40) and (2.41) to get

$$\begin{aligned} \frac{dH}{dt} = & -\frac{1}{4} \int d^3r d^3p_1 d^3p_2 d^3p'_1 d^3p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}_1, \vec{p}_2) \times \\ & \left[\log [f_1(\vec{p}'_1) f_1(\vec{p}'_2)] - \log [f_1(\vec{p}_1) f_1(\vec{p}_2)] \right] \left[f_1(\vec{p}'_1) f_1(\vec{p}'_2) - f_1(\vec{p}_1) f_1(\vec{p}_2) \right] \end{aligned} \quad (2.42)$$

The bottom line of this expression is a function $(\log x - \log y)(x - y)$. It is positive for all values of x and y . Since the scattering rate is also positive, we have the proof of the H-theorem.

$$\frac{dH}{dt} \leq 0 \quad \Leftrightarrow \quad \frac{dS}{dt} \geq 0$$

And there we see the arrow of time seemingly emerging from time-invariant Hamiltonian mechanics! Clearly, this should be impossible, a point first made by Loschmidt soon after Boltzmann's original derivation. But, as we saw earlier, everything hinges on the assumption of molecular chaos (2.22). This was where we broke time-reversal symmetry, ultimately ensuring that entropy increases only in the future. Had we instead decided in (2.21) that the rate of scattering was proportional to f_2 *after* the collision, again assuming $f_2 \sim f_1 f_1$ then we would find that entropy always decreases as we move into the future.

There is much discussion in the literature about the importance of the H-theorem and its relationship to the second law of thermodynamics. Notably, it is not particularly hard to construct states which violate the H-theorem by virtue of their failure to obey the assumption of molecular chaos. Nonetheless, these states still obey a suitable second law of thermodynamics⁴.

The H-theorem is not a strict inequality. For some distributions, the entropy remains unchanged. From (2.42), we see that these obey

$$f_1(\vec{p}'_1) f_1(\vec{p}'_2) - f_1(\vec{p}_1) f_1(\vec{p}_2)$$

But this is simply the requirement of detailed balance (2.25). And, as we have seen already, this is obeyed by any distribution satisfying the requirement of local equilibrium (2.29).

⁴This was first pointed out by E. T. Jaynes in the paper “*Violation of Boltzmann's H Theorem in Real Gases*”, published in Physical Review A, volume 4, number 2 (1971).

2.4 A First Look at Hydrodynamics

Hydrodynamics is what you get if you take thermodynamics and splash it. You know from your first course on [Statistical Mechanics](#) that, at the most coarse grained level, the equilibrium properties of any system are governed by the thermodynamics. In the same manner, low energy, long wavelength, excitations of any system are described by hydrodynamics.

More precisely, hydrodynamics describes the dynamics of systems that are in local equilibrium, with parameters that vary slowly in space in time. As we will see, this means that the relevant dynamical variables are, in the simplest cases,

- Density $\rho(\vec{r}, t) = m n(\vec{r}, t)$
- Temperature $T(\vec{r}, t)$
- Velocity $\vec{u}(\vec{r}, t)$

Our goal in this section is to understand why these are the relevant variables to describe the system and to derive the equations that govern their dynamics.

2.4.1 Conserved Quantities

We'll start by answering the first question: why are these the variables of interest? The answer is that these are quantities which don't relax back down to their equilibrium value in an atomic blink of an eye, but instead change on a much slower, domestic time scale. At heart, the reason for they have this property is that they are all associated to conserved quantities. Let's see why.

Consider a general function $A(\vec{r}, \vec{p})$ over the single particle phase space. Because we live in real space instead of momentum space, the question of how things vary with \vec{r} is more immediately interesting. For this reason, we integrate over momentum and define the average of a quantity $A(\vec{r}, \vec{p})$ to be

$$\langle A(\vec{r}, t) \rangle = \frac{\int d^3p A(\vec{r}, \vec{p}) f_1(\vec{r}, \vec{p}; t)}{\int d^3p f_1(\vec{r}, \vec{p}; t)}$$

However, we've already got a name for the denominator in this expression: it is the number density of particles

$$n(\vec{r}, t) = \int d^3p f_1(\vec{r}, \vec{p}; t) \tag{2.43}$$

(As a check of the consistency of our notation, if you plug the local equilibrium distribution (2.29) into this expression, then the $n(\vec{r}, t)$ on the left-hand-side equals the $n(\vec{r}, t)$ defined in (2.29)). So the average is

$$\langle A(\vec{r}, t) \rangle = \frac{1}{n(\vec{r}, t)} \int d^3p A(\vec{r}, \vec{p}) f_1(\vec{r}, \vec{p}; t) \quad (2.44)$$

It's worth making a couple of simple remarks. Firstly, this is different from the average that we defined earlier in (2.3) when discussing Liouville evolution. Here we're integrating only over momenta and the resulting average is a function of space. A related point is that we're at liberty to take functions which depend only on \vec{r} (and not on \vec{p}) in and out of the $\langle \cdot \rangle$ brackets. So, for example, $\langle nA \rangle = n\langle A \rangle$.

We're interested in how the average of A changes with time. We looked at this kind of question for Liouville evolution earlier in this section and found the answer (2.5). Now we want to ask the same question for the Boltzmann equation. Before we actually write down the answer, you can guess what it will look like: there will be a streaming term and a term due to the collision integral. Moreover, we know from our previous discussion that the term involving the collision integral will vary much faster than the streaming term.

Since we're ultimately interested in quantities which vary slowly, this motivates looking at functions A which vanish when integrated against the collision integral. We will see shortly that the relevant criterion is

$$\int d^3p A(\vec{r}, \vec{p}) \left(\frac{\partial f_1}{\partial t} \right)_{\text{coll}} = 0$$

We'd like to find quantities A which have this property for any distribution f_1 . Using our expression for the collision integral (2.23), we want

$$\int d^3p_1 d^3p_2 d^3p'_1 d^3p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}_1, \vec{p}_2) A(\vec{r}, \vec{p}_1) \left[f_1(\vec{r}, \vec{p}'_1) f_1(\vec{r}, \vec{p}'_2) - f_1(\vec{r}, \vec{p}_1) f_1(\vec{r}, \vec{p}_2) \right] = 0$$

This now looks rather similar to equation (2.38), just with the $\log f$ replaced by A . Indeed, we can follow the steps between (2.38) and (2.41), using the symmetry properties of ω , to massage this into the form

$$\begin{aligned} \int d^3p_1 d^3p_2 d^3p'_1 d^3p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}_1, \vec{p}_2) & \left[f_1(\vec{p}'_1) f_1(\vec{p}'_2) - f_1(\vec{p}_1) f_1(\vec{p}_2) \right] \\ & \times \left[A(\vec{r}, \vec{p}_1) + A(\vec{r}, \vec{p}_2) - A(\vec{r}, \vec{p}'_1) - A(\vec{r}, \vec{p}'_2) \right] = 0 \end{aligned}$$

Now it's clear that if we want this to vanish for all distributions, then A itself must have the property that it remains unchanged before and after the collision,

$$A(\vec{r}, \vec{p}_1) + A(\vec{r}, \vec{p}_2) = A(\vec{r}, \vec{p}'_1) + A(\vec{r}, \vec{p}'_2) \quad (2.45)$$

Quantities which obey this are sometimes called *collisional invariants*. Of course, in the simplest situation we already know what they are: momentum (2.18) and energy (2.19) and, not forgetting, the trivial solution $A = 1$. We'll turn to each of these in turn shortly. But first let's derive an expression for the time evolution of any quantity obeying (2.45).

Take the Boltzmann equation (2.23), multiply by a collisional invariant $A(\vec{r}, \vec{p})$ and integrate over $\int d^3p$. Because the collision term vanishes, we have

$$\int d^3p A(\vec{r}, \vec{p}) \left(\frac{\partial}{\partial t} + \frac{\vec{p}}{m} \cdot \frac{\partial}{\partial \vec{r}} + \vec{F} \cdot \frac{\partial}{\partial \vec{p}} \right) f_1(\vec{r}, \vec{p}, t) = 0$$

where the external force is $\vec{F} = -\nabla V$. We'll integrate the last term by parts (remembering that the force \vec{F} can depend on position but not on momentum). We can't integrate the middle term by parts since we're not integrating over space, but nonetheless, we'll also rewrite it. Finally, since A has no explicit time dependence, we can take it inside the time derivative. We have

$$\frac{\partial}{\partial t} \int d^3p A f + \frac{\partial}{\partial \vec{r}} \cdot \int d^3p \frac{\vec{p}}{m} A f - \int d^3p \frac{\vec{p}}{m} \cdot \frac{\partial A}{\partial \vec{r}} f - \int d^3p \vec{F} \cdot \frac{\partial A}{\partial \vec{p}} f = 0$$

Although this doesn't really look like an improvement, the advantage of writing it in this way is apparent when we remember our expression for the average (2.44). Using this notation, we can write the evolution of A as

$$\frac{\partial}{\partial t} \langle nA \rangle + \frac{\partial}{\partial \vec{r}} \cdot \langle n\vec{v}A \rangle - n \langle \vec{v} \cdot \frac{\partial A}{\partial \vec{r}} \rangle - n \langle \vec{F} \cdot \frac{\partial A}{\partial \vec{p}} \rangle = 0 \quad (2.46)$$

where $\vec{v} = \vec{p}/m$. This is our master equation that tells us how any collisional invariant changes. The next step is to look at specific quantities. There are three and we'll take each in turn

Density

Our first collisional invariant is the trivial one: $A = 1$. If we plug this into (2.46) we get the equation for the particle density $n(\vec{r}, t)$,

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial \vec{r}} \cdot (n\vec{u}) \quad (2.47)$$

where the average velocity \vec{u} of the particles is defined by

$$\vec{u}(\vec{r}, t) = \langle \vec{v} \rangle$$

Notice that, once again, our notation is consistent with earlier definitions: if we pick the local equilibrium distribution (2.29), the $\vec{u}(\vec{r}, t)$ in (2.29) agrees with that defined above. The result (2.47) is the continuity equation, expressing the conservation of particle number. Notice, however, that this is not a closed expression for the particle density n : we need to know the velocity \vec{u} as well.

It's useful to give a couple of extra, trivial, definitions at this stage. First, although we won't use this notation, the continuity equation is sometimes written in terms of the *current*, $\vec{J}(\vec{r}, t) = n(\vec{r}, t) \vec{u}(\vec{r}, t)$. In what follows, we will often replace the particle density with the mass density,

$$\rho(\vec{r}, t) = mn(\vec{r}, t)$$

Momentum

Our next collisional invariant is the momentum. We substitute $A = m\vec{v}$ into (2.46) to find

$$\frac{\partial}{\partial t} \langle mnv_i \rangle + \frac{\partial}{\partial r_j} \langle mnv_j v_i \rangle - \langle nF_i \rangle = 0 \quad (2.48)$$

We can play around with the middle term a little. We write

$$\begin{aligned} \langle v_j v_i \rangle &= \langle (v_j - u_j)(v_i - u_i) \rangle + u_i \langle v_j \rangle + u_j \langle v_i \rangle - u_i u_j \\ &= \langle (v_j - u_j)(v_i - u_i) \rangle + u_i u_j \end{aligned}$$

We define a new object known as the pressure tensor,

$$P_{ij} = P_{ji} = \rho \langle (v_j - u_j)(v_i - u_i) \rangle$$

This tensor is computing the flux of i -momentum in the j -direction. It's worth pausing to see why this is related to pressure. Clearly, the exact form of P_{ij} depends on the distribution of particles. But, we can evaluate the pressure tensor on the equilibrium, Maxwell-Boltzmann distribution (2.28). The calculation boils down to the same one we did in our first [Statistical Physics](#) course to compute equipartition: you find

$$P_{ij} = nk_B T \delta_{ij} \quad (2.49)$$

which, by the ideal gas law, is proportional to the pressure of the gas. Using this definition – together with the continuity equation (2.47) – we can write (2.48) as

$$\rho \left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \right) u_i = \frac{\rho}{m} F_i - \frac{\partial}{\partial r_j} P_{ij} \quad (2.50)$$

This is the equation which captures momentum conservation in our system. Indeed, it has a simple interpretation in terms of Newton’s second law. The left-hand-side is the acceleration of an element of fluid. The combination of derivatives is sometimes called the *material derivative*,

$$D_t \equiv \frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \quad (2.51)$$

It captures the rate of change of a quantity as seen by an observer swept along the streamline of the fluid. The right-hand side of (2.50) includes both the external force \vec{F} and an additional term involving the internal pressure of the fluid. As we will see later, ultimately viscous terms will also come from here.

Note that, once again, the equation (2.50) does not provide a closed equation for the velocity \vec{u} . You now need to know the pressure tensor P_{ij} which depends on the particular distribution.

Kinetic Energy

Our final collisional invariant is the kinetic energy of the particles. However, rather than take the absolute kinetic energy, it is slightly easier if we work with the relative kinetic energy,

$$A = \frac{1}{2} m (\vec{v} - \vec{u})^2$$

If we substitute this into the master equation⁵ (2.46), the term involving the force vanishes (because $\langle v_i - u_i \rangle = 0$). However, the term that involves $\partial E / \partial r_i$ is not zero because the average velocity \vec{u} depends on \vec{r} . We have

$$\frac{1}{2} \frac{\partial}{\partial t} \langle \rho (\vec{v} - \vec{u})^2 \rangle + \frac{1}{2} \frac{\partial}{\partial r_i} \langle \rho v_i (\vec{v} - \vec{u})^2 \rangle - \rho \langle v_i \frac{\partial u_j}{\partial r_i} (\vec{v} - \vec{u})^2 \rangle = 0 \quad (2.52)$$

⁵There is actually a subtlety here. In deriving the master equation (2.46), we assumed that A has no explicit time dependence, but the A defined above does have explicit time dependence through $\vec{u}(\vec{r}, t)$. Nonetheless, you can check that (2.46) still holds, essentially because the extra term that you get is $\sim \langle (\vec{v} - \vec{u}) \cdot \partial \vec{u} / \partial t \rangle = \langle \vec{v} - \vec{u} \rangle \cdot \partial \vec{u} / \partial t = 0$.

At this point, we define the *temperature*, $T(\vec{r}, t)$ of our non-equilibrium system. To do so, we fall back on the idea of equipartition and write

$$\frac{3}{2}mk_B T(\vec{r}, t) = \frac{1}{2}\langle(\vec{v} - \vec{u}(\vec{r}, t))^2\rangle \quad (2.53)$$

This coincides with our familiar definition of temperature for a system in local equilibrium (2.29), but now extends this to a system that is out of equilibrium. Note that the temperature is a close relative of the pressure tensor, $\text{Tr}P = 3m\rho k_B T$.

We also define a new quantity, the *heat flux*,

$$q_i = \frac{1}{2}m\rho\langle(v_i - u_i)(\vec{v} - \vec{u})^2\rangle \quad (2.54)$$

(This actually differs by an overall factor of m from the definition of \vec{q} that we made in Section 1. This has the advantage of making the formulae we're about to derive a little cleaner). The utility of both of these definitions becomes apparent if we play around with the middle term in (2.52). We can write

$$\begin{aligned} \frac{1}{2}m\rho\langle v_i(\vec{v} - \vec{u})^2\rangle &= \frac{1}{2}m\rho\langle(v_i - u_i)(\vec{v} - \vec{u})^2\rangle + \frac{1}{2}m\rho u_i\langle(\vec{v} - \vec{u})^2\rangle \\ &= q_i + \frac{3}{2}\rho u_i k_B T \end{aligned}$$

Invoking the definition of the pressure tensor (2.49), we can now rewrite (2.52) as

$$\frac{3}{2}\frac{\partial}{\partial t}(\rho k_B T) + \frac{\partial}{\partial r_i}\left(q_i + \frac{3}{2}\rho u_i k_B T\right) + mP_{ij}\frac{\partial u_j}{\partial x_i} = 0$$

Because $P_{ij} = P_{ji}$, we can replace $\partial u_j/\partial r_i$ in the last term with the symmetric tensor known as the *rate of strain* (and I promise this is the last new definition for a while!)

$$U_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial r_j} + \frac{\partial u_j}{\partial r_i}\right) \quad (2.55)$$

Finally, with a little help from the continuity equation (2.47), our expression for the conservation of energy becomes

$$\rho\left(\frac{\partial}{\partial t} + u_i\frac{\partial}{\partial r_i}\right)k_B T + \frac{2}{3}\frac{\partial q_i}{\partial r_i} + \frac{2m}{3}U_{ij}P_{ij} = 0 \quad (2.56)$$

It's been a bit of a slog, but finally we have three equations describing how the particle density n (2.47), the velocity \vec{u} (2.50) and the temperature T (2.56) change with time. It's worth stressing that these equations hold for any distribution f_1 . However, the

set of equations are not closed. The equation for n depends on \vec{u} ; the equation for \vec{u} depends on P_{ij} and the equation for T (which is related to the trace of P_{ij}) depends on a new quantity \vec{q} . And to determine any of these, we need to solve the Boltzmann equation and compute the distribution f_1 . But the Boltzmann equation is hard! How to do this?

2.4.2 Ideal Fluids

We start by simply guessing a form of the distribution function $f_1(\vec{r}, \vec{p}; t)$. We know that the collision term in the Boltzmann equation induces a fast relaxation to equilibrium, so if we're looking for a slowly varying solution a good guess is to take a distribution for which $(\partial f_1 / \partial t)_{\text{coll}} = 0$. But we've already met distribution functions that obey this condition in (2.29): they are those describing local equilibrium. Therefore, our first guess for the distribution, which we write as $f_1^{(0)}$, is local equilibrium

$$f_1^{(0)}(\vec{r}, \vec{p}; t) = n(\vec{r}, t) \left(\frac{1}{2\pi m k_B T(\vec{r}, t)} \right)^{3/2} \exp \left(-\frac{m}{2k_B T(\vec{r}, t)} [(\vec{v} - \vec{u}(\vec{r}, t))]^2 \right) \quad (2.57)$$

where $\vec{p} = m\vec{v}$. In general, this distribution is *not* a solution to the Boltzmann equation since it does not vanish on the streaming terms. Nonetheless, we will take it as our first approximation to the true solution and later see what we're missing.

The distribution is normalized so that the number density and temperature defined in (2.43) and (2.53) respectively coincide with $n(\vec{r}, t)$ and $T(\vec{r}, t)$ in (2.29). But we can also use the distribution to compute P_{ij} and \vec{q} . We have

$$P_{ij} = k_B n(\vec{r}, t) T(\vec{r}, t) \delta_{ij} \equiv P(\vec{r}, t) \delta_{ij} \quad (2.58)$$

and $\vec{q} = 0$. We can substitute these expressions into our three conservation laws. The continuity equation (2.47) remains unchanged. Written in terms for $\rho = mn$, it reads

$$\left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \right) \rho + \rho \frac{\partial u_i}{\partial r_i} = 0 \quad (2.59)$$

Meanwhile, the equation (2.50) governing the velocity flow becomes the Euler equation describing fluid motion

$$\left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \right) u_i + \frac{1}{\rho} \frac{\partial P}{\partial r_i} = \frac{F_i}{m} \quad (2.60)$$

and the final equation (2.56) describing the flow of heat reduces to

$$\left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \right) T + \frac{2T}{3} \frac{\partial u_i}{\partial r_i} = 0 \quad (2.61)$$

These set of equations describe the motion of an *ideal* fluid. While they are a good starting point for describing many properties of fluid mechanics, there is one thing that they are missing: dissipation. There is no irreversibility sown into these equations, no mechanism for the fluid to return to equilibrium.

We may have anticipated that these equations lack dissipation. Their starting point was the local equilibrium distribution (2.57) and we saw earlier that for such distributions Boltzmann's H-function does not decrease; the entropy does not increase. In fact, we can also show this statement directly from the equations above. We can combine (2.59) and (2.60) to find

$$\left(\frac{\partial}{\partial t} + u_j \frac{\partial}{\partial r_j} \right) (\rho T^{-3/2}) = 0$$

which tells us that the quantity $\rho T^{-3/2}$ is constant along streamlines. But this is the requirement that motion along streamlines is adiabatic, not increasing the entropy. To see that this is the case, you need to go back to your earlier statistical mechanics or thermodynamics course⁶. The usual statement is that for an ideal gas, an adiabatic transformation leaves $VT^{3/2}$ constant. Here we're working with the density $\rho = mN/V$ and this becomes $\rho T^{-3/2}$ is constant. Note, however, that in the present context ρ and T are not numbers, but functions of space and time: we are now talking about a local adiabatic change.

Sound Waves

It is also simple to show explicitly that one can set up motion in the ideal fluid that doesn't relax back down to equilibrium. We start with a fluid at rest, setting $\vec{u} = 0$ and $\rho = \bar{\rho}$ and $T = \bar{T}$, with both $\bar{\rho}$ and \bar{T} constant. We now splash it (gently). That means that we perturb the system and linearise the resulting equations. We'll analyse these perturbations in Fourier modes and write

$$\rho(\vec{r}, t) = \bar{\rho} + \delta\rho e^{-i(\omega t - \vec{k} \cdot \vec{r})} \quad \text{and} \quad T(\vec{r}, t) = \bar{T} + \delta T e^{-i(\omega t - \vec{k} \cdot \vec{r})} \quad (2.62)$$

Furthermore, we'll look for a particular kind of perturbation in which the fluid motion is parallel to the perturbation. In other words, we're looking for a longitudinal wave

$$\vec{u}(\vec{r}, t) = \hat{k} \delta u e^{-i(\omega t - \vec{k} \cdot \vec{r})} \quad (2.63)$$

The linearised versions of (2.59), (2.60) and (2.61) then read

$$\frac{\omega}{|k|} \delta\rho = \bar{\rho} \delta u$$

⁶See, for example, the discussion of the Carnot cycle in the lectures on [Statistical Physics](#).

$$\begin{aligned}\frac{\omega}{|\vec{k}|}\delta u &= \frac{k_B\bar{T}}{m\bar{\rho}}\delta\rho + \frac{k_B}{m}\delta T \\ \frac{\omega}{|\vec{k}|}\delta T &= \frac{2}{3}\bar{T}\delta u\end{aligned}$$

There is one solution to these equations with zero frequency, $\omega = 0$. These have $\delta u = 0$ while $\delta\rho = -\bar{\rho}$ and $\delta T = \bar{T}$. (Note that this notation hides a small ϵ . It really means that $\delta\rho = -\epsilon\bar{\rho}$ and $\delta T = \epsilon\bar{T}$. Because the equations are linear and homogeneous, you can take any ϵ you like but, since we're looking at small perturbations, it should be small). This solution has the property that $P = mnk_B T$ is constant. But since, in the absence of an external force, pressure is the only driving term in (2.60), the fluid remains at rest, which is why $\delta u = 0$ for this solution.

Two further solutions to these equations both have $\delta\rho = \bar{\rho}$, $\delta T = \frac{2}{3}\bar{T}$ and $\delta u = \omega/|\vec{k}|$ with the dispersion relation

$$\omega = \pm v_s |\vec{k}| \quad \text{with} \quad v_s = \sqrt{\frac{5k_B\bar{T}}{3m}} \quad (2.64)$$

These are sound waves, the propagating version of the adiabatic change that we saw above: the combination $\rho T^{-3/2}$ is left unchanged by the compression and expansion of the fluid. The quantity v_s is the speed of sound.

2.5 Transport with Collisions

While it's nice to have derived some simple equations describing fluid mechanics, as we've seen they're missing dissipation. And, since the purported goal of these lectures is to understand how systems relax back to equilibrium, we should try to see what we've missed.

In fact, it's clear what we've missed. Our first guess for the distribution function was local equilibrium

$$f_1^{(0)}(\vec{r}, \vec{p}; t) = n(\vec{r}, t) \left(\frac{1}{2\pi m k_B T(\vec{r}, t)} \right)^{3/2} \exp\left(-\frac{m}{2k_B T(\vec{r}, t)} [(\vec{v} - \vec{u}(\vec{r}, t))]^2 \right) \quad (2.65)$$

We chose this on the grounds that it gives a vanishing contribution to the collision integral. But we never checked whether it actually solves the streaming terms in the Boltzmann equation. And, as we will now show, it doesn't.

Using the definition of the Poisson bracket and the one-particle Hamiltonian H_1 (2.11), we have

$$\frac{\partial f_1^{(0)}}{\partial t} - \{H_1, f_1^{(0)}\} = \frac{\partial f_1^{(0)}}{\partial t} + \vec{F} \cdot \frac{\partial f_1^{(0)}}{\partial \vec{p}} + \vec{v} \cdot \frac{\partial f_1^{(0)}}{\partial \vec{r}}$$

Now the dependence on $\vec{p} = m\vec{v}$ in local equilibrium is easy: it is simply

$$\frac{\partial f_1^{(0)}}{\partial \vec{p}} = -\frac{1}{k_B T} (\vec{v} - \vec{u}) f_1^{(0)}$$

Meanwhile all \vec{r} dependence and t dependence of $f_1^{(0)}$ lies in the functions $n(\vec{r}, t)$, $T(\vec{r}, t)$ and $\vec{u}(\vec{r}, t)$. From (2.65) we have

$$\begin{aligned} \frac{\partial f_1^{(0)}}{\partial n} &= \frac{f_1^{(0)}}{n} \\ \frac{\partial f_1^{(0)}}{\partial T} &= -\frac{3}{2} \frac{f_1^{(0)}}{T} + \frac{m}{2k_B T^2} (\vec{v} - \vec{u})^2 f_1^{(0)} \\ \frac{\partial f_1^{(0)}}{\partial \vec{u}} &= \frac{m}{k_B T} (\vec{v} - \vec{u}) f_1^{(0)} \end{aligned}$$

Using all these relations, we have

$$\begin{aligned} \frac{\partial f_1^{(0)}}{\partial t} - \{H_1, f_1^{(0)}\} &= \left[\frac{1}{n} \tilde{D}_t n + \left(\frac{m(\vec{v} - \vec{u})^2}{2k_B T^2} - \frac{3}{2T} \right) \tilde{D}_t T \right. \\ &\quad \left. + \frac{m}{k_B T} (\vec{v} - \vec{u}) \cdot \tilde{D}_t \vec{u} - \frac{1}{k_B T} \vec{F} \cdot (\vec{v} - \vec{u}) \right] f_1^{(0)} \end{aligned} \quad (2.66)$$

where we've introduced the notation \tilde{D}_t which differs from the material derivative D_t in that it depends on the velocity \vec{v} rather than the average velocity \vec{u} ,

$$\tilde{D}_t \equiv \frac{\partial}{\partial t} + \vec{v} \cdot \frac{\partial}{\partial \vec{r}} = D_t + (\vec{v} - \vec{u}) \cdot \frac{\partial}{\partial \vec{r}}$$

Now our first attempt at deriving hydrodynamics gave us three equations describing how n (2.59), \vec{u} (2.60) and T (2.61) change with time. We substitute these into (2.66). You'll need a couple of lines of algebra, cancelling some terms, using the relationship $P = nk_B T$ and the definition of U_{ij} in (2.55), but it's not hard to show that we ultimately get

$$\begin{aligned} \frac{\partial f_1^{(0)}}{\partial t} - \{H_1, f_1^{(0)}\} &= \left[\frac{1}{T} \left(\frac{m}{2k_B T} (\vec{v} - \vec{u})^2 - \frac{5}{2} \right) (\vec{v} - \vec{u}) \cdot \nabla T \right. \\ &\quad \left. + \frac{m}{k_B T} \left((v_i - u_i)(v_j - u_j) - \frac{1}{3} (\vec{v} - \vec{u})^2 \delta_{ij} \right) U_{ij} \right] f_1^{(0)} \end{aligned} \quad (2.67)$$

And there's no reason that the right-hand-side is zero. So, unsurprisingly, $f_1^{(0)}$ does not solve the Boltzmann equation. However, the remaining term depends on ∇T and $\partial\vec{u}/\partial\vec{r}$ which means that we if we stick to long wavelength variations in the temperature and velocity then we almost have a solution. We need only add a little extra something to the distribution

$$f_1 = f_1^{(0)} + \delta f_1 \quad (2.68)$$

Let's see how this changes things.

2.5.1 Relaxation Time Approximation

The correction term, δf_1 , will contribute to the collision integral (2.24). Dropping the \vec{r} argument for clarity, we have

$$\begin{aligned} \left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}} &= \int d^3p_2 d^3p'_1 d^3p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}_1, \vec{p}_2) [f_1(\vec{p}'_1) f_1(\vec{p}'_2) - f_1(\vec{p}_1) f_1(\vec{p}_2)] \\ &= \int d^3p_2 d^3p'_1 d^3p'_2 \omega(\vec{p}'_1, \vec{p}'_2 | \vec{p}_1, \vec{p}_2) \left[f_1^{(0)}(\vec{p}'_1) \delta f_1(\vec{p}'_2) + \delta f(\vec{p}'_1) f_1^{(0)}(\vec{p}'_2) \right. \\ &\quad \left. - f_1^{(0)}(\vec{p}_1) \delta f_1(\vec{p}_2) - \delta f(\vec{p}_1) f_1^{(0)}(\vec{p}_2) \right] \end{aligned}$$

where, in the second line, we have used the fact that $f_1^{(0)}$ vanishes in the collision integral and ignored quadratic terms $\sim \delta f_1^2$. The resulting collision integral is a linear function of δf_1 . But it's still kind of a mess and not easy to play with.

At this point, there is a proper way to proceed. This involves first taking more care in the expansion of δf_1 (using what is known as the Chapman-Enskog expansion) and then treating the linear operator above correctly. However, there is a much easier way to make progress: we just replace the collision integral with another, much simpler function, that captures much of the relevant physics. We take

$$\left(\frac{\partial f_1}{\partial t}\right)_{\text{coll}} = -\frac{\delta f_1}{\tau} \quad (2.69)$$

where τ is the *relaxation time* which, as we've already seen, governs the rate of change of f_1 . In general, τ could be momentum dependent. Here we'll simply take it to be a constant.

The choice of operator (2.69) is called the *relaxation time approximation*. (Sometimes it is referred to as the Bhatnagar-Gross-Krook operator). It's most certainly not exact.

In fact, it's a rather cheap approximation. But it will give us a good intuition for what's going on. With this replacement, the Boltzmann equation becomes

$$\frac{\partial(f_1^{(0)} + \delta f_1)}{\partial t} - \{H_1, f_1^{(0)} + \delta f_1\} = -\frac{\delta f_1}{\tau}$$

But, since $\delta f_1 \ll f_1^{(0)}$, we can ignore δf_1 on the left-hand-side. Then, using (2.67), we have a simple expression for the extra contribution to the distribution function

$$\begin{aligned} \delta f_1 = -\tau \left[\frac{1}{T} \left(\frac{m}{2k_B T} (\vec{v} - \vec{u})^2 - \frac{5}{2} \right) (\vec{v} - \vec{u}) \cdot \frac{\partial T}{\partial \vec{r}} \right. \\ \left. + \frac{m}{k_B T} \left((v_i - u_i)(v_j - u_j) - \frac{1}{3} (\vec{v} - \vec{u})^2 \delta_{ij} \right) U_{ij} \right] f_1^{(0)} \end{aligned} \quad (2.70)$$

We can now use this small correction to the distribution to revisit some of the transport properties that we saw in Section 1.

2.5.2 Thermal Conductivity Revisited

Let's start by computing the heat flux

$$q_i = \frac{1}{2} m \rho \langle (v_i - u_i) (\vec{v} - \vec{u})^2 \rangle \quad (2.71)$$

using the corrected distribution (2.68). We've already seen that the local equilibrium distribution $f_1^{(0)}$ gave $\vec{q} = 0$, so the only contribution comes from δf_1 . Moreover, only the first term in (2.70) contributes to (2.71). (The other is an odd function and vanishes when we do the integral). We have

$$\vec{q} = -\kappa \nabla T$$

This is the same phenomenological law that we met in (1.12). The coefficient κ is the thermal conductivity and is given by

$$\begin{aligned} \kappa &= \frac{m\tau\rho}{2T} \int d^3p (\vec{v}_i - \vec{u}_i)^2 (\vec{v} - \vec{u})^2 \left[\frac{m}{2k_B T} (\vec{v} - \vec{u})^2 - \frac{5}{2} \right] f_1^{(0)} \\ &= \frac{m\tau\rho}{6T} \left[\frac{m}{2k_B T} \langle v^6 \rangle_0 - \frac{5}{2} \langle v^4 \rangle_0 \right] \end{aligned}$$

In the second line, we've replaced all $(v - u)$ factors with v by performing a (\vec{r} -dependent) shift of the integration variable. The subscript $\langle \cdot \rangle_0$ means that these averages are to be taken in the local Maxwell-Boltzmann distribution $f_1^{(0)}$ with $u = 0$. These

integrals are simple to perform. We have $\langle v^4 \rangle_0 = 15k_B^2 T^2/m^2$ and $\langle v^6 \rangle_0 = 105k_B^3 T^3/m^3$, giving

$$\kappa = \frac{5}{2} \tau n k_B^2 T$$

The factor of 5/2 here has followed us throughout the calculation. The reason for its presence is that it's the specific heat at constant pressure, $c_p = \frac{5}{2} k_B$.

This result is parameterically the same that we found earlier in (1.13). (Although you have to be a little careful to check this because, as we mentioned after (2.54), the definition of heat flux differs and, correspondingly, κ , differs by a factor of m . Moreover, the current formula is written in terms of slightly different variables. To make the comparison, you should rewrite the scattering time as $\tau \sim 1/m\sigma n \sqrt{\langle v^2 \rangle}$, where σ is the total cross-section and $\langle v^2 \rangle \sim T/m$ by equipartition). The coefficient differs from our earlier derivation, but it's not really to be trusted here, not least because the only definition of τ that we have is in the implementation of the relaxation time approximation.

We can also see how the equation (2.56) governing the flow of temperature is related to the more simplistic heat flow equation that we introduced in (1.14). For this we need to assume both a static fluid $\vec{u} = 0$ and also that we can neglect changes in the thermal conductivity, $\partial\kappa/\partial\vec{r} \approx 0$. Then equation (2.56) reduces to the heat equation

$$\rho k_B \frac{\partial T}{\partial t} = -\frac{2}{3} \kappa \nabla^2 T$$

2.5.3 Viscosity Revisited

Let's now look at the shear viscosity. From our discussion in Section 1, we know that the relevant experimental set-up is a fluid with a velocity gradient, $\partial u_x/\partial z \neq 0$. The shear viscosity is associated to the flux of x -momentum in the z -direction. But this is precisely what is computed by the off-diagonal component of the pressure tensor,

$$P_{xz} = \rho \langle (v_x - u_x)(v_z - u_z) \rangle$$

We've already seen that the local equilibrium distribution gives a diagonal pressure tensor (2.58), corresponding to vanishing viscosity. What happens if we use the corrected distribution (2.68)? Now only the second term in (2.70) contributes (since the first term is an odd function of $(v - u)$). We write

$$P_{ij} = P \delta_{ij} + \Pi_{ij} \tag{2.72}$$

where the extra term Π_{ij} is called the *stress tensor* and is given by

$$\begin{aligned}\Pi_{ij} &= \frac{m\tau\rho}{k_B T} U_{kl} \int d^3p (v_j - u_j)(v_i - u_i) \left((v_k - u_k)(v_l - u_l) - \frac{1}{3}(\vec{v} - \vec{u})^2 \delta_{kl} \right) f_1^{(0)} \\ &= \frac{m\tau\rho}{k_B T} U_{kl} \left[\langle v_i v_j v_k v_l \rangle_0 - \frac{1}{3} \delta_{kl} \langle v_i v_j v^2 \rangle_0 \right]\end{aligned}$$

Before we compute Π_{ij} , note that it is a traceless tensor. This is because the first term above becomes $\langle v^2 v_k v_l \rangle_0 = \delta_{jk} \langle v^2 v_x v_x \rangle_0$ which is easily calculated to be $\langle v^2 v_x^2 \rangle_0 = 5k_B^2 T^2 / m^2 = \frac{1}{3} \langle v^4 \rangle_0$. Moreover, Π_{ij} depends linearly on the tensor U_{ij} . These two facts mean that Π_{ij} must be of the form

$$\Pi_{ij} = -2\eta \left(U_{ij} - \frac{1}{3} \delta_{ij} \nabla \cdot \vec{u} \right) \quad (2.73)$$

In particular, if we set up a fluid gradient with $\partial u_x / \partial z \neq 0$, we have

$$\Pi_{xz} = -\eta \frac{\partial u_x}{\partial z}$$

which tells us that we should identify η with the shear viscosity. To compute it, we return to a general velocity profile which, from (2.73), gives

$$\begin{aligned}\Pi_{xz} &= \frac{m\tau\rho}{k_B T} U_{kl} \left[\langle v_x v_z v_k v_l \rangle_0 - \frac{1}{3} \delta_{kl} \langle v_x v_z v^2 \rangle_0 \right] \\ &= \frac{m\tau\rho}{k_B T} (U_{xz} + U_{zx}) \langle v_x v_z v_x v_z \rangle_0 \\ &= \frac{2m\tau\rho}{15k_B T} U_{xz} \langle v^4 \rangle_0\end{aligned}$$

Comparing to (2.73), we get an expression for the coefficient η ,

$$\eta = nk_B T \tau$$

Once again, this differs from our earlier more naive analysis (1.11) only in the overall numerical coefficient. And, once again, this coefficient is not really trustworthy due to our reliance on the relaxation time approximation.

The scattering time τ occurs in both the thermal conductivity and the viscosity. Taking the ratio of the two, we can construct a dimensionless number which characterises our system. This is called the *Prandtl number*,

$$\text{Pr} = \frac{c_p \eta}{\kappa}$$

With c_p the specific heat at constant pressure which takes the value $c_p = 5k_B/2$ for a monatomic gas. Our calculations above give a Prandtl number $\text{Pr} = 1$. Experimental data for monatomic gases shows a range of Prandtl numbers, hovering around $\text{Pr} \approx 2/3$. The reason for the discrepancy lies in the use of the relaxation time approximation. A more direct treatment of the collision integral, thought of as a linear operator acting on δf_1 , gives the result $\text{Pr} = 2/3$, in much better agreement with the data⁷.

2.6 A Second Look: The Navier-Stokes Equation

To end our discussion of kinetic theory, we put together our set of equations governing the conservation of density, momentum and energy with the corrected distribution function. The equation of motion for density fluctuations does not change: it remains,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{u}) = 0 \quad (2.74)$$

Meanwhile the equation for momentum (2.50) now has an extra contribution from the stress tensor contribution (2.72). Moreover, we typically assume that, to leading order, variations in the viscosity can be neglected: $\nabla \eta \approx 0$. Written in vector notation rather than index notation, the resulting equation is

$$\left(\frac{\partial}{\partial t} + \vec{u} \cdot \nabla \right) \vec{u} = \frac{\vec{F}}{m} - \frac{1}{\rho} \nabla P + \frac{\eta}{\rho} \nabla^2 \vec{u} + \frac{\eta}{3\rho} \nabla (\nabla \cdot \vec{u}) \quad (2.75)$$

This is the *Navier-Stokes* equation. Finally, we have the heat conduction equation. We again drop some terms on the grounds that they are small. This time, we set $\nabla \kappa \approx 0$ and $U_{ij} \Pi_{ij} \approx 0$; both are small at the order we are working to. We're left with

$$\rho \left(\frac{\partial}{\partial t} + \vec{u} \cdot \nabla \right) T - \frac{2}{3} \kappa \nabla^2 T + \frac{2m}{3} P \nabla \cdot \vec{u} = 0$$

We can again look at fluctuations of these equations about a static fluid with $\rho = \bar{\rho}$, $T = \bar{T}$ and $\vec{u} = 0$. Longitudinal fluctuations (2.62) and (2.63) now give rise to the linearised equations of motion,

$$\begin{aligned} \omega \delta \rho &= \bar{\rho} |\vec{k}| \delta u \\ \omega \delta u &= \frac{k_B \bar{T}}{m \bar{\rho}} |\vec{k}| \delta \rho + \frac{k_B}{m} |\vec{k}| \delta T - i \frac{4\eta |\vec{k}|^2}{3\bar{\rho}} \delta u \\ \omega \delta T &= \frac{2}{3} \bar{T} |\vec{k}| \delta u - i \frac{2\kappa |\vec{k}|^2}{3k_B \bar{\rho}} \delta T \end{aligned}$$

⁷You can read about this improved calculations in the lectures by [Daniel Arovas](#).

Notice that terms involving transport coefficients η and κ each come with a factor of i ; this is a sign that they will give rise to dissipation. To compute the frequencies of the different modes, it's best to think of this as an eigenvalue problem for $\omega/|\vec{k}|$; the coefficients of the various terms on the right-hand-side define a 3×3 matrix M , with

$$\det M = \frac{2i}{3} \frac{\kappa |\vec{k}|^4 \bar{T}}{m\bar{\rho}} \quad \text{and} \quad \text{Tr } M = -i \left(\frac{4}{3} \eta + \frac{2}{3} \frac{\kappa}{k_B} \right) \frac{|\vec{k}|^2}{\bar{\rho}}$$

The product of the three eigenvalues is equal to $\det M$. We know that for the ideal fluid, the eigenvalues are zero and $\omega = \pm v_s |\vec{k}|$ where v_s is the sound speed computed in (2.64). Let's first look at the eigenvalue that was zero, corresponding to fluctuations of constant pressure. Working to leading order in κ and η , we must have

$$-v_s^2 |\vec{k}|^2 \omega = \det M \quad \Rightarrow \quad \omega = -\frac{2i}{5} \frac{\kappa}{k_B \bar{\rho}} |\vec{k}|^2$$

The purely imaginary frequency is telling us that these modes are damped. The $\omega \sim i|\vec{k}|^2$ is characteristic of diffusive behaviour.

The remaining two modes are related to the sound waves. These too will gain a dispersive contribution, now with

$$\omega = \pm v_s |\vec{k}| - i\gamma \tag{2.76}$$

Using the fact that the sum of the eigenvalues is equal to the trace, we find

$$\gamma = \left(\frac{2}{3} \eta + \frac{2}{15} \frac{\kappa}{k_B} \right) \frac{|\vec{k}|^2}{\bar{\rho}} \tag{2.77}$$

The fluctuations above are all longitudinal. There are also two shear modes, whose fluctuations are in a direction perpendicular to the velocity. It is simple to check that the linearised equations are solved by $\delta\rho = \delta T = 0$ and $\delta\vec{u} \cdot \vec{k}$, with the frequency given by

$$\omega = -i \frac{\eta |\vec{k}|^2}{\bar{\rho}}$$

Once again, we see that these modes behave diffusively.

Navier Stokes Equation and Liquids

Our derivation of the Navier-Stokes equation relied on the dilute gas approximation. However, the equation is more general than that. Indeed, it can be thought of as the

most general expression in a derivative expansion for momentum transport (subject to various requirements). In fact, there is one extra parameter that we could include:

$$\rho \left(\frac{\partial}{\partial t} + \vec{u} \cdot \nabla \right) \vec{u} = \frac{\rho \vec{F}}{m} - \nabla P + \eta \nabla^2 \vec{u} + \left(\frac{\eta}{3} + \zeta \right) \nabla (\nabla \cdot \vec{u})$$

where ζ is the *bulk viscosity* which vanished in our derivation above. Although the equation above governs transport in liquids, we should stress that first-principles computations of the viscosity (and also thermal conductivity) that we saw previously only hold in the dilute gas approximation.