

# Kinetic Theory

University of Cambridge Graduate Course

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## Recommended Books and Resources

This lecture course covers three topics: kinetic theory, stochastic processes and linear response. Most decent books on statistical mechanics will have a section covering non-equilibrium topics in general. However, if you're looking for details beyond the basics, you'll probably need a different book for each topic. Some good general purpose books are:

- Huang, *Statistical Mechanics*
- Kardar, *Statistical Physics of Particles*
- Reif, *Fundamentals of Statistical and Thermal Physics*

Both Huang and Kardar treat kinetic theory and the Boltzmann equation before they move onto statistical mechanics. Much of Section 2 of these notes follows the path laid down in these books. Reif ends with a much wider ranging discussion of kinetic theory, transport and stochastic processes.

For more details on kinetic theory:

- Chapman and Cowling, *The Mathematical Theory of Non-Uniform Gases*
- Lifshitz and Pitaevskii, *Physical Kinetics*

Both of these are old school. The first was published in 1939 although the latest edition, written in 1970, is modern enough to cover all the developments that we touch upon in this course. The last volume of the course by Landau and Lifshitz covers kinetic theory. This book was written substantially later than the earlier volumes, decades after Landau's death.

For more details on stochastic processes:

- Van Kampen, *Stochastic Processes in Physics and Chemistry*

The topic of linear response is usually covered in books on many body theory or more general condensed matter. Two excellent modern books, both with a chapter on response theory, are

- Altland and Simons, *Condensed Matter Field Theory*
- Chaikin and Lubensky, *Principles of Condensed Matter Physics*

Finally, there are a number of good lecture notes and resources on the web, collated at <http://www.damtp.cam.ac.uk/user/tong/kinetic.html>

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## Acknowledgements

These lecture notes are far from original. They borrow heavily both from the books described above and the online resources listed on the course webpage. My thanks to Daniele Dorigoni for help explaining the tricky factor of  $1/2$  in the path integral for the Fokker-Planck equation.

# 1. Things Bumping Into Other Things

## 1.1 Introduction

The purpose of this course is to describe a number of basic topics in non-equilibrium statistical mechanics.

If you've taken a first course in [Statistical Mechanics](#), you'll know that the whole machinery of ensembles and partition functions only works when applied to systems in equilibrium. Equilibrium is defined to be a state in which, at least on the coarse grained level, things don't change. Of course, if you have a hot system and you look closely enough, everything is flying around on the atomic level. But if you focus only on macroscopic variables then, in equilibrium, all is calm.

At first, the restriction to equilibrium sounds rather limiting. But it's not. This is because the state of equilibrium is very special: if you take any system and wait long enough then it will eventually relax down to equilibrium. (This is sometimes said to be the  $-1^{\text{th}}$  law of thermodynamics).

Of course, this begs the question of why equilibrium is special. Why do all systems eventually reach this state. How do they approach this state? How does such irreversible behaviour arise from the fundamental laws of physics which are, for all intents and purposes, invariant under time reversal? Moreover, what if you're not happy to just sit back and watch an equilibrium system? Suppose you want to stir it or splash it or attach a couple of crocodile clips and zap it. How will it respond? These are the kind of questions that we will begin to answer in this course.

While there is typically only a single equilibrium state, for a system with  $10^{23}$  particles, there are many many ways to be out-of-equilibrium. Most of these states are uninteresting in the sense that they will be so complicated that no general features will emerge. Moreover, such states will be fleeting, rapidly changing to another complicated configuration. If we're to have any chance of making progress, we need to be careful about the kind of states we discuss and the kind of questions that we ask. We would like to identify features in the dynamics of  $10^{23}$  particles that persist for long periods of time. We will see that such features arise for systems that are close to equilibrium. Indeed, throughout this course, the dramatic sounding "non-equilibrium" will really mean "almost-equilibrium".

Each of the four sections in these lecture notes can be read more or less independently. In the rest of this introductory section, we will introduce a few basic tools to describe how quantities change in a gas. This will really be a baby version of kinetic theory, with

nothing more sophisticated than Newtonian thinking applied to a bunch of billiard balls. But it will allow us to develop some basic intuition for the rudiments of the subject. While many of the formulae we derive in this section are rather heuristic, all will be revisited Section 2 where we use the Boltzmann equation to give a more rigorous view on the subject, understanding transport phenomena and deriving the equations of fluid mechanics starting from first principles. Section 3 introduces the subject of random jittery motion, usually called stochastic processes. Finally, in Section 4 we turn the stir-it-splash-it-zap-it question and develop the machinery necessary to describe how systems respond when prodded.

## 1.2 Basics of Collisions

Let's start by considering  $N$  molecules in a gas of volume  $V$ . We will begin by ignoring all interactions between particles. Instead, we will treat the molecules as spheres of a finite size which will allow collisions to occur. For the most part, we won't rely on the results of earlier courses on statistical mechanics. There is, however, one exception: in the rest of this section, we will need the Maxwell-Boltzmann probability distribution for the velocities in a gas<sup>1</sup>.

$$f(\vec{v}) d^3v = \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} d^3v \quad (1.1)$$

The distribution  $f(\vec{v})d^3v$  is the probability that a molecule has velocity within a small volume  $d^3v$  in the neighbourhood of  $\vec{v}$ .

We denote the diameter of the particle as  $d$ . Obviously its radius is  $d/2$ . Viewed head on, the particle appears as a disc with area  $\pi(d/2)^2$ . However, more relevant for our purposes is the effective cross-sectional area of the particle,  $\pi d^2$ . To see why this is, focus on a single particle as it makes its way through the gas. If it travels a distance  $l$ , it will sweep out a volume  $\pi d^2 l$  as shown in Figure 1 and collide with any other particle whose centre lies within this volume.

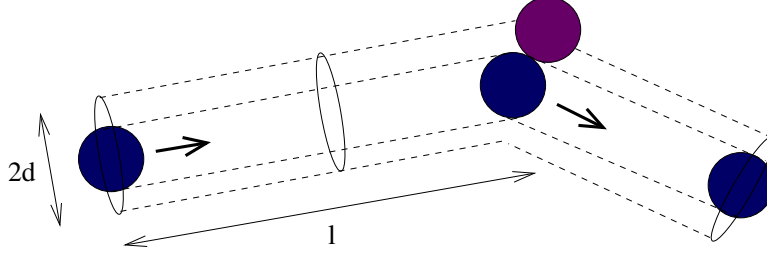
The *mean free path* is defined to be the average distance travelled by the molecule between each collision. This is given by  $\pi d^2 l = V/N$ , or

$$l = \frac{V}{N} \frac{1}{\pi d^2} = \frac{1}{n\pi d^2} \quad (1.2)$$

where  $n = N/V$  is the particle density.

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<sup>1</sup>This result will be re-derived in Section 2 when we discuss the Boltzmann equation. You can also find a simple derivation in the lectures on [Statistical Physics](#).



**Figure 1:** A particle of radius  $d/2$  travels, on average, a length  $l$  between each collision. In this time it sweeps out a volume  $\pi d^2 l$ .

In what follows, we'll assume that our gas is dilute, meaning  $l \gg d$ . For typical gases  $d \sim 10^{-10} \text{ m}$  while, at atmospheric pressure,  $l \sim 10^{-7} \text{ m}$ .

### 1.2.1 Relaxation Time

The average time between collisions is called the *scattering time* or *relaxation time*,

$$\tau = \frac{l}{\bar{v}_{\text{rel}}}$$

You might think that  $\bar{v}_{\text{rel}}$  is the average speed of a given particle. This isn't quite true. Since we're interested in the rate of collisions, the speed of other particles approaching is just as important as the speed of the particle you're looking at. So we should take  $v_{\text{rel}}$  to be the average *relative* speed of the molecules. For two particles with velocities  $\vec{v}$  and  $\vec{v}'$ , the average relative speed is

$$\begin{aligned} \bar{v}_{\text{rel}}^2 &= \langle (\vec{v} - \vec{v}')^2 \rangle = \int d^3\vec{v} \int d^3\vec{v}' (\vec{v} - \vec{v}')^2 f(\vec{v}) f(\vec{v}') \\ &= \langle v^2 \rangle + \langle v'^2 \rangle - 2\langle \vec{v} \cdot \vec{v}' \rangle \end{aligned} \quad (1.3)$$

where  $f(\vec{v})$  in the first line is the Maxwell-Boltzmann distribution (1.1). The fact that we have multiplied the distributions  $f(\vec{v})f(\vec{v}')$  together in the first line means that we are assuming that the velocities of the two particles are uncorrelated. This is an assumption that we shall return to in Section 2.

The last term in (1.3) vanishes:  $\langle \vec{v} \cdot \vec{v}' \rangle = 0$ . This follows on rotational grounds. Because the velocity of each particle is independent, it's enough to know that the average velocity (not speed!) in, say, the  $x$ -direction vanishes:  $\langle v_x \rangle = 0$ . Meanwhile,  $\langle v^2 \rangle = \langle v'^2 \rangle$  which means that  $\bar{v}_{\text{rel}}^2 = 2\langle v^2 \rangle$ . It is a simple exercise to compute  $\langle v^2 \rangle$  from the Maxwell-Boltzmann distribution (1.1) and the answer is the same as you would get



by simply appealing to the equipartition of energy:  $\langle v^2 \rangle = 3k_B T/m$ . We have

$$\bar{v}_{\text{rel}}^2 = \frac{6k_B T}{m}$$

and the relaxation time is given by

$$\tau = \frac{1}{n\pi d^2} \sqrt{\frac{m}{6k_B T}}$$

Notice that as the temperature drops, the mean free path remains unchanged. However, the time between collisions increases.

There is a slightly different interpretation of the relaxation time that it is useful to have in hand. Suppose that the probability that a molecule undergoes a collision between time  $t$  and time  $t + dt$  is given by  $w dt$ , for some constant  $w$ , known as the *collision rate*. Notice that in stating this, we have made more assumptions about the nature of the collisions. In particular, the fact that  $w$  is a constant means that no memory of previous collisions is kept: the chances of being hit again are not affected just because you already were hit a short time ago.

If  $P(t)$  is the probability that the molecule makes it to time  $t$  unharmed, then the probability that it further makes it to time  $t + dt$  without collision is

$$P(t + dt) = P(t)(1 - w dt)$$

Writing this as a differential equation, we have

$$\frac{dP}{dt} = -wP \quad \Rightarrow \quad P(t) = e^{-wt}$$

where we've chosen the normalisation so that  $P(0) = 1$  and  $P(\infty) = 0$ . With this in hand, we can compute the average time between collisions. But this is exactly the quantity that we called the relaxation time above. It is

$$\tau = \int_0^\infty P(t) dt = \frac{1}{w}$$

We learn that  $1/\tau$  is the collision rate.

### 1.3 Basics of Transport

We now turn to the question of how things move. Of course, in a thermal system, the microscopic constituents are always moving, even in equilibrium. Our goal here is to understand how certain macroscopic properties move when out of equilibrium. The properties that we will look at are all associated to a conserved quantity: particle number, energy or momentum. Processes in which these quantities change over time are usually referred to as *transport*. As we will see, all of these quantities typically flow in such a way as to reach the equilibrium state.

### 1.3.1 Diffusion

Drop a blob of ink into a glass of water. How does it spread? More generally, we are interested in the motion of a particular kind of particle – one with a nice colour, or funny smell – as it makes its way through a generic background of liquid or gas. The true dynamics of any particle is, as you might expect, somewhat jittery. Here we'll look at a simple model that captures this physics.

#### Random Walk

Consider a lattice which, for now, we take to be one dimensional. The spacing between the lattice sites is set by the mean free path,  $l$ , and after a time,  $\tau$ , the particle jumps either left or right. The direction of the jump is entirely random: 50% of the time it goes left, 50% right. This model is known as a *random walk*.

The particle starts at the origin and we want to know the probability  $P(x, t)$  that it sits at  $x = ml$  at time  $t = N\tau$ . (Here  $m$  is an integer; it's not the mass of the particle!). We'll start by giving a simple combinatoric derivation of the answer. For simplicity, we'll take  $N$  to be even and we'll look at  $m \ll N$ . To get to  $x = ml$ , the particle must have made  $\frac{1}{2}(N + m)$  forward jumps and  $\frac{1}{2}(N - m)$  backwards jumps. The probability is just the number of different ways we can do this, divided by  $2^N$ , the total number of possible combinations.

$$P(x, t) = \frac{2^{-N} N!}{[\frac{1}{2}(N + m)]![\frac{1}{2}(N - m)]!} \approx \sqrt{\frac{2}{\pi N}} e^{-m^2/2N} = \sqrt{\frac{2\tau}{\pi t}} e^{-x^2\tau/2l^2t} \quad (1.4)$$

where, in the second step, the factorials have been replaced by Stirling's approximation and we've also expanded to leading order in  $m/N$ . (To get the prefactor, we need to go to the third order in the Stirling expansion).

The probability distribution of the particle is an ever-spreading Gaussian ensemble. The mean is simply  $\langle x \rangle = 0$ , reflecting the fact that the particle is equally likely to travel forwards as backwards. The variance is

$$\langle x^2 \rangle = \frac{l^2}{\tau} t \quad (1.5)$$

The root-mean-square (rms) distance travelled by the particle grows as  $\sqrt{\langle x^2 \rangle} \sim \sqrt{t}$ . This is characteristic behaviour of random walks.

It is simple to repeat our analysis of the random walk to three dimensions. For a cubic lattice, we assume that the motion in each of the directions is independent and equally likely. On average, the particle moves in the  $x$ -direction only every  $3\tau$ , so (1.5)

should be replaced by  $\langle x^2 \rangle = l^2 t / 3\tau$ . But this means that the total rms distance covered remains unchanged

$$\langle \vec{x}^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = \frac{l^2}{\tau} t$$

## The Diffusion Equation

We can recast the above discussion in terms of a differential equation for the density of particles,  $n = N/V$ . Away from equilibrium, the density is not a constant. It is, in general, a function of time and space. We expect any gradient,  $\nabla n$ , in the density of particles to lead to a flow, from the high density region to the low.

We'll again restrict first to the case of one-dimension. Consider the density at some fixed time:  $n = n(x, t)$ . We'd like to derive an expression for the density at the point  $x$  a short time  $\Delta t$  later. Of course, some particles will leave, but others will come in to replace them. Any particle which is at  $x$  at time  $t + \Delta t$  must have been sitting at some other position  $x - \Delta x$  at time  $t$ . Here  $\Delta x$  should be viewed as a random variable since some move one way, some the other. This means that we can write an expression for the density at time  $t + \Delta t$  as an average over all the different  $\Delta x$ ,

$$\begin{aligned} n(t + \Delta t, x) &= \langle n(t, x - \Delta x) \rangle \\ &= n(t, x) - \frac{\partial n}{\partial x} \langle \Delta x \rangle + \frac{1}{2} \frac{\partial^2 n}{\partial x^2} \langle \Delta x^2 \rangle + \dots \end{aligned}$$

The term with the first order derivative vanishes because, on average, particles are equally likely to go either way, meaning  $\langle \Delta x \rangle = 0$ . Taylor expanding the left-hand-side, we arrive at the *diffusion equation*

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}$$

where the diffusion constant is  $D = \langle \Delta x^2 \rangle / 2\Delta t$ . We expect this to be related to our two quantities, the mean free path  $l$  and scattering time  $\tau$ . On dimensional grounds, we must have

$$D \sim \frac{l^2}{\tau}$$

Solutions to the diffusion equation evolve so as to iron out any inhomogeneities in particle density. As an example, suppose that all  $N$  particles start out life sitting at the origin, giving us the initial condition  $n(x, t = 0) = N\delta(x)$ . The solution to the diffusion equation with this initial condition is an ever-spreading Gaussian,

$$n(x, t) = N \sqrt{\frac{1}{4\pi Dt}} e^{-x^2/4Dt}$$

This reproduces the discretised result (1.4). Viewing the average distance travelled as the width of the cloud of particles, we again have the result

$$\langle x^2 \rangle = 2Dt$$

It is simple to extend the derivation above to three dimensions. Going through the same steps, we now find the 3d diffusion equation,

$$\frac{\partial n}{\partial t} = D \nabla^2 n$$

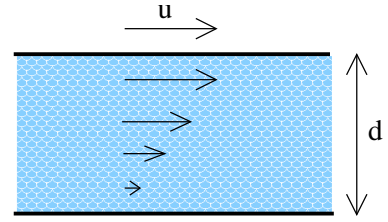
This is also known as *Fick's (second) law*. We again expect that  $D \sim l^2/\tau$ . (Although the overall numerical factor is not necessarily the same as the 1d case. In fact, in simple analysis it is a factor of 3 less). The Gaussian again provides a solution, now with

$$\langle \vec{x}^2 \rangle = 6Dt$$

As we will now show, a number of other processes also follow this general diffusive form.

### 1.3.2 Viscosity

*Viscosity* is a form of internal friction experienced by a fluid. It can be measured by placing a fluid between two plates, a distance  $d$  apart in the  $z$  direction. Holding the lower plate stationary, the top plate is moved at a constant speed,  $u$ , in the  $x$  direction. But you don't get to do this for free: the fluid pushes back. If you want to keep the plate moving at a constant speed, you have to apply a force  $F$ .



**Figure 2:**

Near the upper plate, a friction force causes the fluid to be dragged along with the same speed  $u$ . However, near the lower plate, the fluid remains stationary. This sets up a velocity gradient,  $u_x(z)$ , with  $u_x(d) = u$  and  $u_x(0) = 0$ . Experimentally, it is found that the force per unit area which must be exerted on the upper plate is proportional to this velocity gradient,

$$\frac{F}{A} = \eta \frac{du_x}{dz} \approx \eta \frac{u}{d} \quad (1.6)$$

where the second equality holds for small distances  $d$ . The coefficient of proportionality,  $\eta$ , is called the *viscosity*. (Or, more correctly, the *dynamic viscosity*).

We would like to derive both the force law (1.6) and the viscosity  $\eta$  from first principles. It's simple to get an intuition for what's happening on the atomic level: when the molecules collide with the upper plate, they pick up some  $x$ -momentum. They then collide with other molecules lower down, imparting some of this  $x$ -momentum to new molecules, which then collide with other molecules lower down, and so on. In this way, we set up the velocity gradient in the  $z$  direction.

We'll think of a slab of gas at some fixed value of  $z$ . To figure out the force acting on this slab, we need to work out two things: the number of particles moving through the slab per unit of time; and the extra momentum in the  $x$ -direction that each particle imparts to the molecules in the slab.

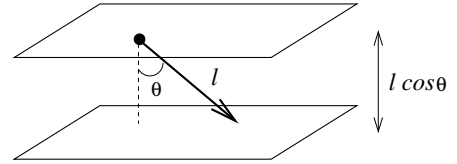
Let's first deal with the number of particles. The density of particles in the fluid is  $n = N/V$ . How many of these pass through a slab in the  $z$ -direction in a given length of time depends on how fast they're travelling in the  $z$ -direction (obv!). But we know how many particles there are with each speed: this is given by the Maxwell-Boltzmann distribution (1.1). The net result is that the number of particles, per unit time, per unit area, whose velocity is lies close to  $\vec{v}$  (in a box of size  $d^3\vec{v}$ ), passing through a horizontal slab is

$$\# \text{ of particles per unit time per unit area} = nv_z f(\vec{v}) d^3v \quad (1.7)$$

Now let's figure out the momentum that each of these molecules imparts. Consider a particle at some position  $z$ . It gets hit from below, it gets hit from above. The hits from above are likely to give it more momentum in the  $x$  direction; those from below, less. Let's consider those arriving from above. If they arrive from a position  $z + \Delta z$ , then they impart  $x$ -momentum

$$\Delta p = m(u_x(z + \Delta z) - u_x(z)) \approx m \frac{du_x}{dz} \Delta z \quad (1.8)$$

What is the distance  $\Delta z$  here? Well, this depends on the angle the particles come in at. They have travelled the mean free path  $l$ , so if they arrive at angle  $\theta$  then we must have



**Figure 3:**

$$\Delta z = l \cos \theta$$

Here  $\theta \in [0, \pi/2)$  for particles arriving from above. But the same argument also holds for particles coming in from below. These have  $\theta \in (\pi/2, \pi]$  and, correspondingly,

$\Delta z < 0$  which, from (1.8), tells us that these particles typically absorb momentum from the layer at  $z$ .

Our goal is to work out the force per unit area acting on any  $z$  slice. This is given by the rate of change of momentum

$$\frac{F}{A} = -\frac{1}{A} \frac{\Delta p}{\Delta t}$$

where the minus sign arises because  $F$  defined in (1.6) is the force you need to apply to keep the flow moving (while  $\Delta p/\Delta t$  is the force of the fluid pushing back). The rate of change of momentum per unit area is simply the product of our two expressions (1.7) and (1.8). We have

$$\begin{aligned} \frac{F}{A} &= -n \int d^3v \Delta p v_z f(\vec{v}) \\ &= -mn \frac{du_x}{dz} \int d^3v v_z \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} l \cos \theta \end{aligned}$$

We've actually done something sly in this second line which is not really justified. We're assuming that the fluid has an average velocity  $\langle v_x \rangle = u_x$  in the  $x$ -direction. Yet, at the same time we've used the Maxwell-Boltzmann distribution for the velocity of the particles which has  $\langle v_x \rangle = 0$ . Presumably this is not too bad if the speed of the flow  $u \ll \langle v \rangle$ , the average speed of the particles in the fluid, but we really should be more careful in quantifying this. Nonetheless, the spirit of this section is just to get a heuristic feel for the physics, so let's push on regardless. Writing the velocity integral in polar coordinates, we have

$$\frac{F}{A} = -mn \frac{du_x}{dz} \int dv v^2 \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi (-v \cos \theta) l \cos \theta \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}} \quad (1.9)$$

At this stage we can trivially do the  $\int d\phi$  integral and  $\int_0^\pi d\theta \cos^2 \theta \sin \theta = 2/3$ . We're left with

$$\frac{F}{A} = \frac{mnl}{3} \frac{du_x}{dz} \int dv 4\pi v^3 \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\beta mv^2/2} \quad (1.10)$$

But the integral  $\int dv$  is simply the expression for the average speed  $\langle v \rangle$  in the gas. We have our final expression,

$$\frac{F}{A} = \frac{1}{3} mnl \langle v \rangle \frac{du_x}{dz}$$

Comparing with (1.6), our expression for the viscosity is

$$\eta = \frac{1}{3} m n l \langle v \rangle \quad (1.11)$$

There is something surprising about the viscosity: it is independent of the density  $n = N/V$  of the gas. At first sight that looks like a wrong statement because, obviously, there is a factor of  $n$  sitting in (1.11). But remember that the mean free path depends inversely on the density,  $l \sim 1/n$ , as we can see from (1.2). The fact that the viscosity does not depend on the fluid density is rather counterintuitive. You might think that denser gasses should be more viscous. But the derivation above provides the explanation for this behaviour: if you halve the density, there are half as many molecules moving down. But each travels twice as far and therefore imparts twice the momentum kick  $\Delta p$  when they finally hit.

The expression (1.11) holds a special place in the history of physics. It was first derived by Maxwell and is arguably the first truly novel prediction that was made using kinetic theory, providing important evidence for the existence of atoms which, at the time, were not universally believed. Indeed, Maxwell himself was surprised by the fact that  $\eta$  is independent of the density of the gas, writing at the time

*“Such a consequence of the mathematical theory is very startling and the only experiment I have met with on the subject does not seem to confirm it”.*

Maxwell rose to the challenge, building the apparatus and performing the experiment that confirmed his own prediction.

### 1.3.3 Thermal Conductivity

The next transport process we will look at is the conduction of heat. Place a fluid between two plates, each held at a different temperature. Empirically, one finds a flow of energy in the fluid. This is described by the heat flow vector,  $\vec{q}$ , defined by the energy per unit time passing through a unit area (which is perpendicular to  $\vec{q}$ ). Empirically, the flow of heat is proportional to the temperature gradient,

$$\vec{q} = -\kappa \nabla T \quad (1.12)$$

where  $\kappa$  is called the *thermal conductivity*. Once again, we would like to derive both this empirical law, as well as an expression for  $\kappa$ .

Our calculation follows the same path that we took to determine the viscosity. Let's set up a temperature gradient in the  $z$ -direction. The number of particles with velocity  $\vec{v}$  that pass through a slab at position  $z$  per unit time per unit area is again given by (1.7). We'll use equipartition and assume that the average energy of a particle at position  $z$  is given by

$$E(z) = \frac{3}{2}k_B T(z)$$

We also need to know how particles deposit or gain energy when they reach the slab. If a particle came from a hot place with temperature  $T(z + \Delta z)$ , we'll assume the particle deposits the difference in energy. Similarly, if the particle arrives from a colder place, we'll assume it absorbs the difference. This means

$$\Delta E = E(z + \Delta z) - E(z) = \frac{3}{2}k_B \frac{dT}{dz} \Delta z$$

Recall that the height  $\Delta z$  from which the particle arrives depends on both the mean free path and the angle at which it comes in:  $\Delta z = l \cos \theta$ .

As in the derivation of the viscosity, there is something a little dodgy in what we've written above. We've equated the energy deposited or gained by a particle with the average energy. But this energy transfer will certainly depend on the velocity of the particle and which is dictated by the Maxwell-Boltzmann distribution in (1.7). As in the derivation of the viscosity, we will simply ignore this fact and proceed. We'll do better in the next section.

Modulo the concerns above, we now have enough information to compute the heat flow. It is

$$|\vec{q}| = n \int d^3v \Delta E v_z f(v)$$

Doing the integrals  $\int d^3v$  using the same steps that took us from (1.9) to (1.10), we derive the law of heat flow (1.12)

$$|\vec{q}| = -\frac{1}{2}k_B n l \langle v \rangle \frac{dT}{dz}$$

The thermal conductivity is the proportionality constant. It is usually expressed in terms of the specific heat,  $c_V$ , of the ideal gas

$$\kappa = \frac{1}{3}c_V l \langle v \rangle \tag{1.13}$$

where

$$c_V = \frac{3}{2}n k_B$$



### 1.3.4 Conservation Means Diffusion

Thermal conductivity is all about the transport of energy; viscosity is about the transport of momentum. But both energy and momentum have a very special property: they are conserved.

What's more, because physics is local, we can make a stronger statement than just “the total energy doesn't change”. If the energy in some region of space,  $E(\vec{x})$ , changes then it must show up in a neighbouring region of space. But that's exactly what the heat flow  $\vec{q}$  is telling us: how energy is moving from one point to the next. This local conservation law is captured by the equation.

$$\frac{dE}{dt} + \nabla \cdot \vec{q} = 0$$

Once again equating energy with the thermal energy,  $E(\vec{x}) = \frac{3}{2}k_B T(\vec{x})$ , the continuity equation reads

$$\frac{dT}{dt} = -\frac{1}{c_V} \nabla \cdot \vec{q} = \frac{\kappa}{c_V} \nabla^2 T \quad (1.14)$$

This is the *heat equation*. It tells us that any inhomogeneities in temperature are smoothed out through diffusion with diffusion constant  $D = \kappa/c_V = \frac{1}{3}l\langle v \rangle \sim l^2/\tau$ .

There is a similar story for momentum,  $p^i$  where  $i = 1, 2, 3$  labels the three directions of space. The continuity equation reads

$$\frac{dp^i}{dt} + \frac{\partial P^{ji}}{\partial x^j} = 0$$

where  $P^{ji}$  is the *pressure tensor* which describes the flux of  $i$ -momentum in the  $j$ -direction.

But looking back at our derivation of the viscosity in Section 1.3.2, this is precisely what we equated to the force  $F/A$ : the flux of  $x$ -momentum in the  $z$ -direction. (Actually there's an extra minus sign that follows from our previous definition of  $F$ ). Combining the continuity equation with our earlier expression for the viscosity, we find

$$\frac{dp^x}{dt} = mn \frac{du_x}{dt} = \eta \frac{d^2 u_x}{dz^2}$$

where, as in Section 1.3.2, we've restricted to situations with no velocity gradients in the  $x$  and  $y$  directions. The result is once again a diffusion equation, this time for gradients in velocity. And, once again, the diffusion constant given by  $D = \eta/mn = \frac{1}{3}l\langle v \rangle \sim l^2/\tau$ .

We learn that all roads lead to diffusion. For any conserved quantity – whether particle number, energy or momentum – any inhomogeneities in the system are smoothed away through the diffusion equation.

The equations that we’ve written down in this final section are rather hand-waving and, in cases, missing some interesting physics. The proper equations are those of hydrodynamics. The goal of the next section is to do a better job in deriving these.