PHYSICAL THERMODYNAMICS
HILARY TERM 2015

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Books We will frequently refer to two books:

- *Concepts in Thermal Physics* by Blundell and Blundell, published by Oxford University Press. (Hereafter **BB**)
- *Fundamentals of Physics* by Halliday, Resnick, and Walker, published by John Wiley. (Hereafter **HRW**)

You are encouraged to purchase these for use during the course, for consultation during future courses at Oxford, and as a reference throughout your career in science. Both books are available at University and college libraries.

Lectures There will be about three lectures per week for the first four weeks of term. Please see the lecture schedule for details.

Lecture topics (Subject to modification)

Lecture 1 Preliminaries. Motivation; key concepts; the Ideal Gas law; temperature and heat; the Zeroth law of thermodynamics; review of probability.

Lecture 2 Kinetic theory I. Microstates vs. macrostates; a statistical definition of temperature; the Boltzmann distribution; geophysical application: isothermal atmosphere; the velocity distribution.

Lecture 3 Kinetic theory II. The Maxwell-Boltzmann distribution; pressure and the Ideal Gas law; mean-free path.

Lecture 4 Kinetic theory III. Diffusion of heat; diffusion of chemical species; the heat equation.

Lectures 5 Classical thermodynamics I. Internal energy; First law of thermodynamics; adiabatic and isothermal processes; geophysical application: adiabatic atmosphere.

Lectures 6 Classical thermodynamics II. Second law of thermodynamics; heat engines; the Carnot cycle.

Lecture 7 Classical thermodynamics III. Entropy; internal energy revisited; geophysical application: adiabatic mantle and potential temperature.

Lecture 8 Classical thermodynamics IV. Phase transitions; latent heat; Clausius-Clapyron; phase diagrams.

Lecture 9 Spill-over from previous lectures. Questions and discussion.

Practice sheets There will be three assigned practice sheets, to be distributed at the third lecture each week. Each sheet will consist of several quantitative problems, and several essay questions. The sheets are intended to help you develop, clarify, and assess your understanding of the material. *You should complete them carefully and thoroughly,*

taking the time neccessary to learn the requisite material. Do not expect that this will be easy! At the end of this series of lectures, you should schedule a tutorial to discuss your results. The names of possible tutors will be made available in lecture. *Note that these problems will not neccessarily cover the full scope of the taught material—they are merely representative of the depth of understanding that is expected of you.*

Problem classes There are three scheduled problem classes, one per week, starting in week 2. *Come to these sessions prepared: having read, understood, and planned how to solve the problems.*

Other important points Please read carefully:

- **These notes** are not a complete description of the information that is to be understood as part of the course. The complete description is contained in the union of these notes, the lectures themselves, and the book-sections referred to below and in the lectures. *The level of mathematics that will be required on an examination of this material is approximately equivalent to that of the assigned problems.*

- **Questions** in the notes are meant as a check on your understanding. Try to answer them; if a question confuses you, it is an indication that you should review the course materials and, perhaps, seek help from a peer, a tutor, or the lecturer.

- **You are responsible** for developing and assessing your own understanding of the material by completing the problem sheets and discussing them with your tutors.

Contents

1 Preliminaries

In this lecture we consider the motivation for a study of thermodynamics. We learn basic concepts that form the basis for the rest of the material. We introduce the Ideal Gas law, heat capacity, the Zeroth law of thermodynamics. There is a brief review of probability.

1.1 Why study thermal physics?

Material From the top of the atmosphere, to the centre of the inner core, to the first forms life, Earth science is concerned with materials and how they behave under variable conditions.

Energy Energy drives all terrestrial processes, and it links them together. From the nucleus of an atom, the metabolism of an organism, the climate, the production and eruption of molten rock, to the tectonic motions of the Earth's surface plates, energy is the key physical connection.

Mathematics Mathematics is the language that can best describe the physical world. Words are a starting point, a means for communicating mathematical results, and a fall-back in cases where we are yet unable to develop mathematical models.

1.2 Physics, mathematics, and this course

The purpose of this course of lectures is to introduce you to the physics of energy. We will describe this physics with words, diagrams, and mathematics. *The equations we will write down are not recipes for obtaining a numerical answer to a problem; instead they encapsulate the physical concepts, giving them a concise expression that can be manipulated using mathematical rules.* Hence the derivation of these equations is the process by which we go from a physical idea to a mathematical expression. It will not be required that you reproduce these derivations. However you should understand the physical concepts and assumptions that go into them, and the mathematical results that come out, and how the two are connected.

1.3 Key concepts

Mole A mole is a quantity of discrete objects. To be specific, a mole is equal to an *Avogadro number* of objects: $N_A = 6.022 \times 10^{23}$. This is the number of atoms that are contained in 12 g of the isotope ^{12}C. It is merely a reference number.

The molar mass of an object is the mass of one object times the Avogadro number. For example, the molar mass of British one-pound coins is 9.5 g $\times N_A = 57.2 \times 10^{23}$ g.

Number density The number density n is the number of particles within a given volume. If you have N molecules of gas in a volume V then the number density of molecules is $n = N/V$.

Pressure A force applied over an area is called a pressure, and has units of Pascals:

$$\text{pressure} = \frac{\text{force}}{\text{area}}, \qquad \left[\frac{\text{kg-m/s}^2}{\text{m}^2} \equiv \text{Pa}\right].$$

Thermodynamic limit (See the raindrops-on-roof analogy, **BB 1.2**) A very large number of instances of a random variable, such that the differences of that variable from its mean value average to nought.

Infinitessimal An infinitessimal is a mathematical representation of a vanishingly small quantity. For some variable x, an infinitessimal change in x is written as $\mathrm{d}x$. We can take $\mathrm{d}x$ as being *arbitrarily small*: as small as we need it to be for the computation at hand. The ratio of infinitessimal quantities is a derivative, e.g. $\mathrm{d}y/\mathrm{d}x$.

Extensive variable A quantity that scales with the size of the body it measures. Examples (think of a container of a gas): volume, mass, kinetic energy. If you cut the container in half, each new container will contain half the volume, mass, and kinetic energy.

Intensive variable A quantity that does NOT scale with the size of the body it measures. Examples (again, think of a container of a gas): temperature, pressure, density. If you cut the container in half, each half will have the same temperature, pressure, and density as the original container of gas.

Classical thermodynamics deals with macroscopic properties of a system such as its pressure, temperature, and volume. It consists of laws relating variations among these quantities.

Kinetic theory of gasses considers the microscopic motions of molecules in a gas and uses statistical averages to derive, in the *thermodynamic limit*, the macroscopic properties of the gas.

1.4   The Ideal Gas Law

The following are known from experiments on confined gasses

$$\begin{array}{ll} p \propto V^{-1} & \text{Boyle's law} \\ V \propto T & \text{Charles' law} \\ p \propto T & \text{Gay-Lussac's law} \end{array}$$

Putting these together gives $pV \propto T$. We might also expect the pressure and the volume to scale with the *number of molecules N* of the gas. Incorporating this and including a constant of proportionality gives

$$pV = Nk_BT, \tag{1}$$

where $k_B = R/N_A$ J K^{-1} is *Boltzmann's constant* ($R = 8.315$ J mol^{-1} K^{-1} is the Universal Gas Constant). Verify that substitution for k_B gives the familiar form $pV = n_m RT$, where $n_m = N/N_A$ is the number of moles of gas molecules.

The Ideal Gas law is an *equation of state*, and is very useful. It tells us, for an ideal gas, how any one property of the gas changes as we change other properties. It raises several questions and comments:

- This law was stated based on empirical measurements. How does it follow from first principles? We will address this question using Kinetic Theory, starting in Lecture 2.

- What is an "ideal gas" anyway? Kinetic Theory will define this rigorously. For now, lets say it is a *dilute gas* (i.e. there is a lot of empty space between molecules) in which intermolecular forces and molecular diameter are both negligibly small. As it turns out, these assumptions apply (approximately) to many gasses of interest.

- Not all gasses are well-described by this law. Not all materials that will concern us are gasses.

- Consider the variables in equation (1): p, V, N, and T. The first three are rather clear in their meaning: p is pressure or force per unit area; V is volume; N is the number of molecules of gas. We can imagine simple ways to measure these. Temperature T, although intuitively obvious, is not so clear, when you consider it carefully. *What is temperature?*

1.5 Temperature and heat

(A temporary definition) **Temperature** is a measure of "hotness" or "coldness."

But what are "hotness" and "coldness?" To answer this question, consider two identical blocks of material: block one possesses "hotness," and block two possesses "coldness" (both are completely insulated from the rest of existence). Now put these two blocks into *thermal contact* with each other and leave them for a while—the blocks become indistinguishable. The hot block (block one) has lost its hotness and the cold block (block two) has lost its coldness, and hence the two are at the same *temperature*. The blocks are then said to be in *thermal equilibrium*. **BB 4.1 HRW 18-7**

How did the process of *thermalisation* between our two blocks of different temperature occur? Thermal energy flowed from block one to block two. **BB 2.1**

Thermal energy in transit is called **heat Q**.

The transfer of heat raised the temperature of block two and lowered the temperature of block one until they were in thermal equilibrium.

How much heat was transferred? That depends on the difference in temperature between the blocks, the mass of the blocks, as well as the *specific heat capacity* of the material in the blocks. **BB 2.2 HRW 18-8**

Specific heat capacity is the amount of heat dQ required to change the temperature of a unit mass of material by a specified, small amount dT.

From this definition, we can write that for a block of mass M kg, $dQ = cM\,dT$ or

$$c = \frac{1}{M}\frac{dQ}{dT},$$

where c is the specific heat capacity in J K^{-1} kg^{-1}.

Now if blocks one and two were initially at temperatures T_1 and T_2, respectively, with $T_1 > T_2$, then we can calculate their final temperatures, and the amount of heat transferred. As stated above, the blocks are identical, so they have the same c and M, and we'll assume that c is independent of temperature. At thermal equilibrium, they both have the same temperature, T_f. Because they are in thermal contact and otherwise insulated, the heat transferred into each block must sum to zero. Thus we can write

$$Q_1 + Q_2 = cM(T_f - T_1) + cM(T_f - T_2) = 0$$

and solve to obtain $T_f = (T_1 + T_2)/2$. The heat transferred out of block one is thus $Q_1 = cM(T_2 - T_1)/2$ J; Q_1 is negative because block one lost heat.

Question: Suppose blocks one and two start with different specific heat capacities (c_1 and c_2) and different masses (M_1 and M_2). What are their final temperatures and how much heat was transferred?[*]

BB 2.2

There's just one small complication to be added to the discussion of heat capacity above: we know that materials tend to expand or contract as they change temperature. We did not specify whether our two-block thought experiment was carried out at constant pressure or at constant volume (in a rigid container). In fact, there is a different specific heat for each of these cases[†]. They are defined as:

$$c_p = \frac{1}{M}\left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_p, \tag{2a}$$

$$c_V = \frac{1}{M}\left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_V. \tag{2b}$$

1.6   The Zeroth law of thermodynamics

The concept of thermal equilibrium, introduced above, allows us to state the 0th law.

> **Zeroth law of thermodynamics**: Two systems, each separately in thermal equilibrium with a third, are in equilibrium with each other.

This is exactly as simple as it sounds. Suppose the two systems are blocks, and the third is a thermometer. If both blocks are in thermal equilibrium with the same thermometer, then both blocks are at the same temperature, and hence they are in thermal equilibrium with each other. (N.B. the thermometer is a system with a temperature; in thermal equilibrium that temperature is the same as the system that it is used to measure.) Another way to state the 0th law: thermometers work.

1.7   Basic probability

Read: Chapter 3 of **BB**.

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[*]Answer: when the blocks reach thermal equilibrium, they have the *same temperature*—let's call it T_f. As before, the heat transferred into each block must sum to zero, since the system is isolated. Hence we can write:

$$c_1 M_1(T_f - T_1) + c_2 M_2(T_f - T_2) = 0,$$

and we can solve this equation for T_f.

[†]This distinction is especially important if the blocks are actually containers of gas.

A *discrete probability distribution* gives the likelihood that a discrete random variable will take on any given value. Consider a 6-sided die; let the discrete random variable x_i represent the different results of rolling and P_i the likelihood of obtaining the value x_i (assume the die is not "crooked."). Then

$$x_i = \{1, 2, 3, 4, 5, 6\},$$
$$P_i = \left\{ \frac{1}{6}, \frac{1}{6}, \frac{1}{6}, \frac{1}{6}, \frac{1}{6}, \frac{1}{6} \right\}.$$

Note that the sum of the probabilities must be equal to unity

$$\sum_i P_i = 1, \tag{3}$$

and that the *mean* (or *average*, or *expected value*) of x is

$$\langle x \rangle = \sum_i x_i P_i, \tag{4}$$

and the mean of any function of x is given by

$$\langle f(x) \rangle = \sum_i f(x_i) P_i. \tag{5}$$

Question: What are $\langle x \rangle$, $\langle ax + b \rangle$, and $\langle x^2 \rangle$ for the die example above? (*a* and *b* are constants.)

A continuous probability distribution gives the likelihood that a continuous random variable x will take on a value with a given range (say $x_1 \le x \le x_2$):

$$\int_{x_1}^{x_2} P(x)\mathrm{d}x.$$

Analogous to the discrete distribution,

$$\int P(x)\mathrm{d}x = 1, \tag{6}$$

$$\langle x \rangle = \int x P(x)\mathrm{d}x, \tag{7}$$

$$\langle f(x) \rangle = \int f(x) P(x)\mathrm{d}x. \tag{8}$$

Be sure to familiarise yourself with the properties of a *Gaussian distribution*, example 3.3 in **BB**. Also review the variance (**BB** 3.4) and the mean of the product of two independent random variables (**BB** 3.6).

2　Kinetic theory I

The purpose of the next three lectures is to introduce the *Kinetic Theory* of gasses. This is a theory that aims to explain how macroscopic features of a gas system (pressure, temperature, volume) arise from the microscopic motions and forces of molecules. We will see that many macroscopic properties arise from the *kinetic energy* of molecules—this is the same kinetic energy that you learned about in the lectures on Mechanics.

In this lecture　we derive a statistical definition of temperature. We learn how, for a gas, temperature determines the probability distribution of molecular velocities.

2.1　Microstates vs. macrostates

How can we describe the state of a collection of molecules that compose a closed box of gas? For kinetic theory, we will need two descriptions: one that accounts for each individual molecule, and another that accounts for the system as a whole. Before we talk about the gas, let's consider two simpler systems, dice and coins.

A *microstate* is a description of the state of each individual element of a system at a given instant. In a system consisting of three individually labelled, six-sided dice on a table, the microstate would be given by:

$$\text{microstate } s = [\text{Die A: 3,}\quad \text{Die B: 1,}\quad \text{Die C: 6}],$$

where the number corresponds to the face of each die that is pointing upward.

A *macrostate* is a description of the state of a system as a whole. In the dice example, the macrostate could be definied as the *sum* of the three dice. In that case, for the given microstate above, the macrostate would be

$$\text{macrostate } S = 3 + 1 + 6 = 10.$$

BB 4.3

Next consider a system composed of five randomised coins, numbered one through five, but otherwise indistinguishable. One *microstate* of the system is $s = [H, T, T, T, T]$, where a H indicates "heads" and a T indicates "tails." Clearly there are five different microstates s that correspond to the *macrostate* $S = 1$, which indicates that one of the five coins is heads. These are:

$$\text{Microstates corresponding to } S = 1:$$
$$s_1 = [H, T, T, T, T]$$
$$s_2 = [T, H, T, T, T]$$
$$s_3 = [T, T, H, T, T]$$
$$s_4 = [T, T, T, H, T]$$
$$s_5 = [T, T, T, T, H]$$

In total, there are $2^5 = 32$ distinct microstates of this 5-coin system. *Key concept: each distinct microstate is equally probable!* In contrast, there are only six macrostates $S_i = \{0, 1, 2, 3, 4, 5\}$; these have different probabilities.

What is the probability of each macrostate? There is only one microstate corresponding to the macrostate $S = 0$ so it has probability $P_0 = 1/32$. There are $5!/(3!\,2!)$ microstates corresponding to three heads $S = 3$ (why?), so it has $P_3 = 10/32$. The probabilities of all macrostates are $P_i = \left\{ \frac{1}{32}, \frac{5}{32}, \frac{10}{32}, \frac{10}{32}, \frac{5}{32}, \frac{1}{32} \right\}$.

Question: Consider a system composed of three tetrahedral (4-sided) dice. (a) How many microstates does this system have? (b) What is the probability that after rolling the dice, the system is in the microstate $s = [4, 4, 4]$? (c) What is the probability that it is in the macrostate $S = 4$?*

2.2   A statistical definition of temperature

How can we understand temperature in terms of the motion of a collection of molecules?

Consider a container of gas with N total molecules; this system has a microstate and a macrostate. The microstate might be defined as the kinetic energy ϵ of each molecule in the system at a given instant,

$$ s = [\epsilon_1,\ \epsilon_2,\ \epsilon_3, ...,\ \epsilon_N], $$

while the macrostate could be the temperature of the system at the same time. In general, **BB 4.4** the microstate is unknowable, but *we can assume that number of possible microstates depends on the total energy E of the system*; we denote the number of possible microstates for a given total energy as $\Omega(E)$.

Now consider two containers of gas, each with N molecules. Suppose that initially, each container has a different quantity of energy, E_1 and E_2, corresponding to a different number of microstates, $\Omega_1(E_1)$ and $\Omega_2(E_2)$. The containers are brought into thermal contact but are otherwise isolated so the total energy $E = E_1 + E_2$ is fixed. The number of microstates of the combined system is $\Omega_1(E_1)\Omega_2(E_2)$.

How will the total energy be distributed in thermal equilibrium? E_1 and E_2 will take on values *such that the combined system obtains the macrostate that corresponds to the largest possible number of microstates*. Why does this occur?

1. The system is rapidly changing from one microstate to another;

2. each of the $\Omega_1\Omega_2$ microstates is equally likely;

3. over a long enough time interval, the system will spend an equal amount of time in each microstate. Its macrostate will be that which corresponds to the largest number of different microstates.

So we seek the maximum of $\Omega_1(E_1)\Omega_2(E_2)$ for all values of E_1 and E_2. We know that these energies are not independent, however; in fact, $E_1 + E_2 = E$ and so $dE_1 = -dE_2$. To find the maximum, we can thus search over all values of E_1:

$$ \frac{\mathrm{d}}{\mathrm{d}E_1}\left(\Omega_1(E_1)\Omega_2(E_2)\right) = 0. \tag{9} $$

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*Answers: (a) 64 microstates, (b) $P = 1/64 = 0.015625$, (c) $P = 3/64 = 0.046875$.

Using the product rule and the relationship between dE_1 and dE_2 we can write

$$\frac{d\ln\Omega_1}{dE_1} = \frac{d\ln\Omega_2}{dE_2}. \tag{10}$$

This condition will hold when the blocks are in thermal equilibrium. We know that in thermal equilibrium the temperature of each block is equal to the other. This motivates us to define the temperature as

$$\frac{1}{k_B T} = \frac{d\ln\Omega}{dE}. \tag{11}$$

You can verify that combining equations (10) and (11) gives $T_1 = T_2$. The choice of the constant k_B means that T has units of Kelvin and that our definition will have a useful physical interpretation, as we shall see later.

2.3   The Boltzmann distribution

In a gas of temperature T, how much kinetic energy does any given molecule have? Since all the molecules are bouncing around in the gas with different speeds, we can only answer this in terms of a probability distribution, the *Bolzmann distribution*.

The Boltzmann distribution describes the probability that a single molecule within our container of gas will have a given kinetic energy ϵ. Consider a microscopic system (one molecule, chosen at random) in thermal contact with a huge energy reservoir (the reservoir is huge because it contains many molecules, and *much* more energy than ϵ). There are several **BB 4.6** important points to note

- The total energy of the reservoir plus microscopic system (our one molecule) is fixed at E. The reservoir has energy $E - \epsilon$.

- Since $\epsilon \ll E$, fluctuations of ϵ have a minuscule effect on the energy of the reservoir, and we can assume the reservoir is at a fixed temperature, T.

- The one molecule, as a system by itself, is so simple that for each allowed value of its energy, there is only one associated microstate: $\Omega(\epsilon) = 1$.

- For a given energy ϵ, the total number of microstates available to the coupled reservoir and microscopic system is $\Omega(E-\epsilon) \times 1$. The probability that the microsystem has energy ϵ is therefore given by $P(\epsilon) \propto \Omega(E - \epsilon)$.

Since $\epsilon \ll E$, we can make a simple, linear approximation of the quantity $\ln\Omega(E - \epsilon)$

$$\ln\Omega(E - \epsilon) \approx \ln\Omega(E) + \frac{d\ln\Omega}{d(E)}(-\epsilon), \tag{12}$$

which is actually quite accurate because ϵ is very very small compared to E. Using our definition of temperature from equation (11), we can write

$$\ln\Omega(E - \epsilon) \approx \ln\Omega(E) - \frac{\epsilon}{k_B T}, \tag{13}$$

where T is the temperature of the reservoir. Exponentiating equation (13) and using $P(\epsilon) \propto \Omega(E - \epsilon)$ we have

$$P(\epsilon) \propto \mathrm{e}^{-\epsilon/(k_B T)}. \tag{14}$$

When properly normalised, equation (14) is the Boltzmann distribution.

> A single molecule is coupled to a reservoir at temperature T. The probability P that the single molecule has energy ϵ is proportional to the **Boltzmann factor**: $P(\epsilon) \propto \mathrm{e}^{-\beta \epsilon}$, where $\beta = (k_B T)^{-1}$.

The Boltzmann factor states that the probability of our single molecule having an energy ϵ decreases as ϵ gets larger, and that *the rate at which probability decreases with increasing ϵ is determined by the temperature of the gas reservoir*. This is best understood with a graph, Figure 1. In this figure, we compare the probability density functions for a single molecule in two different containers: one at temperature T_a and one at temperature T_b.
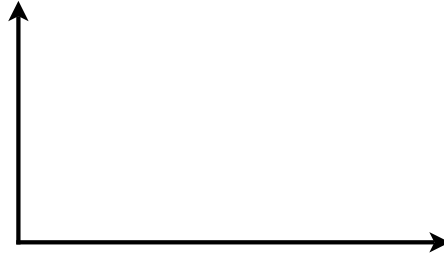
Figure 1: A plot of the Boltzmann factor for two different temperatures, T_a and T_b. (Axis labels and lines to be added by the student).

The *Boltzmann distribution* is

$$P(\epsilon) = C\mathrm{e}^{-\beta \epsilon}, \tag{15}$$

where C is a normalisation factor, which ensures that $\int_0^\infty P(\epsilon)\mathrm{d}\epsilon = 1$. We will use this important formula in the next lecture.

2.4   Geophysical application: isothermal atmosphere

We can use the Boltzmann factor to construct a model for the density of the atmosphere as a function of height. To do so, we assume that the atmosphere is isothermal, with temperature T.   **BB 4.7**

Method 1 – using the Boltzmann distribution   The potential energy of a molecule with mass m at height z in a gravity field with acceleration g is mgz. Hence we can write

$$P(z) \propto \mathrm{e}^{-mgz/(k_B T)}.$$

The number density of molecules at height z in the atmosphere will be proportional to the probability $P(z)$. This means that the number density (molecules per cubic meter) is

$$n(z) = n(0)\mathrm{e}^{-mgz/(k_B T)},$$

where $n(0)$ is the number density at the surface of the Earth.

Method 2 – using the Ideal Gas law   We can check this result by trying to derive it
with a different approach. Consider a layer of the atmosphere between z and $z + dz$ that has
number density of particles n. The downward pressure exerted by this layer is

$$dp = -nmg\,dz.$$

Now recall equation (1), the ideal gas law. Dividing both sides by V gives $p = nk_BT$, where
n is, again, the number density of molecules. Differentiating both sides gives

$$dp = dn\,k_BT.$$

Combining this with our previous expression for dp gives

$$\frac{dn}{n} = -\frac{mg}{k_BT}dz,$$

which we can integrate to give, again,

$$n(z) = n(0)e^{-mgz/(k_BT)},$$

which is consistent with our earlier result.

We predict that the number density of the atmosphere decreases exponentially with height.
This turns out to be wrong, because our assumption of an isothermal atmosphere is wrong.
We will return to this problem later in the course.

2.5   The probability distribution for velocity

We now apply the Boltzmann distribution to determine the probability distribution g that a
molecule of gas will have a given velocity $\mathbf{v} = (v_x, v_y, v_z)$. To do so, we make three important
BB 5.1   assumptions.

- Molecular size is much smaller that intermolecular spacing, so collisions between
  molecules are rare and negligiable.

- There are no intermolecular forces.

- Each molecule behaves like a microsystem coupled to a thermal reservoir at temperature
  T, composed of all the other molecules in the gas.

Recall that the kinetic energy of a molecule is given by

$$\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 = \frac{1}{2}mv^2, \tag{16}$$

where $v = |\mathbf{v}|$. We can use the kinetic energy in each direction to define the Boltzmann factor;
for example, in the x-direction we have

$$g(v_x) \propto e^{-mv_x^2/(2k_BT)}. \tag{17}$$
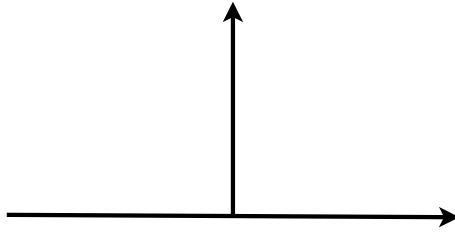
Figure 2: A Gaussian distribution. (Axis labels and lines to be added by the student).

To find the normalisation factor for the Boltzmann distribution, we evaluate the integral

$$\int_{-\infty}^{\infty} e^{-mv_x^2/(2k_BT)}dv_x = \sqrt{\frac{2\pi k_BT}{m}}. \tag{18}$$

Then, since we require that $\int_{-\infty}^{\infty} g(v_x)dv_x = 1$, we have

$$g(v_x) = \sqrt{\frac{m}{2\pi k_BT}}\, e^{-mv_x^2/(2k_BT)}. \tag{19}$$

This is a Gaussian distribution with a mean of zero and a variance of $\sigma_x^2 = \left\langle (v_x - \langle v_x \rangle)^2 \right\rangle = k_BT/m$; it is shown in Figure 2.

Note that there is nothing special about the x-direction; the distributions for the y- and z-directions are exactly the same as equation (19).

$$g(v_y) = \sqrt{\frac{m}{2\pi k_BT}}\, e^{-mv_y^2/(2k_BT)}. \tag{20}$$

$$g(v_z) = \sqrt{\frac{m}{2\pi k_BT}}\, e^{-mv_z^2/(2k_BT)}. \tag{21}$$

In the next lecture, we'll consider a slightly more complex quantity, the distribution of molecular *speeds*. The above results will be useful to keep in mind.

3   Kinetic theory II

In this lecture   we derive the probability distribution of molecular speeds in a gas, a result that will be very useful to us. We then examine how this distribution gives rise to a statistical definition of gas pressure. We also introduce the concept of molecular collisions, and define the mean free path.

In the last lecture we derived an expression for the distribution of velocity in each of the three Cartesian directions,

$$g(v_j) = \sqrt{\frac{m}{2\pi k_B T}}\, e^{-mv_j^2/(2k_B T)}, \tag{22}$$

where j can be replaced with x, y, or z. We can use this result to determine the fraction of molecules with velocity between $\mathbf{v} = (v_x, v_y, v_z)$ and $\mathbf{v} + d\mathbf{v} = (v_x + dv_x, v_y + dv_y, v_z + dv_z)$ by simply multiplying them together:

$$g(v_x)dv_x g(v_y)dv_y g(v_z)dv_z \propto e^{-mv_x^2/(2k_B T)}dv_x\, e^{-mv_y^2/(2k_B T)}dv_y\, e^{-mv_z^2/(2k_B T)}dv_z,$$

$$\propto e^{-m(v_x^2+v_y^2+v_z^2)/(2k_B T)}\, dv_x\, dv_y\, dv_z, \tag{23}$$

$$\propto e^{-mv^2/(2k_B T)}\, dv_x\, dv_y\, dv_z. \tag{24}$$

3.1   The Maxwell-Boltzmann distribution

BB 5.2   A more useful quantity, however, is the distribution of molecule *speed* $v = |\mathbf{v}|$. In particular, we can ask: what is the fraction of molecules that is travelling with speed between v and $v + dv$? In velocity space, this corresponds to the spherical shell between radii v and $v + dv$, shown in Figure 3.
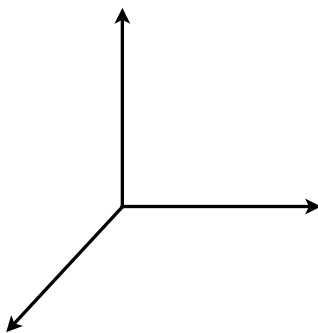

Figure 3: Velocity space. (Axis labels and lines to be added by the student).

What is the volume of velocity-space between the two shells? The volume of each spherical shell is

$$V(v) = \frac{4}{3}\pi v^3.$$

Therefore the volume between the two shells is

$$dV = \frac{dV}{dv}dv = 4\pi v^2 dv.$$

Now we can define the probability distribution f such that the probability that a molecule will have speed between v and $v + dv$ is given by

$$f(v)dV \propto v^2 e^{-mv^2/(2k_BT)} dv, \tag{25}$$

where the factor 4π has been dropped since this is a statement of proportionality, not equality.

As with the velocity distribution, we need to normalise the function f such that $\int_0^\infty f(v)dv = 1$. (Note that we integrate from zero because speed is the absolute value of velocity and thus *cannot be negative*.)

$$\int_0^\infty v^2 e^{-mv^2/(2k_BT)} dv = \frac{1}{4}\sqrt{\frac{\pi}{[m/(2k_BT)]^3}}, \tag{26}$$

and thus we can write an equation for $f(v)$ as

$$f(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2} v^2 e^{-mv^2/(2k_BT)}. \tag{27}$$

This very important result is the **Maxwell-Boltzmann speed distribution**. A graph is shown in Figure 4.

Figure 4: The Maxwell-Boltzmann probability distribution. (Axis labels and lines to be added by the student).

We can calculate the expected values of equation (27) as

$$\langle v \rangle = \int_0^\infty v f(v)\, dv = \sqrt{\frac{8k_BT}{\pi m}}, \tag{28}$$

$$\langle v^2 \rangle = \int_0^\infty v^2 f(v)\, dv = \frac{3k_BT}{m}. \tag{29}$$

Note that $\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3\langle v_j^2 \rangle = 3k_BT/m = \langle v^2 \rangle$, from equation (19).

Question: Calculate the mean $\langle v \rangle$ and root-mean-square $\sqrt{\langle v^2 \rangle}$ velocity of an oxygen molecule (O_2) at room temperature (300 K).

3.2   The mean kinetic energy of a gas molecule

The mean kinetic energy of a molecule in the gas described above is $\langle E_{KE} \rangle = \frac{1}{2}m\langle v^2 \rangle$. Using the result in equation (29) we can calculate that

$$\langle E_{KE} \rangle = \frac{3}{2}k_BT. \tag{30}$$

This equation states the the average kinetic energy of a molecule in a gas depends only on the temperature of the gas.

> The **mean kinetic energy** of a gas molecule is independent of its mass. It is directly proportional to the temperature of the gas.

3.3   Pressure and the Ideal Gas law revisited

HRW
19-4

Consider a cubic box of gas, shown in Figure 5, with volume $V = L^3$. The box is full of gas molecules with number density n (so there are $N = nV$ molecules in the box). Each molecule has a mass m and velocity $\mathbf{v}$, and the distribution of these velocities is given by equations (19), (20), and (21).
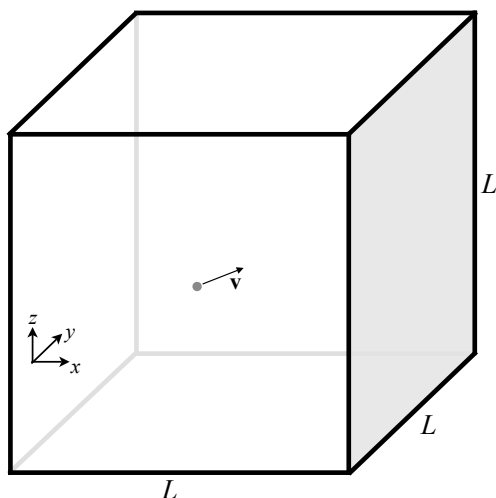
Figure 5: A cubic box filled with gas. One molecule of the gas is shown, with its velocity vector. The edges are of length L.

We can assume that the particles don't collide with each other; they only hit the walls. Each time a molecule hits a wall, it undergoes a perfect elastic rebound. For example, if a molecule that has velocity $\mathbf{v}_{before} = (v_x, v_y, v_z)$ hits the shaded wall in Figure 5, it rebounds with velocity $\mathbf{v}_{after} = (-v_x, v_y, v_z)$. In the process in imparts some momentum onto the wall. The momentum imparted is $m\,\Delta v_x = 2mv_x$. Since the molecule doesn't lose any speed in the collision with the wall, it will return to the same wall every $\Delta t = 2L/v_x$.

Since force is given by $F = \mathrm{d}(momentum)/\mathrm{d}(time)$, the force of one molecule on the shaded wall is

$$F = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}. \tag{31}$$

To find the total force on the shaded wall, we must sum the forces of all the N molecules on that wall:

$$F_{tot} = \sum_{i=1}^{N} \frac{m(v_x^2)_i}{L}, \tag{32}$$

but we can replace the sum with the total number of molecules times the mean-squared velocity to give

$$F_{tot} = \frac{m}{L} N \left\langle v_x^2 \right\rangle . \tag{33}$$

We can also use the following

- Pressure equals force divided by area. In this case, the area is L^2.

- Since N is large and all three directions are equivalent, the mean-squared speed in any one direction is one third the mean squared speed: $\left\langle v_x^2 \right\rangle = \left\langle v^2 \right\rangle /3$.

Applying both these points gives

$$p = \frac{mN}{3L^3} \left\langle v^2 \right\rangle = \frac{mN}{3V} \left\langle v^2 \right\rangle , \tag{34}$$

a statistically derived expression for the pressure of a gas.

Finally, using our result from equation (29), $\left\langle v^2 \right\rangle = 3k_B T/m$, and rearranging gives

$$pV = Nk_B T, \tag{35}$$

the Ideal Gas law!

To review the path that we took to this point:

1. We assumed a dilute gas with no intermolecular forces and no intermolecular collisions.

2. We used the idea that each molecule is coupled to the thermal reservoir of gas at temperature T to derive a probability distribution for molecular energy.

3. We used this result to derive the probability distribution of molecular speed in the gas.

4. We calculated the mean-squared molecular speed.

5. We calculated the pressure exerted by the gas on the wall of a box in terms of the frequency and momentum change of molecular collisions with the wall.

6. We used our expression for the mean-squared molecular speed to write the pressure in terms of temperature.

And hence we derived, from first principles, the empirically known Ideal Gas equation.

3.4 The frequency of collisions and the mean free path

Molecules in a gas are not points of zero diameter, they are objects with finite size and hence they sometimes collide. This has important consequences for molecular transport (diffusion), **HRW** as we shall see in the next lecture. Now we quantify occurrence of collisions. We assume that **19-6** collisions between molecules are perfectly elastic, like collisions between molecules and walls.

1. Consider a molecule in a gas with speed v_0 and cross-sectional area $\sigma = \pi d^2$, where d is the molecule radius. For now, *assume that all the other molecules are not moving and have zero diameter.* As our molecule bounces around within the gas, it sweeps out a (zigzag) cylindrical path behind it.

2. In a time Δt, the molecule goes a distance $v_0 \Delta t$ and thus sweeps through a volume of $\sigma v_0 \Delta t$.

BB 8.1

3. The number of collisions per Δt is equal to the number of other molecules that are in the swept volume. For a gas with particle density n, this number is, on average, $n\sigma v_0 \Delta t$. Thus the mean *frequency of collisions* for our molecule is $n\sigma v_0$; the mean *time between collisions* is $\tau_0 = (n\sigma v_0)^{-1}$.

4. The average distance travelled between collisions by the molecule that we are watching is the mean free path λ_0. For *this one molecule* the mean free path is its speed times the time-interval between collisions: $\lambda_0 = v_0 \tau_0 = (n\sigma)^{-1}$.

BB 8.3

5. However, we are interested in the mean free path for *all molecules in the gas*. In that case, we need the mean speed: $\lambda = \langle v \rangle \tau$.

6. Furthermore, we must substitute the mean time between collisions for *all molecules in the gas*. In this case, all the molecules are moving, and the collision interval is determined by the *mean relative speed* $\langle v_r \rangle = \langle |\mathbf{v}_r| \rangle$. In this case

$$\mathbf{v}_r = \mathbf{v}_1 - \mathbf{v}_2,$$
$$v_r^2 = \mathbf{v}_r \cdot \mathbf{v}_r = v_1^2 + v_2^2 - 2\mathbf{v}_1 \cdot \mathbf{v}_2.$$

When we take the mean of v_r^2 we must handle the cross term carefully:

$$\langle \mathbf{v}_1 \cdot \mathbf{v}_2 \rangle = 0 \text{ because } \langle \cos\theta \rangle = 0$$

where θ is the angle between the two velocity vectors. Since the vectors are independent and can point in any direction, θ ranges from zero to π. The mean value of $\cos\theta$ over this interval is zero, so the cross term drops out and we have

$$\langle v_r^2 \rangle = \langle v_1^2 \rangle + \langle v_2^2 \rangle = 2\langle v^2 \rangle,$$

where the second equality is true because $\mathbf{v}_1$ and $\mathbf{v}_2$ are drawn from the same probability distribution. We can then make two approximations[*]:

$$\langle v_r \rangle \approx \sqrt{\langle v_r^2 \rangle} \approx \sqrt{2}\langle v \rangle.$$

From this we have $\tau \approx \left(\sqrt{2}n\sigma\langle v\rangle\right)^{-1}$, which we can substitute into $\lambda = \langle v\rangle \tau$ to give

$$\lambda \approx \frac{1}{\sqrt{2}n\sigma}, \tag{36}$$

the (approximate) mean free path for all molecules in the gas.

---

[*]recall that

$$\langle v_r \rangle = \int v_r f(v_r) \mathrm{d}v$$

while

$$\sqrt{\langle v_r^2 \rangle} = \sqrt{\int v_r^2 f(v_r)\mathrm{d}v}.$$

7. We can use the Ideal Gas law $pV = Nk_BT$ to put this into a more useful form (recall that $n = N/V$)

$$\lambda \approx \frac{k_BT}{\sqrt{2}p\sigma}. \tag{37}$$

> The mean free path in an ideal gas is directly proportional to the temperature and indirectly proportional to the pressure of the gas.

In the next lecture, we will use this result to predict how energy and chemistry diffuse through a gas.

4   Kinetic theory III

In this lecture we explore how the motion of molecules within a gas gives rise to the diffusion of energy, temperature, and chemical species. We derive a macroscopic *diffusion equation* based on kinetic theory.

Recall that heat is defined as thermal energy in transit, and that the transport of energy is caused by a spatial *gradient* in temperature. Below we will show how this occurs at the molecular level in an ideal gas.

4.1   Aside: partial derivatives

A mathematical aside is required before we can discuss diffusion. This concerns a new notation for derivatives. You are used to seeing derivatives of functions of one variable. For example, for the function $f(x) = \sin(cx)$ with c constant, we can write

$$\frac{\mathrm{d}f}{\mathrm{d}x} = c\cos(cx),$$

and we know that this derivative is the *slope* of the curve $f(x)$. We have learned in this course that we can also write this as

$$\mathrm{d}f = c\cos(cx)\,\mathrm{d}x.$$

You can read this as "an infinitessimal change in x leads to a change in f of size $c\cos(cx)\mathrm{d}x$."

Often in physics, we need functions of more than one variable! We live in four dimensions, and many things that we're interested vary in all four. Consider temperature, for example: it changes with height, with distance to the North, with distance to the East, and with time. We could thus write $T = T(x, y, z, t)$. We could then ask: what is the rate of change in temperature with respect to time t? What is the rate of change of temperature with respect to height z? And so forth. We write each of these derivatives with a different *notation*:

$$\frac{\partial T}{\partial x}, \ \ \frac{\partial T}{\partial y}, \ \ \frac{\partial T}{\partial z}, \ \ \text{and} \ \frac{\partial T}{\partial t}.$$

These are called *partial derivatives*. They are just like regular derivatives, except for the different symbol! We've simply replaced the symbol d with the symbol ∂ to emphasise that T is a function of more than one variable.

Let's consider an example. The surface elevation h over some landscape is a function of distance East, which we'll call x, and distance North, which we'll call y. In fact, the landscape is very simple, and its surface height (meters above sea level) is described by the equation

$$h(x, y) = 300 + 100\sin(2\pi x/L)\cos(2\pi y/M). \tag{38}$$

This function is plotted in Figure 6 for $L = 10$ and $M = 6$. If we were planning a walk across this landscape, we might like to know its slope. Suppose that we expect to walk in the x-direction, along the line AA'; what is the slope of this line? We use the partial derivative
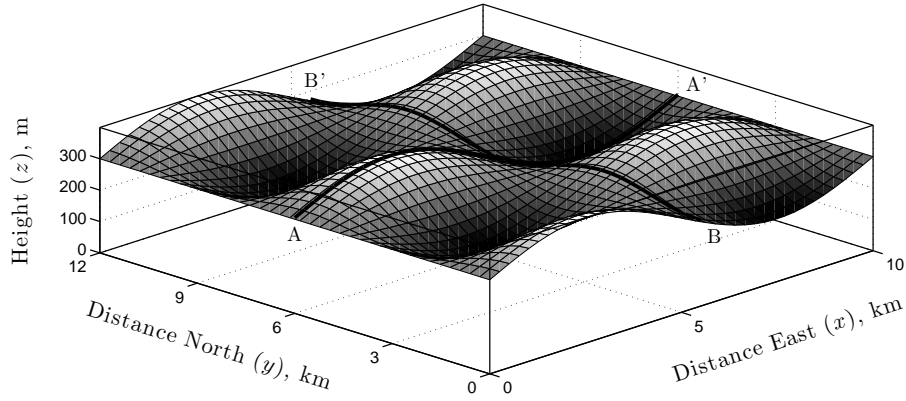
Figure 6: A plot of equation (38) representing the height of the landscape above sea level as a function of distance to the East (x) and distance to the North (y), for $L = 10$ and $M = 6$. Lines AA' and BB' are thicker curves.

with respect to x to find out:

$$\frac{\partial h}{\partial x} = \frac{\partial}{\partial x} \left[300 + 100 \sin(2\pi x/L) \cos(2\pi y/M) \right],$$

$$= 100 \cos(2\pi y/M) \frac{\partial}{\partial x} \sin(2\pi x/L),$$

$$= \frac{200\pi}{L} \cos(2\pi y/M) \cos(2\pi x/L).$$

Note that we treated $\cos(2\pi y/M)$ as a constant, even though y is a variable! The $\frac{\partial}{\partial x}$ tells us that we are only considering the result of variations in x. Since we are interested in the line AA', which is at $y = M$, we can further calculate that

$$\left. \frac{\partial h}{\partial x} \right|_{y=6} = \frac{200\pi}{L} \cos(2\pi x/L),$$

since $\cos(2\pi) = 1$.

We can do the same for the y-direction:

$$\frac{\partial h}{\partial y} = \frac{\partial}{\partial y} \left[300 + 100 \sin(2\pi x/L) \cos(2\pi y/M) \right],$$

$$= 100 \sin(2\pi x/L) \frac{\partial}{\partial y} \cos(2\pi y/M),$$

$$= -\frac{200\pi}{M} \cos(2\pi x/L) \sin(2\pi y/M).$$

In this case, we treated $\cos(2\pi x/L)$ as a constant because the partial derivative was with respect to y.

Question: What is the partial derivative of h from Equation 38 along the line BB', at $x = 5.5$?

Question: Calculate the following derivatives

$$\frac{\partial^2 h}{\partial x^2}, \quad \frac{\partial^2 h}{\partial y^2}, \quad \frac{\partial^2 h}{\partial x \partial y}$$

for $h(x, y)$ as defined in Equation 38.

When writing the partial derivative of a function in which the variables are *not independent*, it is sometimes neccessary to specify which variables are being held constant. For the above example this was not neccessary because x and y are independent variables: a change in x does not imply any change in y. In contrast, consider the ideal gas law, $pV = n_m RT$. Suppose we're interested in the change of pressure with respect to temperature $\partial p/\partial T$. Now recall that Charles' law states that $V \propto T$. So should we incorporate that derivative too? For clarity, we can write

$$\left(\frac{\partial p}{\partial T} \right)_V$$

to indicate that the volume is being held constant. The result is $(\partial p/\partial T)_V = n_m R/V$, of course. This corresponds to the case where the ideal gas is held within a rigid container of constant volume.

Question: Calculate, for an ideal gas, $(\partial V/\partial p)_T$. Describe the corresponding physical conditions.

4.2 Thermal transport in an ideal gas

BB 9.2

Consider an ideal gas with a linear gradient in temperature along the z-axis, as shown in Figure 7. The flux of thermal energy, J goes from the region of higher temperature to the region of lower temperature. We know that the average kinetic energy of a molecule in an ideal gas is proportional to the temperature, so a gradient in temperature must be equivalent to a gradient in kinetic energy, and therefore in mean molecular speed $\langle v \rangle$.
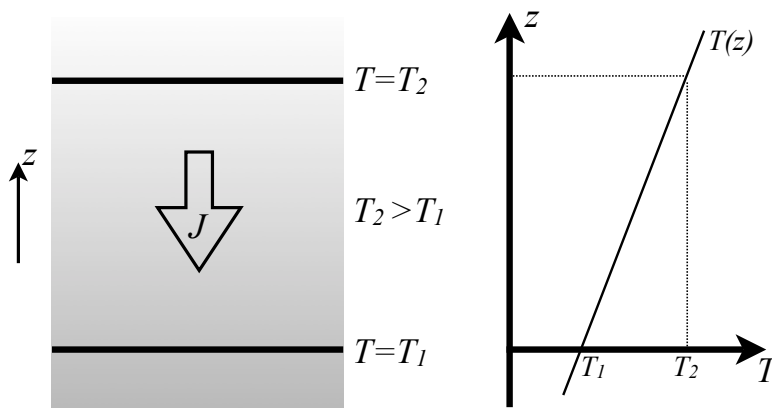

Figure 7: Thermal gradient in the z direction. The left panel shows the gas with temperature marked at two levels. The heat flux J is downward, from hot to cold. The grey-scale corresponds to temperature, with darker shades being colder. The right panel shows a plot of z versus temperature.

It is the molecules of the gas that transport heat. As the molecules bounce around randomly, higher KE molecules spread downward, and lower KE molecules spread upward. To calculate J, we can make the following steps of logic.

1. Consider a gas molecule at height z and temperature T. Between collisions, that molecule moves a distance that is the mean free path λ. In general, its velocity is at an angle θ to the z-direction, and hence the vertical distance moved is $\lambda \cos \theta$ (Fig. 8). It thus moves over a temperature difference

$$\Delta T = \lambda \cos \theta \frac{\mathrm{d}T}{\mathrm{d}z}.$$
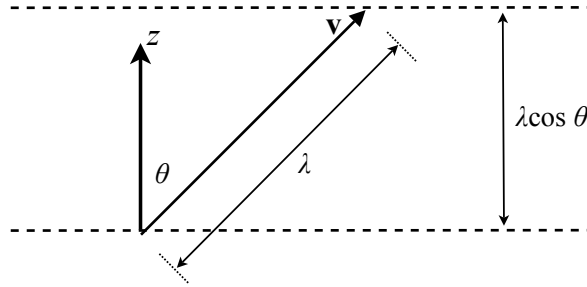
Figure 8: A schematic diagram showing the vertical transport distance $\lambda \cos \theta$ for a single molecule in the gas.

2. The excess (or deficit) of energy carried by the molecule as it moves is proportional to ΔT. The constant of proportionality is $C_{molecule}$, the heat capacity of a single molecule. Hence the excess energy transported by the molecule is

$$\Delta E = -C_{molecule} \Delta T = -C_{molecule} \lambda \cos \theta \frac{\mathrm{d}T}{\mathrm{d}z}.$$

3. Recall that the distribution of molecular speeds is given by the Maxwell-Boltmann distribution, $f(v)$. The mean speed in the vertical direction is then the average $\int_0^\infty v \cos \theta f(v) \, \mathrm{d}v = \langle v \rangle \cos \theta$.

4. And, of course, there are many molecules doing the same thing. In fact, there is a number density n of molecules.

5. Putting this all together, we can write down an expression for the thermal energy transport per unit area and unit time as

$$\begin{aligned} J &= -\frac{1}{3} n \langle v \rangle \lambda C_{molecule} \frac{\mathrm{d}T}{\mathrm{d}z} \\ &= -\frac{1}{3} \langle v \rangle \lambda C_V \frac{\mathrm{d}T}{\mathrm{d}z}, \end{aligned} \tag{39}$$

where $C_V = n C_{molecule}$. To get rid of the $\cos^2 \theta$, we have integrated with respect to θ from zero to π to obtain the $1/3$ in front (see **BB 9.2** for details).

Note that J is a *heat flux* and has units of energy/time/area (J s^{-1} m^{-2} = W m^{-2}). We can rewrite[*] it in terms of a *thermal conductivity* κ:

$$J_z = -\kappa \frac{\partial T}{\partial z}. \tag{40}$$

By comparison with equation (39) it is evident that for an ideal gas, $\kappa = \langle v \rangle \lambda C_V / 3$.

> **Fourier's law** states that the **rate of heat transport** is proportional to the temperature gradient and the diffusivity.

We can learn about thermal transport in an ideal gas by substituting our expressions for λ and $\langle v \rangle$. Using equations (28) and (36) we obtain

$$\kappa \propto \frac{C_{molecule}}{d^2} \left(\frac{k_B T}{m} \right)^{1/2}. \tag{41}$$

So we predict that thermal conductivity of an ideal gas is proportional to $\sqrt{T}$ and $1/(\sqrt{m}d^2)$. Both of these predictions compare well with data, as shown in Figure 9.
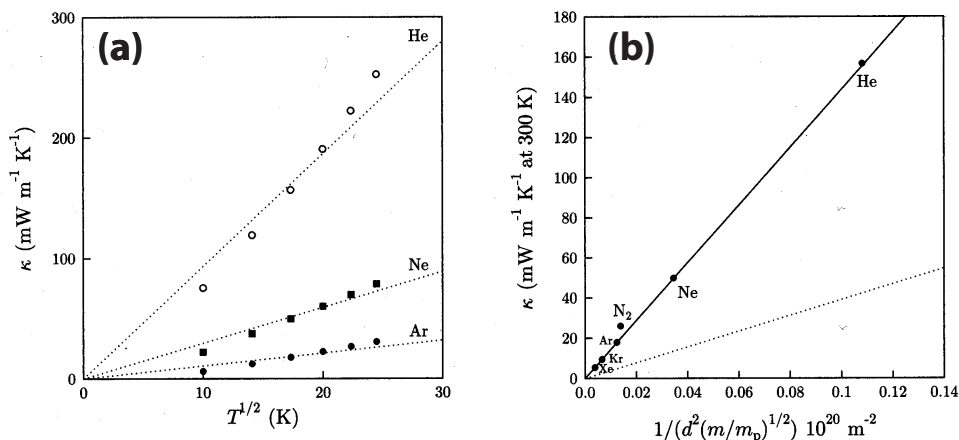
Figure 9: Figures copied from **BB 9.2**. A comparison between experiments on thermal conductivity of gasses and predictions from theory. **(a)** shows an approximately linear relationship between κ and $T^{1/2}$ for various gasses. **(b)** shows an approximately linear relationship between κ and $m^{-1/2}d^{-2}$. Both of these relationships are consistent with equation (41).

> **Thermal diffusivity in an ideal gas** increases with temperature and mean free path of the gas molecules.

4.3   Chemical diffusion

BB 9.3

Now suppose that we're interested in the transport of the molecules themselves, rather than the energy they carry. For example, a spray of perfume is released in one corner of a room with still air at constant temperature; an Oxford student, standing in the opposite corner,

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[*]We use the *partial derivative* because in general, temperature can vary in three directions and in time, not just in z, as with the example above.

will eventually smell the perfume. The molecules travelled across the room by diffusion. How does this work[†]?

Imagine that all the molecules are identical, and that the perfume molecules are marked with a smell. The direction across the room is z and the number density of perfumed molecules is n^*; the total number density is still n. According to kinetic theory, there is a flux of perfumed molecules Φ_z in the z-direction,

$$\Phi_z = -\lambda \frac{\partial n^*}{\partial z} \int_0^\infty v f(v) \mathrm{d}v \int_0^\pi \cos^2 \theta \frac{\sin \theta}{2} \mathrm{d}\theta,$$

$$= -\frac{1}{3} \lambda \langle v \rangle \frac{\partial n^*}{\partial z}, \tag{42}$$

$$= -D \frac{\partial n^*}{\partial z} \quad \text{(Fick's first law)}. \tag{43}$$

with units m^{-2} s^{-1}. This is analogous to equation (40) (the integral over θ is shown in this case). The difference from equation (39), of course, is that we're not tracking energy transport, so there is no heat capacity factor. Still, the flux is proportional to the gradient $(\partial n^*/\partial z)$ times a coefficient; here D is the *coefficient of self-diffusion*.

Question: For an ideal gas, how does D depend on pressure p and temperature T?
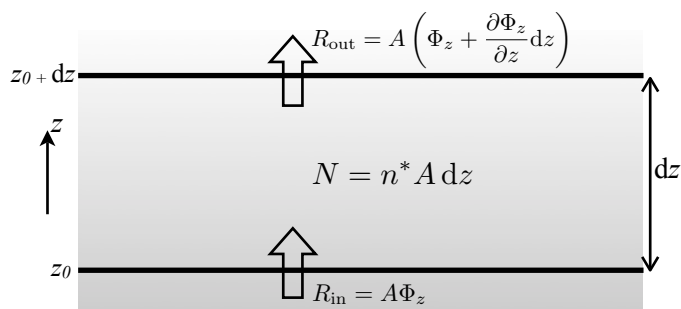
Figure 10: Slab of gas with area A and thickness $\mathrm{d}z$. (When $\Phi_z > 0$) there is a flux of perfumed molecules into the slab at $z = z_0$ and out of the slab at $z = z_0 + \mathrm{d}z$.

Now consider a slab of air that is perpendicular to the z-direction with thickness $\mathrm{d}z$ and area A, as shown in Figure 10. As molecules diffuse, the total number of perfumed particles in the slab is changing with time. At any given time, the number of molecules in the slab is given by the quantity $n^* A \, \mathrm{d}z$. The rate at which molecules are entering the slab is

$$R_{\mathrm{in}} = A \Phi_z, \tag{44}$$

while the rate at which molecules are leaving the slab is

$$R_{\mathrm{out}} = A \left(\Phi_z + \frac{\partial \Phi_z}{\partial z} \mathrm{d}z \right). \tag{45}$$

[†]Download a fun, visual demonstration of molecular transport by Johannes Kottonau at
http://lsvr12.kanti-frauenfeld.ch/KOJ/Java/Diffusion.html
[The program requires a working installation of NetLogo, which is freely available and runs on a variety of platforms]

The rate of change of the number of particles within the slab is equal to the net flux into the slab:

$$\frac{\partial}{\partial t}(n^* A \, \mathrm{d}z) = R_{\mathrm{in}} - R_{\mathrm{out}},$$

$$= -A \frac{\partial \Phi_z}{\partial z} \mathrm{d}z.$$

Cancelling $A \, \mathrm{d}z$ on both sides gives

$$\frac{\partial n^*}{\partial t} = -\frac{\partial \Phi_z}{\partial z},$$

and, finally, substitution of equation (43) gives the one-dimensional[‡] *diffusion equation*

$$\frac{\partial n^*}{\partial t} = D \frac{\partial^2 n^*}{\partial z^2}. \tag{46}$$

> The **diffusion equation** (also called Fick's second law) states that the change in time of the concentration of a diffusing species is proportional to the second derivative with respect to position (the *curvature*) of the species concentration.

Often we are interested in the diffusion of a chemical within a liquid (or even a solid). Although the Ideal Gas law doesn't hold in such cases, the diffusion equation (46) is still valid; in general, D must be determined empirically.

4.4 Thermal diffusion

BB 10.1   Now we return to the transport of heat to talk about thermal diffusion. Recall equation (40),

$$J_z = -\kappa \frac{\partial T}{\partial z},$$

and note the similarity to equation (43). The flux of heat is proportional to the conductivity times the temperature gradient. To derive a thermal diffusion equation, we must follow an argument analogous to that above, for the rate of change of species number density. Consider a slab with area A and thickness $\mathrm{d}z$, as shown in Figure 10. Since J is a flux of *heat*, it will change the total amount of *energy* in the slab. The total energy in the slab is given by

$$E = A \rho c_P T \, \mathrm{d}z.$$

[‡]In three dimensions, the diffusion equation is

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

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

The rate of change of the energy is given by the net flux of energy into or out of the slab. Hence we can write

$$\frac{\partial E}{\partial t} = \frac{\partial}{\partial t}(A\rho c_P T\, \mathrm{d}z) = R_{\mathrm{in}} - R_{\mathrm{out}},$$

$$= AJ_z - A\left(J_z + \frac{\partial J_z}{\partial z}\mathrm{d}z\right),$$

$$= -A\frac{\partial J_z}{\partial z}\mathrm{d}z.$$

Using equation (40) and assuming that ρ and c_P are constants gives the heat diffusion equation,

$$\frac{\partial T}{\partial t} = D\frac{\partial^2 T}{\partial z^2}, \tag{47}$$

where the *thermal diffusivity* is defined as $D = \kappa/(\rho c_P)$. Just as for the coefficient of self-diffusion in equation (43), the thermal diffusivity has units of $\mathrm{m}^2\ \mathrm{s}^{-1}$. Compare equations (46) and (47) and note their similarity.

> The one-dimensional **diffusion equation** for the molecular transport of stuff has the general form
>
> $$\frac{\partial}{\partial t}(\mathrm{stuff}) = D\frac{\partial^2}{\partial x^2}(\mathrm{stuff}),$$
>
> where D is the diffusivity coefficient of stuff, with units of $\mathrm{m}^{-2}\ \mathrm{s}^{-1}$.

5 Classical thermodynamics I

Having developed an intuition (and a bunch of theory) for the microscopic processes that underlie macroscopic thermodynamic variables, we come to Classical Thermodynamics, in which we study how these variables are interrelated, and how they are constrained by physical laws.

In this lecture We introduce the *internal energy*, which is the most important example of a *function of state*. The internal energy is used to define the *First law of thermodynamics*. This law is used as we revisit *heat capacity* and consider its value for an ideal gas. We then explore the first law in the context of *isothermal and adiabatic expansions* of an ideal gas. This leads us to reconsider our model of the isothermal atmosphere.

5.1 Internal energy

**BB 11.2,
HRW
18-10**

The most important quantity in classical thermodynamics is the *internal energy U*, which is the sum of the energy of all the internal degrees of freedom that the system possesses. For example, thermal energy contributes to the internal energy of a system, but potential energy does not (a can of beans on top of a hill at temperature T has the same internal energy as a can of beans with the same temperature at sea-level). For a monatomic ideal gas, the only degree of freedom for a gas molecule is its speed, and so the molecular kinetic energy is the only contribution to the internal energy. We know the mean kinetic energy of a single molecule from equation (30), and so for N molecules we can write

$$U = N \langle E_{KE} \rangle = \frac{3}{2} n_m R T, \qquad \text{(ideal gas only)} \qquad (48)$$

which applies to n_m moles of an ideal monatomic gas.

5.1.1 Functions of state

**BB 11.1
HRW
18-9**

The macroscopic properties of a thermodynamic system that is at equilibrium are called *functions of state*. A function of state is a physical quantity that has a well-defined value for each equilibrium state of the system. Examples:

Extensive functions of state Internal energy, volume, mass.

Intensive functions of state Temperature, pressure, density, internal energy per mole.

Recall that extensive properties scale with the system size, while intensive properties do not.

Functions of state do NOT depend on the path taken to achieve that state. For example, you can get to the same thermodynamic state of having warm hands by rubbing them together (work) or by putting them near a fire (heat). As noted by **BB 11.1**, a toaster would also do the trick (toasting).

Now let's give a mathematical definition to a function of state. If a system is described by a number of parameters $\mathbf{x} = (x_1, x_2, ...)$ then a function of state f is some function of

those parameters $f(\mathbf{x})$. Furthermore, for f to be a function of state, $\mathrm{d}f$ must be an *exact differential*. It must be true that

$$\Delta f = \int_{\mathbf{X}_a}^{\mathbf{X}_b} \mathrm{d}f = f(\mathbf{x}_b) - f(\mathbf{x}_a), \tag{49}$$

that is, the change in the function of state must be given by the difference between its final value and its initial value; *the path taken does not matter.*

5.2 The first law of thermodynamics

The internal energy of a system changes when heat Q or work W are added to the system (or extracted from it). Once the internal energy has changed, however, it is impossible to distinguish its source. This leads us to the first law

> **The first law of thermodynamics:** Energy is conserved; heat and work are both forms of energy.

This law means that there is a strict accounting for energy. The change in internal energy of a system is given by the amount of added heat and work[*]

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W. \tag{50}$$

If a system is *thermally isolated* then $\mathrm{d}Q = 0$, while if a system is in a rigid container, then $\mathrm{d}W = 0$. Note that both $\mathrm{d}Q$ and $\mathrm{d}W$ are inexact differentials.

Consider a frictionless piston with area A in a container of gas. To cause an infinitesimal displacement of the piston $\mathrm{d}x$ requires a force $F = pA$, where p is the pressure of the gas. This yields a volume change of the gas of $\mathrm{d}V = -A\mathrm{d}x$. We can then calculate the work as[†]

$$\mathrm{d}W = F\mathrm{d}x = -p\mathrm{d}V. \tag{51}$$

Since the gas is being compressed, $\mathrm{d}V < 0$; the negative sign in equation (51) thus insures that $\mathrm{d}W > 0$, consistent with the definition used in equation (50).

Since the amount of work done in this case is infinitesimally small, it is fine to assume that p remains constant. If the amount of volume change is large, say $\Delta V = V_2 - V_1$, then we must integrate a series of infinitesimal steps

$$\Delta W = - \int_{V_1}^{V_2} p\mathrm{d}V.$$

Because we are NOT integrating a function of state, this does NOT reduce to the difference between the initial and final states. The integral is, in fact, path dependent. To evaluate

---

[*]Note that **HRW** and **BB** use different notation for internal energy, and different sign convections for the first law. **HRW** says that $\mathrm{d}E_{\mathrm{int}} = \mathrm{d}Q - \mathrm{d}W$. **HRW** then defines $\mathrm{d}W = p\mathrm{d}V$, which is again opposite from the convection adopted by **BB**. The two sign differences cancel, and the two books are consistent. We will use the **BB** convention. If in doubt about which to use, just choose one, state it explicitly, and make sure it is consistent with a change in internal energy in the first law.

[†]Again, note that the sign convection here is consistent with **BB**, and opposite that of **HRW**.

it, we would need an equation of state (such as the Ideal Gas law) for the material being compressed.

Furthermore, for equation (51) to hold, we must ensure that the application of force is done *reversibly*. If we apply pressure very rapidly, it could cause shock-waves in the gas, which would dissipate some of the force as heat, and hence the amount of work done would be less than predicted by (51). We'll study this in more detail later.

5.3   Application of the first law: heat capacity

BB 11.3
With this understanding of internal energy, we can return to the concept of heat capacity and define it with more rigour. Recall that heat capacity is the amount of heat dQ required to change the temperature of a mass by an infinitesimal amount dT. Mathematically, $C = dQ/dT$.

We can see from equations (50) and (51) that the internal energy will be a function of temperature and volume, so we can write $U = U(T, V)$. Small changes in T and V can thus drive small changes in U:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV. \tag{52}$$

Recall that the notation

$$\left(\frac{\partial U}{\partial T}\right)_V dT$$

means "for an infinitesimal change in temperature dT, the change in internal energy is given by the rate of change of U with respect to T *while holding volume constant* times temperature change dT."

Combining equations (50) and (51) gives

$$dQ = dU + pdV, \tag{53}$$

and combining that with (52) gives

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV. \tag{54}$$

To get closer to an expression for the heat capacity, we divide both sides by the infinitesimal change in temperature

$$\frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \frac{dV}{dT}. \tag{55}$$

Now review (2) and recall that we require expressions for the heat capacity at *constant pressure* and at *constant volume*. For the latter we write

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V. \tag{56}$$

Looking back at equation (55), we see that setting $dV = 0$ removes the second term. Hence we have

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V. \tag{57}$$

In contrast, at constant pressure we have

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p, \tag{58}$$

$$= \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p. \tag{59}$$

These heat capacities are measured in J K^{-1}, whereas normally we will need to know the heat capacity per mole (J K^{-1} mol^{-1}), the heat capacity per volume (J K^{-1} m^{-3}), or the specific heat capacity c (J K^{-1} kg^{-1}). For the latter, $c_V = C_V/M$ and $c_p = C_p/M$, where M is the mass of the object that C refers to.

The *adiabatic index* $\gamma = C_p/C_V$ will be a useful quantity for later calculations.

5.3.1   Heat capacity of an ideal gas

For an ideal, monatomic gas, the internal energy is stored solely in the translational kinetic energy of the molecules. Thus, using equation (30), we have $U = N_A \langle E_{KE} \rangle = \frac{3}{2}RT$ per mole (units of J mol^{-1}; note that we have used $N_A k_B = R$). This means that for an ideal gas, $U = U(T)$; it does not depend on volume and so

$$\left(\frac{\partial U}{\partial V}\right)_T = 0. \tag{60}$$

We can immediately find that

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left[\frac{\partial}{\partial T}\left(\frac{3}{2}RT\right)\right]_V = \frac{3}{2}R \;\; \text{per mole}. \tag{61}$$

For one mole of ideal gas, $n_m = 1$ and $V = RT/p$ and thus

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}. \tag{62}$$

Then, substituting equations (61), (60), and (62) into equation (59) gives

$$C_p = C_V + (0 + p)\frac{R}{p}, \tag{63a}$$

$$= C_V + R, \tag{63b}$$

$$= \frac{3}{2}R + R = \frac{5}{2}R \;\; \text{per mole}. \tag{63c}$$

The adiabatic index for an ideal monatomic gas is thus $\gamma = 5/3$.

Note that it is not generally true that $dU = CdT$; the ideal gas (in particular, equation (60)) is a special case. In general,

$$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV. \tag{64}$$

An equation of state such as the Ideal Gas law is required to go beyond this equation.

5.4   Reversibility

BB 12.1

The laws of physics are reversible, and so we would expect that physical processes are too. Consider the molecules of a gas bouncing around within a container. A film of their motions, played in reverse, would look equally plausible as the film played forward[‡].

Now visit the kinetic simulation of diffusion at
http://lsvr12.kanti-frauenfeld.ch/KOJ/Java/Diffusion.html. Start the background motion of molecules by clicking on "go/stop." The motions and collisions of the particles are reversible. Now click on "Release the perfume molecules" and watch what happens. The perfumed molecules spread throughout the entire box, and their distribution reaches a statistical steady state. It is plausible that they could spontaneously reassemble in the corner where they started, but the *probability that this could occur is vanishingly small.* Diffusion is an example of an irreversible process.

Consider a battery that drives a current I through a resistance R and dissipates heat $I^2 R$. It never occurs that that heat is absorbed by the resistor, recharging the battery! Most irreversible processes are like this: potential, chemical, or kinetic energy gets converted into thermal energy that is *dissipated* into the environment. The energy cannot be restored, and hence the (dissipative) process is irreversible.

> **Irreversibility** arises from the dissipation of energy into the environment as heat. The reason that energy is dissipated as heat is that this is by far *the most probable outcome.*

As an analogy, consider 100 coins, place head-side up in a box. The box is shaken vigorously and then opened: of course the coins are now a mixture of heads and tails. Shaking the box again, even in the exact reverse of the way it was first shaken, will not return the coins to their original state of all heads. The reason is simply that the probability of this occurring is $1/2^{100} \approx 10^{-30}$.

So statistics seems to drive processes in an irreversible direction. So how can we achieve reversibility (even if just in theory)? The answer is: very carefully.

> **Reversibility** in a thermodynamic process is achieved by running the process sufficiently slowly that *the material remains in thermodynamic equilibrium at all times.* Such a process is said to be *quasistatic.*

Note that reversibility does not mean that heat cannot be absorbed or emitted by the process. We will see that in the next section.

[‡]So what is the real direction of time? What is the difference between past and future? This question was famously addressed by Richard Feynman in a lecture on physics to students at Cornell University in 1964. Watch it here (Lecture 5):
http://research.microsoft.com/apps/tools/tuva/

5.4.1 Application of the first law: reversible isothermal expansion of an ideal gas

Isothermal means constant temperature. A reversible isothermal expansion is then an expansion at constant temperature, i.e. one where $\Delta T = 0$, that is performed reversibly, i.e. without dissipation.   **BB 12.2**

For an ideal gas, we showed above that $dU = C_V dT$. Since $dT = 0$ for an isothermal change, $dU = 0$. Then, from equation (50) we have

$$dW = -dQ. \tag{65}$$

This means that *the work done by the expansion of the gas is energetically equivalent to the heat that is absorbed by the gas.*

> In an **isothermal process**, the heat absorbed is equal to the work done by the system, and the temperature of the system doesn't change.

We know that for an increment of reversible work, $dW = -pdV$. Hence we can calculate the total amount of heat absorbed by one mole of gas during an isothermal expansion from V_1 to V_2 at temperature T as:

$$\Delta Q = \int dQ, \tag{66a}$$

$$= -\int dW, \tag{66b}$$

$$= \int_{V_1}^{V_2} p dV, \tag{66c}$$

$$= \int_{V_1}^{V_2} \frac{RT}{V} dV, \tag{66d}$$

$$= RT(\ln V_2 - \ln V_1) = RT \ln \frac{V_2}{V_1} \quad \text{per mole.} \tag{66e}$$

Now since $V_2 > V_1$ we know that $\Delta Q > 0$. In fact, exactly enough heat was absorbed by the system to balance the expenditure of energy on doing work while keeping temperature fixed.

5.4.2 Application of the first law: adiabatic expansion of an ideal gas

An *adiabatic* expansion is both reversible and *adiathermal*. Adiathermal means "without flow   **BB 12.3,** of heat," so an adiathermal system is said to be *thermally isolated*. Hence, for an adiabatic   **HRW** expansion we have   **18-11**

$$dQ = 0. \tag{67}$$

Then the first law states that

$$dU = dW. \tag{68}$$

> In an **adiabatic process**, there is no heat flow into or out of the system. The change in internal energy of the system is due entirely to work done on or by the system.

Into this equation we can substitute $dU = C_V dT$, which is true for an ideal gas, and $dW = -p dV$, which is true for a reversible change. For one mole of gas,

$$C_V dT = -p dV \tag{69a}$$

$$= -\frac{RT}{V} dV. \tag{69b}$$

Integrating this equation from (T_1, V_1) to (T_2, V_2) gives

$$\ln \frac{T_2}{T_1} = -\frac{R}{C_V} \ln \frac{V_2}{V_1}. \tag{70}$$

From equation (63b), $C_p = C_V + R$. Dividing by C_V and rearranging gives $-R/C_V = 1 - \gamma$. Equation equation (70) the becomes

$$\ln \frac{T_2}{T_1} = (1 - \gamma) \ln \frac{V_2}{V_1}. \tag{71}$$

Exponentiating both sides we find that

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}, \tag{72}$$

or

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} = T V^{\gamma-1} = \text{constant}. \tag{73}$$

Figure 11: Comparison of decompression paths under adiabatic and isothermal conditions. (Axis labels and lines to be added by the student).

Finally, we can use $T \propto pV$ from the Ideal Gas law to rewrite equation (73) as

$$pV^\gamma = \text{constant}. \tag{74}$$

This tells us that if we start with a gas at some initial pressure and volume and then allow it to expand adiabatically, the final pressure and volume will be related to the initial one by equation (74); the temperature can be determined with the Ideal Gas law. Figure 11 shows a comparison between adiabatic and isothermal decompression of an ideal gas for the same initial conditions.

5.5   Geophysical application: adiabatic atmosphere

BB 12.4

We can extend our model of the atmosphere (notes 2.4) by using results on adiabatic expansion. The hydrostatic equation for the atmosphere is

$$\mathrm{d}p = -\rho g \mathrm{d}z, \tag{75}$$

which states that over an increment of height in the atmosphere, the pressure decreases by the mass per unit area within that increment. We're interested in finding the integral of this equation, but we don't yet know how density ρ varies with height.

Begin by recalling that $p = n k_B T$ and $\rho = nm$, where m is the mass of one molecule. Combining these two gives $\rho = mp/(k_B T)$, and plugging this into equation (75) and rearranging gives

$$T\frac{\mathrm{d}p}{p} = -\frac{mg}{k_B}\mathrm{d}z. \tag{76}$$

For an isothermal atmosphere, T is constant and we can integrate this equation immediately for $p(z)$. We know that T varies with height, however, so as a better approximation, we could assume that parcels of air move through the atmosphere without exchanging heat with their neighbours, $\mathrm{d}Q = 0$. So if a parcel rises, it expands adiabatically.

We have learnt that for an ideal gas undergoing an adiabatic processes, pV^γ is a constant. Using the Ideal Gas law ($pV \propto T$), we can rewrite this as $p^{1-\gamma}T^\gamma = $ constant and differentiate to give

$$(1-\gamma)\frac{\mathrm{d}p}{p} + \gamma\frac{\mathrm{d}T}{T} = 0. \tag{77}$$

Substituting this into equation (76) gives

$$\frac{\mathrm{d}T}{\mathrm{d}z} = -\frac{\gamma-1}{\gamma}\frac{mg}{k_B}. \tag{78}$$

This equation predicts a linear thermal gradient with height. We can simplify it by substituting $(\gamma-1)/\gamma = R/C_p$ and using $R = k_B N_A$ and writing the molar mass as $M_{\mathrm{molar}} = mN_A$ to give

$$\frac{\mathrm{d}T}{\mathrm{d}z} = -\frac{M_{\mathrm{molar}}g}{C_p}. \tag{79}$$

The quantity $M_{\mathrm{molar}}g/C_p$ is the *adiabatic lapse rate*. For dry air it is about 10 K/km, though for the real atmosphere (which is humid), it is measured at about 6-7 K/km.

Question: What is $T(z)$ for the atmosphere, assuming a lapse rate of 6.5 and $T(0) = 288$ K?

6   Classical thermodynamics II

In this lecture   We introduce the concept of an *engine* that converts heat into work. We show that the *Carnot engine* is the most efficient such engine, but that it does not achieve 100% efficiency. We then generalise this result to the Second law of thermodynamics. We reexamine the Carnot engine and derive a new and useful function of state.

6.1   The Carnot engine

We have seen in the last lecture that heat and work are both forms of energy that can be added or taken away from a thermodynamic system. Since this is the case, it should be possible to make a machine that converts heat into work; such a machine is called an *engine*, of which the *Carnot engine* is the simplest example.

BB 13.2,
HRW
20-5

Ideally, we'd like to put some amount of heat Q into the machine and get out an equivalent amount of work W, such that $Q = W$. This engine would be perfect in the sense that it would not waste any heat. Unfortunately, however, a perfect engine is physically impossible.
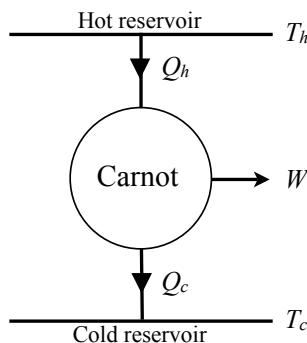

Figure 12: A schematic diagram of the Carnot engine. Heat flows into the gas piston from the hot reservoir and out to the cold reservoir. The piston does work. Variables Q_h, Q_c, and W represent *magnitudes* of the heat input, heat output, and work output, respectively, and are thus all greater than zero.

The Carnot engine is physically possible and now we consider it in detail. The process consists of a four-part, cyclical path. Two parts are isotherms (at temperatures T_h and T_c), and two parts are adiabats (connecting T_h to T_c and vice versa). Although the cycle is a theoretical construct, you can imagine it as a gas within a piston that is coupled to a hot reservoir (at T_h) and a cold reservoir (at T_c), as shown in Figure 12.

This is shown in Figure 13.

In detail, the four parts of the Carnot cycle are:

A→B In the first stage of a Carnot cycle, the gas is at temperature T_h; heat Q_h enters the system from the hot reservoir and drives an isothermal volume-expansion ($V_A \rightarrow V_B$). The piston goes from its initial, fully compressed position to a partially extended one.
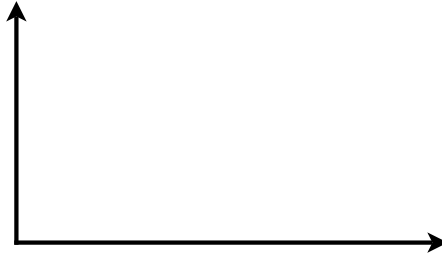
Figure 13: The Carnot cycle shown in pressure-volume space. (Axis labels and lines to be added by the student).

For one mole of an ideal monatomic gas, we can write

$$Q_h = RT_h \ln \frac{V_B}{V_A}. \tag{80a}$$

B→C The second stage is an adiabatic expansion, so no heat enters or leaves the system, but the pressure and volume change along an adiabatic curve. At the end of this adiabatic change ($V_B \to V_C$), the volume is at its maximum (the piston is fully extended) and the temperature has been reduced to T_c. We can write

$$\frac{T_h}{T_c} = \left(\frac{V_C}{V_B}\right)^{\gamma - 1}. \tag{80b}$$

C→D In the third stage, the gas is compressed ($V_C \to V_D$) isothermally at temperature T_c; heat Q_c flows out of the system into the cold reservoir. This allows the piston to return part of the way to its original position. For this stage we can write[*]

$$Q_c = RT_c \ln \frac{V_C}{V_D}. \tag{80c}$$

D→A The final step of the cycle takes the piston back to its original, fully compressed position. This stage is an adiabatic compression ($V_D \to V_A$), thus there is no exchange of heat with the reservoirs. The gas is compressed, so its pressure increases. The temperature of the gas increases from T_c to T_h. We can write

$$\frac{T_c}{T_h} = \left(\frac{V_A}{V_D}\right)^{\gamma - 1}. \tag{80d}$$

Combining equations (80b) and (80d) gives

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}. \tag{81}$$

Dividing equation (80a) by equation (80c) and substituting equation (81) then gives

$$\frac{Q_h}{Q_c} = \frac{T_h}{T_c}, \tag{82}$$

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[*]Note that we have inverted the fraction V_D/V_C in this equation. The reason is that we want the magnitude of the heat output, Q_c, which should be a positive quantity.

which will be useful below.

Question: How does the Carnot cycle look on a plot of temperature vs. pressure? How does it look on a plot of temperature vs. volume?

6.1.1   Efficiency of the Carnot cycle

Because the Carnot process is cyclic, the internal energy (a function of state) returns to its initial value after each cycle. There is a net output of work done in each cycle. To find the net work, we could do the integral

$$W = \int_{A\to B\to C\to D\to A} \mathrm{d}W = -\oint p\mathrm{d}V, \tag{83}$$

for the area within the cycle in Figure 13 (the special integration symbol $\oint$ signifies integration around a closed loop). Another approach is to equate the net work done with the net heat added to the system (since $\Delta U = 0$ over the cycle). For the Carnot cycle,

$$W = Q_{\mathrm{net}} = Q_h - Q_c. \tag{84}$$

Recall that the perfect engine is 100% efficient: it converts all the heat added to the system Q_h into work W such that the efficiency $\eta_{\mathrm{perfect}} = W/Q_h = 1$. In reality, for a Carnot engine,

$$\eta_{\mathrm{Carnot}} = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h}, \tag{85}$$

and using equation (82),

$$\eta_{\mathrm{Carnot}} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h}. \tag{86}$$

Hence the efficiency of a Carnot engine is less than 100%. Real engines are much less efficient than Carnot engines.

Question: Why are real engines less efficient than Carnot engines?

It turns out that the Carnot engine is the most efficient heat engine that can exist, hence η_{Carnot} is an upper limit on the efficiency of a heat engine. (This is proven in **BB 13.3** but is not required knowledge for the course.)

> **Carnot's theorem:** Of all the heat engines working between two given temperatures, none is more efficient than a Carnot engine. All cycles composed of reversible processes have the same efficiency as the Carnot cycle.

HRW
20-5   **Question:** What is a Stirling engine? How does it look on a *p-V* plot?

6.2   The second law of thermodynamics

BB 13.1   Having studied the example of a Carnot engine, we can generalise and state the second law

> **The second law of thermodynamics:**
> **(Clausius')** No process is possible whose sole result is the transfer of heat from a colder body to a hotter body;
> or
> **(Kelvin's)** No process is possible whose sole result is the complete conversion of heat into work.

Although these sound like different statements, they are actually equivalent. Another equivalent statement would be "no engine can be 100% efficient."

For reasons discussed above in the section on reversibility, heat always flows from high temperatures to low temperatures. The second law states that this must be the case in all isolated processes.

We can show that Clausius' and Kelvin's statements are equivalent by showing that if a system violates one, it violates the other.
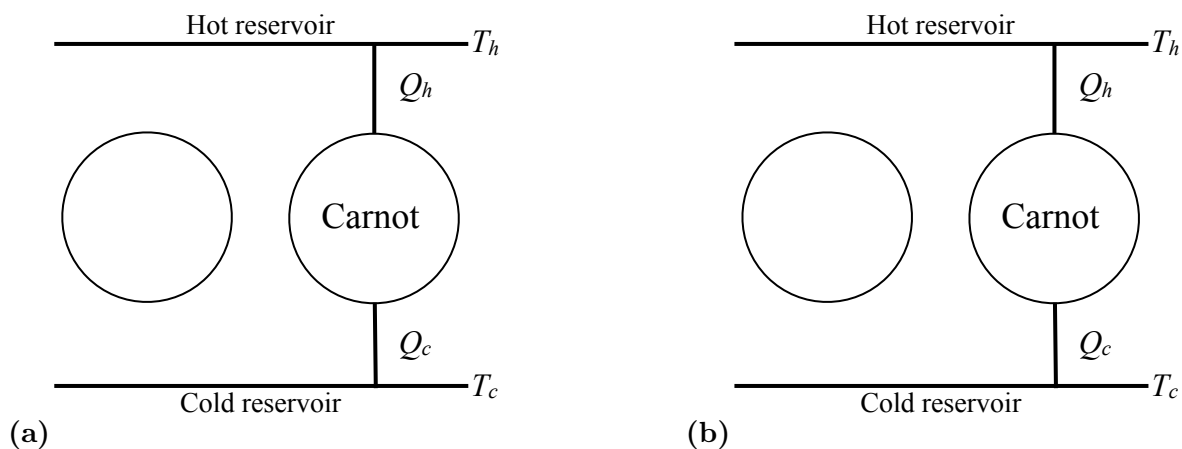

(a)   **(b)**

Figure 14: **a** Schematic diagram of a Kelvin violator connected to a Carnot engine (to be completed by the student). **(b)** Schematic diagram of a Clausius violator connected to a Carnot engine (to be completed by the student).

- First consider a machine that violates Kelvin's statement of the second law (a "Kelvin violator"). This machine is an engine with the sole result of complete conversion of heat into work: $Q'_h = W$. You can connect this engine with a Carnot engine as shown in Figure 14a. The work W drives the Carnot engine in reverse, allowing it to pump heat from the cold reservoir to the hot reservoir. Equation (84) says that $W = Q_h - Q_c$; equating this with the work from the Kelvin violator gives $Q_c = Q_h - Q'_h$. This means that the combined Carnot-Kelvin violator machine has the sole result of pumping Q_c heat from the cold reservoir to the hot reservoir. This violates Clausius' statement of the second law.

- Now consider a machine that violates Clausius' statement of the second law (a "Clausius violator"). This machine has the sole result of pumping heat Q_c from the cold reservoir to the hot reservoir. It is connected with a Carnot engine in Figure 14b. Evidently, the net heat lost from the hot reservoir is $Q_h - Q_c$, while the net heat lost from the

cold reservoir is zero. Hence, the combined Carnot-Clausius violator machine has the sole result is the *complete* conversion of heat $Q_h - Q_c$ into work. This violates Kelvin's statement of the second law.

Hence we have shown the equivalence of Kelvin's and Clausius' statements of the second law of thermodynamics.

6.3   Clausius' theorem

Recall that for the Carnot cycle, the amount of heat that leaves the cycle Q_c is different from the amount of heat that enters it Q_h, thus heat is not conserved and Q is not a function of state (as we already knew). However, we found that for the Carnot cycle

BB 13.7

$$\frac{Q_h}{Q_c} = \frac{T_h}{T_c} \tag{87}$$

and this motivates us to consider a new quantity that turns out to be very important in thermodynamics: the ratio of heat input to temperature at which it is input. For the Carnot cycle we have

$$\sum_{\text{cycle}} \frac{\Delta Q}{T} = \frac{Q_h}{T_h} + \frac{-Q_c}{T_c} = 0. \tag{88}$$

We could take each heat addition as being the integral of an infinite number of infinitessimal additions $\mathrm{d}Q$ and write equation (88) as an integral

$$\oint \frac{\mathrm{d}Q}{T} = 0. \tag{89}$$

The Carnot cycle is an idealised process in that it is perfectly reversible. In reality, no process is perfectly reversible. As we learned above (section 5.4), in irreversible processes some heat is *dissipated*. Thus we can modify equation (89) to accomodate irreversible processes by writing

$$\oint \frac{\mathrm{d}Q}{T} \leq 0, \tag{90}$$

where the equality only holds if the cycle is reversible. We can now write *Clausius' theorem.*

Clausius' theorem: For any closed cycle, $\oint \mathrm{d}Q/T \leq 0$, where equality neccessarily holds for a reversible cycle.

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7   Classical thermodynamics III

In this lecture   In this lecture we introduce the concept of *entropy* and give it several complementary definitions. We examine the question of *reversibility* in thermodynamic processes, and consider the causes and consequences of *irreversibility*. Finally, we use our understanding of entropy to reexamine the first law of thermodynamics, and to model the thermal gradient of rock in the mantle.

7.1   A definition of Entropy

BB 14.1

In the last lecture we studied the quantity $\mathrm{d}Q/T$ and found that for a *reversible* process

$$\oint \frac{\mathrm{d}Q}{T} = 0.$$

This tells us that the integral is path independent and that $\mathrm{d}Q/T$ is an exact differential of a function of state.

This new function of state is called *entropy* and is defined by

$$\mathrm{d}S = \frac{\mathrm{d}Q_{\mathrm{rev}}}{T}, \tag{91}$$

such that

$$\int_{\mathrm{A}}^{\mathrm{B}} \frac{\mathrm{d}Q_{\mathrm{rev}}}{T} = \int_{\mathrm{A}}^{\mathrm{B}} \mathrm{d}S = S(\mathrm{B}) - S(\mathrm{A}). \tag{92}$$

> **Entropy** is a function of state whose exact differential is the ratio of a reversible input of heat $\mathrm{d}Q_{\mathrm{rev}}$ to the temperature T at which that input occurs.

Recall that an *adiabatic process* is thermally isolated and hence $\mathrm{d}Q_{\mathrm{rev}} = 0$. This means that there is no change in entropy during an adiabatic process, and so an adiabatic process is also *isentropic*.

7.1.1   Entropy in the Carnot cycle

Another way to visualise the Carnot cycle is to plot it in terms of temperature vs. *entropy S*. We'll go into more detail about entropy below, but for now, just remember the *entropy is constant along an adiabatic path*. Hence we have two isothermal paths and two *isentropic* paths, as shown in Figure 15.

7.2   Irreversible changes and entropy

Recall from Clausius' theorem that $\oint \mathrm{d}Q/T \leq 0$ where the equality only holds if the process is reversible. Suppose that a cycle is composed of two steps:

BB 14.2

$$\mathrm{A} \to \mathrm{B}: \ \text{irreversible,}$$
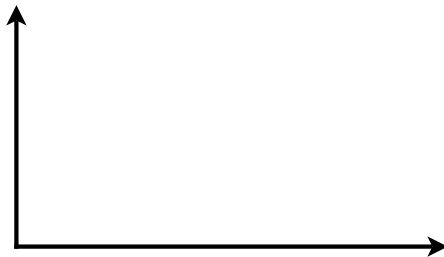$$\mathrm{B} \to \mathrm{A}: \ \text{reversible.}$$

Figure 15: The Carnot cycle shown in temperature-entropy space. (Axis labels and lines to be added by the student).

This cycle is, overall, irreversible. Hence we write

$$\oint \frac{dQ}{T} \leq 0$$

$$\int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ_{rev}}{T} \leq 0, \tag{93}$$

and we can rearrange to give

$$\int_A^B \frac{dQ_{rev}}{T} \geq \int_A^B \frac{dQ}{T} \tag{94}$$

(note that the limits of the integration for the reversible integral have been switched).

We are free to shrink the cycle until it is arbitrarily (infinitessimally) small, and so we can rewrite equation (94) as

$$dS = \frac{dQ_{rev}}{T} \geq \frac{dQ}{T}. \tag{95}$$

This equation states that *the increase in entropy for a process is always at least as big as the heat added divided by the temperature at which it is added.*

Furthermore, we can consider a thermally isolated system where $dQ = 0$. For reversible changes within this system $dS = 0$, however for any *irreversible* change,

$$dS \geq 0. \tag{96}$$

This is an extremely profound result. It states that the entropy of a thermally isolated system can only increase. Suppose that the system is the Universe; equation (96) says that the entropy of the Universe can only increase with time. This sounds dangerous... what is entropy, physically?

> **Second law, incognito:** the entropy of the Universe is always increasing (as is the entropy of any thermally isolated system that undergoes irreversible processes).

7.3   Entropy in kinetic theory

HRW 20-8   For a physical picture we return to kinetic theory, and to the ideal gas. Consider a thermally isolated, rigid box of gas with two volumetrically equal halves, L and R. The box contains N

gas molecules, numbered one through N, each of which can be in either L or R at any given moment.

At any given instant there are N_L molecules in volume L and N_R molecules in volume R, such that $N_L + N_R = N$, the total number of molecules. This is a case of microstates and macrostates[*], as we explored in lecture 2 (section 2.1). Each possible distribution of molecules 1 through N is a microstate. There are 2^N microstates, but only $N + 1$ macrostates. The macrostates, in terms of (N_L, N_R), are

$$(N, 0), \ (N - 1, 1), \ ..., \ (0, N).$$

Recall that each macrostate has a different probability because each macrostate corresponds to a different number of microstates. For example, the macrostate with all the molecules in one half of the box $(N, 0)$ corresponds to only one microstate, and thus has a very low probability. In our example, the number of microstates that corresponds with a macrostate (N_L, N_R) is

$$\Omega = \frac{N!}{N_L! \, N_R!}, \tag{97}$$

and this quantity is called the *multiplicity*. The probability of being in a macrostate i : $(N - i, i)$ is then given by

$$P_i = \frac{\text{multiplicity of } i}{\text{total \# of microstates}} = \frac{\Omega_i}{2^N}. \tag{98}$$

For very large N the number of microstates N is enormous, but most of them correspond to the macrostate $i = N/2$, so the system spends most of its time with half the molecules on one side of the box and half on the other side. This is consistent with what we learned in lecture 2: the system seeks the macrostate with the largest number of microstates. It is also true that *the system seeks the state with the largest entropy*. In fact, the entropy of a gas is defined as

$$S = k_B \ln \Omega. \tag{99}$$

This equation states that the *entropy of a gas* is proportional to the logarithm of the number of microstates corresponding to its macrostate.

You can think of entropy as being a measure of disorder. For our example: a state where all the molecules of gas are in L is highly ordered and hence has low entropy, while a state where some randomly chosen molecules are in R is less ordered and has higher entropy. The most disordered state has half the molecules in each half of the box, and thus has the highest entropy.

> **Entropy** is a measure of the disorder of a system, in terms of the number of microstates that correspond to its observed macrostate. Systems tend to exist in the highest-entropy (most disordered) state that is available.

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[*]In **HRW**, macrostates are called *configurations*.

7.4   Entropy, internal energy, and the first law

Armed with our new concept of entropy, we can reconsider the first law of thermodynamics, which is

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W. \tag{100}$$

For a *reversible* change we have the definition of entropy

$$\mathrm{d}Q = T\mathrm{d}S$$

and that of work

$$\mathrm{d}W = -p\mathrm{d}V.$$

Combining these three equations we find that

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V. \tag{101}$$

This equation states that changes in internal energy are caused by changes in entropy and changes in volume (or density). We can see from this that the *natural variables* that control U are S and V, hence we can write $U = U(S, V)$. From this definition we can take the total differential of U and compare it with equation (101):

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V, \tag{102}$$

$$= T\mathrm{d}S - p\mathrm{d}V. \tag{103}$$

Hence we can see that temperature and pressure can be interpreted in a new way:

$$T = \left(\frac{\partial U}{\partial S}\right)_V, \tag{104}$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_S. \tag{105}$$

This says that temperature is the rate of change of internal energy with entropy at constant volume, and that pressure is minus the rate of change of internal energy with volume at constant entropy. Clear? Not really... but sometimes useful.

Going back to equation (101), we can make another important observation that pertains to irreversible processes. For an irreversible process,

$$\text{irrev:}\ \ \mathrm{d}Q \leq T\mathrm{d}S\ \ \text{and}\ \ \mathrm{d}W \geq -p\mathrm{d}V.$$

Fortunately, *the amount that each of these differs from the reversible limit is the same, so the differences cancel out. Equation (101) applies even for irreversible processes.*

> **The first law revisited:** Energy is conserved; heat and work are both forms of energy; and all of this can be accounted for with the simple formula $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$, which holds for reversible and irreversible changes.

7.4.1   Entropy: kinetic & classical

Let's rewrite equation (104) as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V, \tag{106}$$

and rearranging equation (11) slightly gives

$$\frac{1}{T} = \frac{\mathrm{d}(k_B \ln \Omega)}{\mathrm{d}E}. \tag{107}$$

Comparing these two equations (while squinting) leads us, again, to the definition of entropy,

$$S = k_B \ln \Omega.$$

Joy!

7.5   Geophysical application: adiabatic mantle

As you may have learned in another lecture, the rock in the Earth's mantle is convecting slowly but inexorably, and this leads to plate tectonics. It also leads to melting and volcanism. To address these latter topics, thermodynamics is an essential tool. For example, what are the thermal conditions in the mantle where melting occurs?

As you will learn in more detail in your lectures on Planet Earth, mantle convection is vigorous. Flow of rock in the mantle occurs at a rate that is of order 10 cm/year, about the same rate that your fingernails grow. However, relative to this slow creeping flow, diffusion of heat is even slower. Hence we say that mantle convection is vigorous. We can also then assume that flow in most places in the mantle is adiabatic, because it occurs without (much) diffusion of heat.

Recall that an adiabatic process is also isentropic. Entropy thus provides a starting point for our study of temperature in the convecting mantle.

More advanced thermodynamics tells us that entropy S can be written as a function of pressure and temperature: $S = S(p, T)$; its total differential is then

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p. \tag{108}$$

We can then use an equality that you will derive in MMES problem set 8, $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$, to substitute into equation (108) to obtain

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T - \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p. \tag{109}$$

To simplify this further, we need to make a couple of asides.

Aside: specific heat   Recall that the specific heat capacity is given in equation (2) as

$$c_p = \frac{1}{M}\left(\frac{\partial Q}{\partial T}\right)_p,$$

where the units of c_P are J K^{-1} kg^{-1}. Note that for a reversible change, we can substitute our definition of entropy $dQ = TdS$ and rearrange to obtain

$$\frac{c_p M}{T} = \left(\frac{\partial S}{\partial T}\right)_p. \tag{110}$$

Aside: thermal expansion   You may already know that solids expand when you heat them. A solid with initial volume V_0 at temperature T_0 will expand nearly linearly with temperature. This can be written

$$V(T) = \frac{M}{\rho}[1 + \alpha(T - T_0)], \tag{111}$$

such that when $T = T_0$, $V = M/\rho$. The constant α is called the *coefficient of thermal expansion*; ρ is the density of mantle rock. We can use this to evaluate the partial derivative in equation (109),

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{\alpha M}{\rho}. \tag{112}$$

Now we can return to equation (109) and substitute equations (110) and (112). This gives

$$dS = \frac{c_p M}{T}dT - \frac{\alpha M}{\rho}dp. \tag{113}$$

Then, dividing both sides by mass M and writing the *specific entropy* as $s = S/M$ we have

$$ds = \frac{c_p}{T}dT - \frac{\alpha}{\rho}dp. \tag{114}$$

Now let's recall our earlier statement about mantle convection: it is isentropic. We can therefore set $ds = 0$ and rearrange equation (114) to read

$$\left(\frac{dT}{dp}\right)_s = \frac{\alpha T}{\rho c_P}. \tag{115}$$

Finally, writing z for depth in the mantle, we can write the change in pressure with depth as $(dp/dz) = \rho g$ and substitute to obtain

$$\left(\frac{dT}{dz}\right)_s = \left(\frac{dT}{dp}\right)_s \frac{dp}{dz}$$
$$= \frac{\alpha g T}{c_P}. \tag{116}$$

Taking values representative of the shallow mantle ($T = 1600$ K, $\alpha = 3 \times 10^{-5}$ K^{-1}, $c_P = 1$ kJ kg^{-1} K^{-1}, and $g = 10$ m s^{-2}) gives a value for the adiabatic temperature gradient in the mantle of $(dT/dz)_s = 0.5$ K km^{-1}.
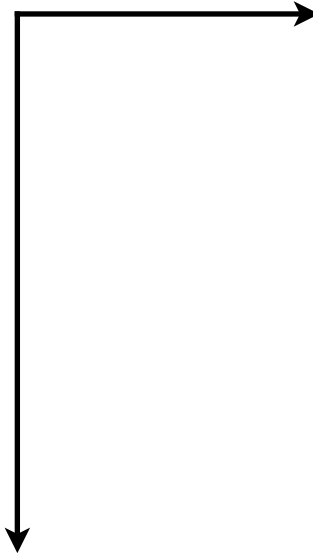
Figure 16: Temperature as a function of depth through the Earth. (Axis labels and lines to be added by the student).

We can integrate equation (116) with respect to z to obtain $T(z)$ in the mantle

$$T(z) = T(0)\, e^{\alpha g z / c_P}, \tag{117}$$

where $T(0)$ is value the mantle temperature would have if if could rise adiabatically all the way to the surface of the Earth (which is clearly impossible). Nonetheless, $T(0)$ is such a useful quantity that we give it a special name, the *mantle potential temperature*. A plot of $T(z)$ is shown in Figure 16.

The **mantle potential temperature** is the temperature that a parcel of mantle would have if it were brought to the surface adiabatically.

8   Classical thermodynamics IV

In this lecture   we consider *phase changes* of pure substances (such as H_2O). We quantify the latent heat, the amount of energy required to convert between phases. We then discuss the concept of *phase diagrams*, which map out the conditions under which various phases are stable. Finally, we consider the *Clausius-Clapeyron equation*, a quantitative model of the boundaries between these regions of stability.

8.1   Latent heat and phase transitions

BB 28.1,
HRW
18-8

Water freezes and boils, solid CO_2 (dry ice) sublimes, solid metals can be melted; these are all examples of phase transitions.   We know from experience that phase transitions occur when a material reaches a certain temperature; for example, water boils at 100°C. To change the temperature of a substance requires supplying it with sufficient heat to increase the entropy, as we saw in the last lecture. This is quantified by the heat capacity,

$$C_x = T \left(\frac{\partial S}{\partial T} \right)_x, \tag{118}$$

where x is the quantity that is held constant (e.g. p or V).

Now suppose that our thermodynamic system is composed of water and steam, in equilibrium at constant pressure and at $T_b = 100$°C. To convert water to steam requires that we *supply extra heat ΔQ to overcome the difference in entropy between the two phases*. This extra heat is known as the *latent heat* and is defined by

$$L = \Delta Q = T_b S_{\text{steam}} - T_b S_{\text{water}} = T_b \Delta S. \tag{119}$$

So in a plot of S vs. T, as shown in Figure 17, the slope of the line for $T < T_b$ is proportional to the specific heat capacity of liquid water. For $T > T_b$ the slope is proportional to the specific heat capacity of steam. At $T = T_b$, the entropy changes discontinuously over a jump $\Delta S = L/T_b$.

Figure 17: Entropy as a function of temperature for a water–steam system in thermodynamic equilibrium at constant pressure. (Axis labels and lines to be added by the student).

> The **latent heat** associated with a phase transition is the amount of heat that must be supplied to (or extracted from) the system to convert material from one phase to another.

8.1.1 Latent heat of vaporisation for an ideal gas

In general, the latent heat for different materials is empirically known—it is obtained by carefully measured experiments. For the case of an ideal gas, we can make a theoretical estimate.

First we must assume that the number of microstates Ω available to a gas molecule is proportional to the system volume[*] V. With this assumption, we can write, for one mole of vapour and one mole of liquid,

$$\frac{\Omega_{\text{vapour}}}{\Omega_{\text{liquid}}} = \left(\frac{V_{\text{vapour}}}{V_{\text{liquid}}}\right)^{N_A}, \tag{120}$$

$$= \left(\frac{\rho_{\text{liquid}}}{\rho_{\text{vapour}}}\right)^{N_A}, \tag{121}$$

$$\approx \left(10^3\right)^{N_A}, \tag{122}$$

since the density of the vapour is roughly 10^3 times smaller than the density of the liquid.

Now recall that $S = k_B \ln \Omega$, and so we can calculate that

$$\Delta S = \Delta(k_B \ln \Omega) = k_B \ln \left(10^3\right)^{N_A} = R \ln \left(10^3\right) \approx 7R. \tag{123}$$

This result allows us to estimate the latent heat as

$$L = T_b \Delta S \approx 7RT_b. \tag{124}$$

This relationship is known as *Trouton's rule*, and is reasonably accurate for a range of gasses.

8.2 Phase diagrams

Phase diagrams are an important tool used in Earth Sciences where phase changes are important (i.e. almost everywhere). They represent graphically the phases that can be present at a given set of conditions. For example, given the pressure and temperature of a pure H_2O system, a phase diagram allows us to determine which of the solid, liquid and vapour phases of H_2O should coexist in equilibrium.

A phase diagram for H_2O is shown in Figure 18. Pressure increases on the y-axis and **BB 28.3** temperature on the x-axis. The conditions that we are most familiar with are atmospheric pressure over a range of temperatures from less than 0ºC to greater than 100ºC. These conditions lie along a horizontal line in the diagram.

A thermodynamic system with pressure of 1 bar (1 atm) and temperature of 200 K sits within the solid *field* on this plot, and hence we expect to find only solid H_2O in our thermodynamic system under those conditions. A thermodynamic system with pressure of 1 bar and temperature of 500 K, in contrast, would be entirely gas (water vapour). At 1 bar and 273 K, the system would plot exactly on the boundary between solid and liquid, and hence we could find both phases present under those conditions.

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[*]This assumption can be proven rigorously with more advanced kinetic theory.
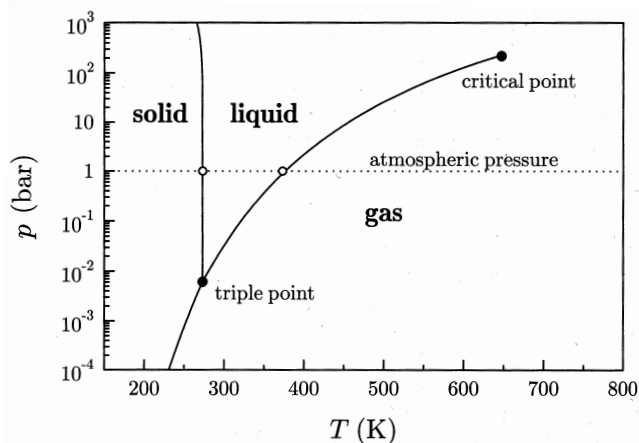
Figure 18: The phase diagram of H_2O copied from **BB 28.3**. Open circles indicate the freezing and boiling points of water at atmospheric pressure.

Notice that with decreasing pressure, there is a decreasing range of temperatures in which the liquid phase is stable. At a pressure of 6.12×10^{-3} bars and a temperature of 273.16 K, this range is zero and the system is on a *triple point*. At the triple point, all three phases can coexist[†]. For pressures below the triple point, liquid water is not stable at any temperature. In this case, supplying heat to a system on the solid–vapour boundary leads to phase change by *sublimation*.

Finally, following the liquid–vapour phase boundary upwards in pressure and temperature, eventually the critical point is reached. Beyond this point, there is no sharp physical (i.e. entropic) difference between gas and liquid; they grade smoothly into each other[‡].

A **phase diagram** is a plot of the boundaries between different phases of a material. The point where two phase boundaries join together is called a **triple point**. The point where a lone phase boundary terminates is called a **critical point**.

8.3   The Clausius-Clapeyron equation

Thermodynamic theory can be used to predict the slope of the lines on a phase diagram. The derivation relies on advanced topics, but the result is straightforward

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_2 - S_1}{V_2 - V_1}, \tag{125}$$

where the subscript on entropy S and volume V refers to each of the phases present. Since $L = T\Delta S$,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T(V_2 - V_1)}. \tag{126}$$

[†]You can watch a video of an experiment on Tert-Butyl Alcohol at its triple point at 0.06 atm pressure on YouTube:
http://www.youtube.com/watch?v=BLRqpJN9zeA

[‡]For a good time with supercritical fluids, dial http://www.youtube.com/watch?v=yBRdBrnIlTQ

This is the *Clausius-Clapeyron equation.* It says that the slope of the phase boundary in p-T space is entirely determined by the latent heat, the temperature at the phase boundary, and the difference in volume (density) between the two phases.

> The **Clausius-Clapeyron equation** states that the slope of a phase boundary in p-T space is determined by the latent heat of the phase change, the temperature at the phase boundary, and the difference in density of the two phases.

8.3.1 Phase boundary for a liquid $\leftrightarrow$ ideal gas transition

We can easily calculate the phase boundary between a liquid and an ideal gas by assuming that the latent heat L is a constant, independent of temperature. Also, we assume that the volume of the gas is much greater than that of the liquid, $V \gg V_{\text{liq}}$. For one mole of ideal gas $pV = RT$, and we can write

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{TV}, \tag{127}$$

$$= \frac{Lp}{RT^2}, \tag{128}$$

$$\frac{\mathrm{d}p}{p} = \frac{L\mathrm{d}T}{RT^2}. \tag{129}$$

Integrating equation (129) and rearranging we obtain

$$p(T) = p_0 \, e^{-L/(RT)}. \tag{130}$$

If we know a point on the phase boundary empirically, we can determine p_0 and hence plot the curve, as shown in Figure 19.

Figure 19: The phase diagram of a hypothetical pure substance. (Axis labels and lines to be added by the student).

8.3.2 Phase boundary for a solid $\leftrightarrow$ liquid transition

For a solid–liquid phase transition, the change in volume ΔV is nearly constant. The Clausius-Clapeyron equation can be rearranged to give

$$\mathrm{d}p = \frac{L\mathrm{d}T}{T\Delta V}, \tag{131}$$

which can be integrated assuming constant L to obtain

$$p = p_0 + \frac{L}{\Delta V} \ln \left(\frac{T}{T_0} \right), \tag{132}$$

where (p_0, T_0) is a point on the solid–liquid phase boundary. Because ΔV is very small, the phase boundary in the p-T plane is very steep. This is evident in Figure 19.

Question: Would you expect the slope of the solid–liquid phase boundary to be positive or negative for most pure substances? What about for water?

Summary of key equations and concepts

Ideal gas law Equation of state for a dilute gas without intermolecular forces

$$pV = Nk_BT, \text{ or } p = nk_BT, \text{ or } pV = n_mRT,$$

where p is pressure, V is volume, N is the number of molecules, k_B is the Boltzmann constant, T is temperature, $n = N/V$ is the number density of molecules, n_m is the number of moles of molecules, and R is the Universal Gas Constant.

Heat capacity Proportionality between heat added to an object and change in temperature of the object.

$$C_x = \left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_x$$

where $\mathrm{d}Q$ is an infinitessimal addition of heat, $\mathrm{d}T$ is an infinitessimal change in temperature, x is the quantity held constant, either p or V. The *specific* heat capacity is C per mass of object, hence

$$c_x = \frac{1}{M}\left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_x.$$

Definition of temperature This formula gives rigorous meaning to the temperature.

$$\frac{1}{k_BT} = \frac{\mathrm{d}\ln\Omega}{\mathrm{d}E},$$

where Ω is the multiplicity: the number of microstates corresponding to the observed macrostate of the system.

Boltzmann distribution Is the probability distribution for the energy of a molecule that is coupled to a large reservoir (e.g. a gas at temperature T)

$$P(\epsilon) = A\mathrm{e}^{-\epsilon/(k_BT)},$$

where A is a constant, and ϵ is the energy of the molecule.

Maxwell-Boltzmann distribution Probability distribution of molecular speed in a gas at temperature T

$$P(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2k_BT}\right)^{3/2} v^2 \exp\left(\frac{-mv^2}{2k_BT}\right),$$

where m is the mass of a single molecule and v is the speed.

Mean kinetic energy The average kinetic energy of a molecule in a gas at temperature T,

$$\langle E_{KE}\rangle = \frac{3}{2}k_BT.$$

Mean free path The average distance that a molecule in a gas travels between collisions

$$\lambda = \left(\sqrt{2}n\sigma\right)^{-1},$$

where σ is the molecular cross-sectional area.

Conduction and diffusion The flux of heat through a gas in the x-direction is given by

$$J_x = -\kappa \frac{\partial T}{\partial x},$$

where κ is the thermal conductivity. The diffusion equation in the x-direction is

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

where D is the diffusivity. For chemical diffusion, these are given by

$$\Phi_x = -D \frac{\partial n^*}{\partial x}, \quad \text{and} \quad \frac{\partial n^*}{\partial t} = D \frac{\partial^2 n^*}{\partial x^2},$$

where n^* is the number density of the diffusing molecules.

Function of state A variable describing a system in thermodynamic equilibrium that is path-independent. For a change from state a to state b it has the property

$$\Delta f = \int_{\mathbf{x}_a}^{\mathbf{x}_b} \mathrm{d}f = f(\mathbf{x}_b) - f(\mathbf{x}_a),$$

where $\mathbf{x}$ is a list of system paramters describing the state (e.g. pressure, temperature, etc). $\mathrm{d}f$ must be an exact differential.

First law of thermodynamics Energy is conserved; heat and work are both forms of energy

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W,$$

where $\mathrm{d}U$ is an infinitessimal change in internal energy, and $\mathrm{d}W$ is an infinitessimal quantity of work done by the system (sign convection following **BB**).

Work Work is force times distance, or in the case of a thermodynamic system,

$$\mathrm{d}W = -p\mathrm{d}V,$$

where $\mathrm{d}V$ is an infinitessimal change in volume (sign convection following **BB**).

Reversible isothermal expansion of an ideal gas For an ideal gas, $U = U(T)$, hence if $\mathrm{d}T = 0$ then $\mathrm{d}U = 0$ and $\mathrm{d}Q = -\mathrm{d}W$. Using this and the ideal gas law gives

$$\Delta Q = RT \ln \frac{V_2}{V_1}$$

per mole of gas.

Adiabatic expansion of an ideal gas Adiabatic means reversible and adiathermal ($\mathrm{d}Q = 0$). Using this, $\mathrm{d}U = C_V \mathrm{d}T$ for an ideal gas, and the ideal gas law gives

$$pV^\gamma = \text{const.}$$

Efficiency of an engine cycle Engines are supposed to convert heat into work. The efficiency is given by the work output of the engine divided by the heat input

$$\eta = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h},$$

where Q_h is the heat input and Q_c is the (waste) heat output.

Efficiency of a Carnot engine The Carnot engine is the most efficient engine possible between two thermal reservoirs. It is composed of two isothermal paths and two adiabatic paths. Its efficiency is

$$\eta_{\text{carnot}} = 1 - \frac{T_c}{T_h},$$

where T_h and T_c are the temperatures of the hot and cold reservoirs, respectively.

Second law of thermodynamics No process is possible with the sole result of complete conversion of heat into work, **or**, no process is possible with the sole result of transfer of heat from a colder to a hotter body.

Entropy A function of state defined by the exact differential

$$dS = \frac{dQ_{\text{rev}}}{T},$$

where dQ_{rev} is the amount of heat added to the system reversibly. For any process, $dS \geq 0$, where the equality holds if the process is reversible. The definition of entropy from kinetic theory is

$$S = k_B \ln \Omega,$$

which is consistent with the definition of temperature from kinetic theory.

Latent heat The energy associated with a phase change is called the latent heat. It is given by

$$L = T \Delta S,$$

where T is the temperature of the phase change and ΔS is the entropy difference between the two phases.

Clausius-Clapeyron equation This equation describes the slope of phase boundaries on a phase diagram

$$\frac{dp}{dT} = \frac{L}{T \, \Delta V},$$

where ΔV is the change in volume (or the change in specific volume) between the two phases.