5 Kinetic theory

The problems are roughly in order of difficulty. The ones with ♣ are the hardest ones, which might only occur as a "sting in the tail" at the end of a long examination question.

Problem 5.1 **Two-level gas**
Consider a volume of gas at $27°$C. The atoms of the gas can exist in only two energy states, one being an energy E above the other. Calculate the fraction of atoms in the higher energy state

1. if $E = 1$ eV,
2. if $E = 0.1$ eV and
3. if $E = 0.01$ eV.

Problem 5.2 **Sketching Maxwell-Boltzmann**
Sketch the probability distribution for the y-component of velocity of the molecules of a gas at temperature T.

Problem 5.3 **Speed versus velocity**
Sketch the probability distribution for the speed of the molecules of a gas at temperature T. Why is the shape of this distribution different from that of (2) above ?

Problem 5.4 **Internal energy of a gas**
Internal energy of a gas,

$$U(T) = (\tfrac{1}{2}k_{\text{B}}T) \times (?) \times \text{ (number of molecules) .}$$

What is the missing term? What is its value for a monatomic gas?

The next problem is a little mathematical so has a ♣, but the *results* can be used straightforwardly – for example in the following questions.

♣*Problem 5.5* **Approximations for probabilities**
As was observed in the lectures, it is impossible in general to provide an exact, analytic, expression for the probability that a molecule in a gas at temperature T is travelling faster than v_0, say. This must be determined numerically.

However if $v_0 \gg \langle |v| \rangle$ or if $0 < v_0 \ll \langle |v| \rangle$, useful approximations may be made.

Two results from integration (which are illustrations of general techniques for approximating integrals) follow. Consider the function $f(x) = \mathrm{e}^{-\alpha x^2}$, so there is a natural scale for x, $\alpha^{-1/2}$. We will now approximate

$$F(x) = \int_x^\infty \mathrm{d}y \ f(y) \ ,$$

(i) $\boldsymbol{x \gg \alpha^{-1/2}}$.. Write

$$F(x) = \int_x^\infty \mathrm{d}y\ \mathrm{e}^{-\alpha y^2} = \int_x^\infty \mathrm{d}y\ \frac{-2\alpha y}{-2\alpha y}\mathrm{e}^{-\alpha y^2}\ ,$$

then judiciously group symbols and integrate by parts twice to show that:

$$F(x) = \frac{\mathrm{e}^{-\alpha x^2}}{2\alpha x} - \frac{1}{(2\alpha)^2}\frac{\mathrm{e}^{-\alpha x^2}}{x^3} + \cdots \tag{5.1}$$

$$\simeq \frac{\mathrm{e}^{-\alpha x^2}}{2\alpha x}\left(1 - \frac{1}{2\alpha x^2}\right)\ . \tag{5.2}$$

Note that $\alpha^{1/2}x \gg 1$ so this expansion looks useful.

(ii) $\boldsymbol{x \ll \alpha^{-1/2}}$. Firstly rewrite $F(x)$, with $x > 0$,

$$F(x) = \int_x^\infty \mathrm{d}y\ \mathrm{e}^{-\alpha y^2}$$

$$= \int_0^\infty \mathrm{d}y\ \mathrm{e}^{-\alpha y^2} - \int_0^x \mathrm{d}y\ \mathrm{e}^{-\alpha y^2}\ .$$

The first term is known, and for the second term note the region of integration, $x \ll \alpha^{-1/2}$. How may we exploit that to evaluate the integral approximately? Hence show that

$$F(x) \underset{x\to 0}{\sim} \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} - x + \frac{\alpha x^3}{3} - \cdots$$

$$\simeq \frac{1}{\sqrt{\alpha}}\left(\frac{\sqrt{\pi}}{2} - \alpha^{1/2}x + \frac{\left(\alpha^{1/2}x\right)^3}{3}\right)\ . \tag{5.3}$$

Since $\alpha^{1/2}x \ll 1$ this approximation also appears useful.

Problem 5.6 **A languid cyclist**

A cyclist is cycling at 5 ms^{-1} in a straight line in the x-direction. What fraction of the molecules in the atmosphere have $v_x < 5$ ms^{-1}? [Decide which approximation from the previous problem to use.]

Problem 5.7 **Hot air – the leaky Earth**

What is the escape velocity from Earth?

Assuming molecules of nitrogen, $^{14}N_2$, in the atmosphere do not collide with each other and have a Maxwell-Boltzmann distribution at room temperature (say 300 K), what fraction will escape from the Earth's gravitational field?

How does this fraction differ for ^{3}He, ^{4}He and $^{14}N_2$ molecules? Is this a credible reason for the disparities of of abundance of these entities in the atmosphere? (Consult the Web to find the Earthly isotopic abundances.)

Problem 5.8 **Counterpart to equipartition for different potential shapes**

The aim is to derive the counterpart to $\frac{1}{2}k_{\mathrm{B}}T$ per degree of freedom for potential energy of the form $V_n(x) = V_0|x|^n$, with $n > 0$ and $V_0 > 0$.

The Boltzmann factor for $V_n(x)$ is

$$\exp\left(-\frac{V_0|x|^n}{k_{\mathrm{B}}T}\right) .$$

So the *normalised* probability for the particle being $x_0 \le x \le x_0 + \mathrm{d}x$, $p(x)\mathrm{d}x$, is

$$p(x)\ \mathrm{d}x = \frac{\exp\left(-\frac{V_0|x|^n}{k_{\mathrm{B}}T}\right)\ \mathrm{d}x}{\displaystyle\int_{-\infty}^{\infty} \mathrm{d}x\ \exp\left(-\frac{V_0|x|^n}{k_{\mathrm{B}}T}\right)} .$$

It is convenient to define the quantity Z_n:

$$Z_n = \int_{-\infty}^{\infty} \mathrm{d}x\ \exp\left(-\frac{V_0|x|^n}{k_{\mathrm{B}}T}\right) .$$

And the average value for the potential energy is

$$\langle V_n\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\ V_0|x|^n p(x) = \frac{\displaystyle\int_{-\infty}^{\infty} \mathrm{d}x\ V_0|x|^n\ \exp\left(-\frac{V_0|x|^n}{k_{\mathrm{B}}T}\right)\ \mathrm{d}x}{\displaystyle\int_{-\infty}^{\infty} \mathrm{d}x\ \exp\left(-\frac{V_0|x|^n}{k_{\mathrm{B}}T}\right)} .$$

We will break the derivation of this quantity into a number of stages.

(i) Firstly a general result on Z_n. Let us define $\beta = 1/(k_{\mathrm{B}}T)$. Then show, using the chain rule, that

$$-\frac{\partial \ln Z_n}{\partial\beta} = \langle V_n\rangle . \tag{5.4}$$

(ii) Rewrite the the expression for Z_n, by defining a new variable of integration $y = (\beta V_0)^{1/n}\, x$ to show

$$Z_n = (\beta V_0)^{-1/n} \int_{-\infty}^{\infty} \mathrm{d}y\ \mathrm{e}^{-|y|^n} . \tag{5.5}$$

(iii) Now use Eq. (5.4) and apply to Eq. (5.5). Hence show that

$$\langle V_n\rangle = \frac{1}{n}k_{\mathrm{B}}T .$$

What value of n corresponds to the harmonic oscillator?

(iv) What is the result for particles in the "flat Earth" gravitational potential which we considered in analysing the density profile of the atmosphere?

Problem 5.9 **A two-level heat engine – magnetic cooling**

Consider a two-level system where the energy difference between the levels is $2\mu H$, with $E_- = -\mu H$ and $E_+ = +\mu H$.

The physical setting for this is an atomic (or nuclear) magnetic dipole, μ, which has two quantum states. In the presence of an applied magnetic field, $H\hat{\mathbf{z}}$, the states are split to give $E_\pm$. I.e. the magnetic moment is either parallel or anti-parallel to the field.

The average magnetisation, $M(T, H)$, is defined as

$$M(T, H) = \mu p(E_-) - \mu p(E_+) \ .$$

Constructing the probabilities $p(E_\pm)$ using the corresponding Boltzmann factors and hence calculate $M(T, H)$. This plays the role of the equation of state for the two-level system.

Work may be performed on the system by changing H. It can be placed in contact with heat baths to exchange heat.

Derive the "internal energy", U defined via

$$U(T, H) = \langle E \rangle \ ,$$

where we assume the two-level system is in equilibrium at temperature T. This is a function of state, as in the ideal gas, but note it depends on the applied field, H, as well as the temperature.

Consider the thermodynamic cycle depicted in Fig. (5.1). Along section 1 the magnetic

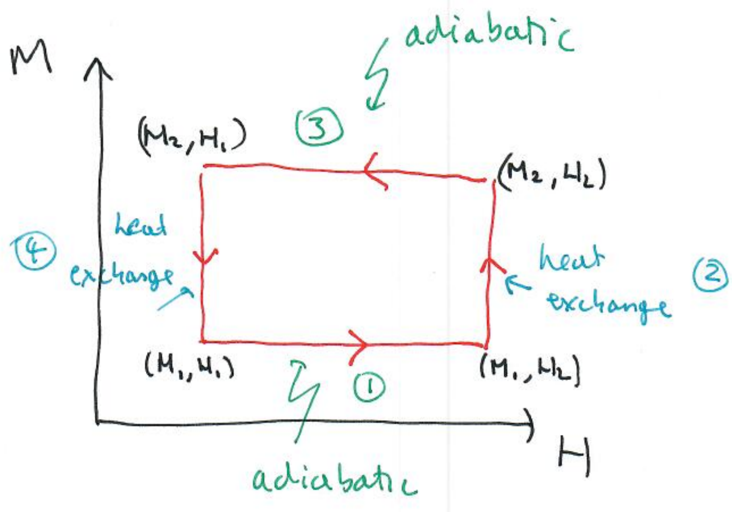

Figure 5.1: A magnetic refrigeration cycle.

field is increased adiabatically; there is a heat exchange in section 2 where the two level system cools to come to equilibrium at T_3; along section 3 there is an adiabatic decrease in the applied field; finally in section 4 there is a heat exchange with the cold heat bath at T_1 and the two level system heats up.

(i) Start at (M_1, H_1). What is the initial temperature, T_1?

(ii) Increase the magnetic field, H, to H_2, keeping M fixed. What is the change in the internal energy?

(iii) What is the temperature, T_2, at this point (M_1, H_2)?

(iv) Then at fixed $H = H_2$ let the system come to equilibrium at the temperature, $T_3 < T_2$. Calculate the magnetisation M_2, and the change in U.

(v) Reduce the field adiabatically back to H_1. What is the resulting temperature T_4? Is it larger or smaller than T_1?

(vi) Finally exchange heat with the medium at T_1.

(vii) Is this cycle a refrigeration of heating cycle. Why?

(viii) Sketch the isotherms through the vertices of the thermodynamic cycle. Indicate the ordering of the temperatures associated with them.

(ix) Show the isotherms for $T = 0$ and $T = \infty$ on the diagram.

Problem 5.10 **Self-diffusion constant for an almost ideal gas**

We employ the same logic as in section 10 to determine the self diffusion constant, D, of an almost ideal gas. We define the concentration of the atomic species as $n(y)$, then experimentally we find the number crossing a plane of area A per unit time,

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -D\frac{\partial n}{\partial y}A \ .$$

By considering planes a distance $y \pm \lambda$ away from that at y, show the net transfer of atoms is

$$-2\lambda A\langle v_y^+\rangle\frac{\partial n}{\partial y} \ .$$

Hence show

$$D = 2\lambda\langle v_y^+\rangle \ .$$

For air at s.t.p., one finds $D \sim 10^{-5}$ m^{2}s^{-1}.