

5 Kinetic theory – solutions

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

Assume the gas is in thermal equilibrium, implied by the statement it is at 27°C.

Let the lower state be denoted E_0 and the higher by E_1 , then the probability of each is the associated Boltzmann factor:

$$p(E_1) = Ae^{-E_1/k_B T} \quad \text{and} \quad p(E_2) = Ae^{-E_2/k_B T} .$$

Here A is determined by normalisation. To obtain the relative fraction of the atoms being in the first or second state, p_{rel} :

$$p_{\text{rel}} = \frac{p(E_1)}{p(E_2)} = \frac{Ae^{-E_1/k_B T}}{Ae^{-E_0/k_B T}} = e^{-(E_1-E_0)/k_B T} = e^{-E/k_B T} .$$

Note $0 \leq p_{\text{rel}} \leq 1$.

Now at $T = 27^\circ\text{C}$,

$$\begin{aligned} k_B T &= 1.38 \times 10^{-23} \text{ JK}^{-1} \times [300 \text{ K}] \\ &= 4.14 \times 10^{-21} \text{ J} \\ &= \frac{4.14 \times 10^{-21}}{1.6 \times 10^{-19}} \text{ eV} \\ &= 2.5 \times 10^{-2} \text{ eV} . \end{aligned}$$

Now for the three cases,

1. if $E = 1 \text{ eV}$, i.e. $E \gg k_B T$,

$$e^{-E/k_B T} = \exp\left(-\frac{1}{2.5 \times 10^{-2}}\right) = e^{-40} = 4.3 \times 10^{-18} .$$

And we may immediately deduce that

$$p(E_0) \simeq 1 \quad \text{and} \quad p(E_1) = 4.3 \times 10^{-18} .$$

2. if $E = 0.1 \text{ eV}$, i.e. $E > k_B T$,

$$e^{-E/k_B T} = \exp\left(-\frac{0.1}{2.5 \times 10^{-2}}\right) = 0.018 .$$

One might assume that this result implies that $p(E_0) \simeq 1$, but we can check:

$$\begin{aligned} \frac{p(E_1)}{1 - p(E_1)} &= 0.018 \\ \Rightarrow p(E_1)(1 - 0.018) &= 0.018 \\ \Rightarrow p(E_1) &\simeq 0.018 , \end{aligned}$$

where we used the first term of the binomial expansion for $(1 - 0.018)^{-1}$.

3. if $E = 0.01$ eV, i.e. $E < k_B T$,

$$\frac{p(E_1)}{p(E_0)} = \exp\left(-\frac{0.01}{2.5 \times 10^{-2}}\right) = 0.67$$

$$\text{so } \frac{p(E_1)}{1 - p(E_1)} = 0.67$$

$$\Rightarrow p(E_1) = 0.40$$

So in the third case, the probabilities are roughly equal.

Problem 5.2 Sketching Maxwell-Boltzmann

The probability distribution for the y -component of velocity of the molecules of a gas at temperature T is sketched below in Fig. (5.1).

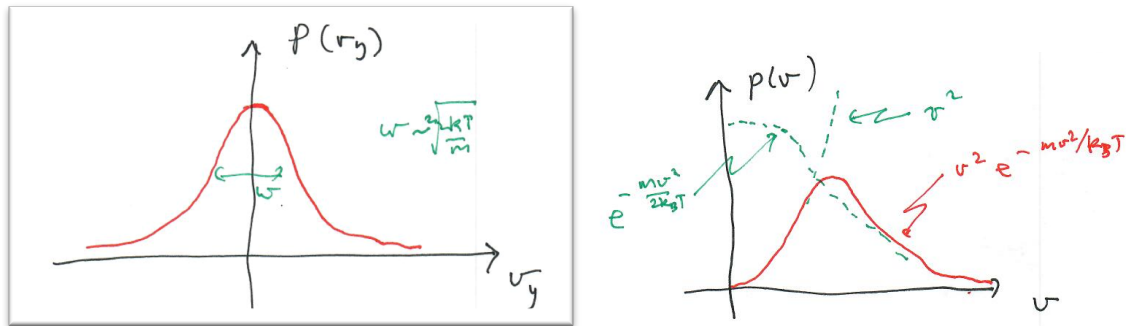


Figure 5.1: Left: The Maxwell-Boltzmann distribution for the y component of the velocity. Right: the probability distribution for the speed, v , in three dimensions.

Problem 5.3 Speed versus velocity

A sketch of the probability distribution for the speed of the molecules of a gas in three dimensions at temperature T is in figrefmaxbcom.

The distribution reflects all three components of $\mathbf{v} = (v_x, v_y, v_z)$, and the probability of all three components being small vanishes as $|\mathbf{v}| \rightarrow 0$.

Problem 5.4 Internal energy of a gas

If we write the internal energy of a gas,

$$U(T) = \left(\frac{1}{2}k_B T\right) \times (?) \times (\text{number of molecules}),$$

then the missing term is the number of degrees of freedom.

For a monatomic gas experiencing no external force, this number is the number of dimensions. For three dimensions the missing number is 3.

♣ Problem 5.5 Approximations for probabilities

The following techniques can be used on other problems. For example the first technique may be used for $x \gg \alpha^{-1}$ in this integral

$$\int_x^\infty dy \frac{e^{-\alpha y}}{y}.$$

And an example for the second technique might be, for $\alpha^{1/8}x \ll 1$,

$$\int_0^x dy e^{-\alpha y^8}.$$

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

$$\begin{aligned} F(x) &= \int_x^\infty dy e^{-\alpha y^2} \\ &= \int_x^\infty dy \frac{-2\alpha y}{-2\alpha y} e^{-\alpha y^2} \\ &= \left[\frac{e^{-\alpha y^2}}{-2\alpha y} \right]_x^\infty - \left(-\frac{1}{2\alpha} \right) \int_x^\infty dy \left(-\frac{1}{y^2} \right) e^{-\alpha y^2} \\ &= \frac{e^{-\alpha x^2}}{2\alpha x} - \frac{1}{2\alpha} \int_x^\infty dy \frac{-2\alpha y e^{-\alpha y^2}}{y^2} \\ &= \frac{e^{-\alpha x^2}}{2\alpha x} - \frac{1}{(2\alpha)^2} \frac{e^{-\alpha x^2}}{x^3} - \frac{3}{(2\alpha)^2} \int_x^\infty dy \frac{e^{-\alpha y^2}}{y^4} \\ &\simeq \frac{e^{-\alpha x^2}}{2\alpha x} \left(1 - \frac{1}{2\alpha x^2} \right). \end{aligned} \quad (5.1)$$

Since $\alpha x^2 \gg 1$, this approximation is useful. One may continue this process more times – but there is a catch (see Y3 *Perturbation Theory and Asymptotics*).

(ii) $x \ll \alpha^{-1/2}$. the key idea is to approximate the integrand by Taylor expansion as the function does not vary much over the region of integration.

$$\begin{aligned} F(x) &= \int_x^\infty dy e^{-\alpha y^2} \\ &= \int_0^\infty dy e^{-\alpha y^2} - \int_0^x dy e^{-\alpha y^2} \\ &= \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} - \int_0^x dy (1 - \alpha x^2 + \dots) \\ &\simeq \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} - \left(x - \frac{\alpha x^3}{3} \right) \\ &= \frac{1}{\sqrt{\alpha}} \left(\frac{\sqrt{\pi}}{2} - \sqrt{\alpha} x + \frac{1}{3} [\sqrt{\alpha} x]^3 \right). \end{aligned} \quad (5.2)$$

Since $\sqrt{\alpha}x \ll 1$ this is a good approximation.

Problem 5.6 A languid cyclist

To set the scale of the cyclist's speed, v_{cyc} , versus the air molecules, we might remember they were close to the speed of sound, or calculate it. At room temperature the average value of $|v_x|$ is

$$\langle |v_x| \rangle = \sqrt{\frac{2k_B T}{\pi m}}.$$

For the majority component of the atmosphere, N_2 , at room temperature this was determined in the lecture notes to be $v_{\text{nit}} \simeq 500 \text{ ms}^{-1}$.

Thus the cyclist is moving very slowly compared to the typical velocity of the air molecules at room temperature. We are in the second limit above Eq. (5.2), although we only want the second or perhaps third term as

$$\text{fraction of molecules slower than cyclist} = \int_0^{v_{\text{cyc}}} dv_x p(v_x) .$$

The normalised MB distribution for one component of the velocity is

$$p(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{mv_x^2}{2k_B T}\right) .$$

Thus we may use the second term in the expansion, so

$$\text{fraction of molecules slower than cyclist} \simeq v_{\text{cyc}} \sqrt{\frac{m}{2\pi k_B T}} = \frac{1}{\pi} \frac{v_{\text{cyc}}}{v_{\text{nit}}} \simeq \frac{1}{\pi} \frac{5}{500} \simeq 0.3\% .$$

i.e. a small fraction.

Problem 5.7 Hot air – the leaky Earth

The escape velocity of the earth is

$$\frac{1}{2}mv_e^2 = \frac{GMm}{R} \quad \Rightarrow \quad v_e = \sqrt{\frac{2GM}{R}} .$$

Here $M \simeq 6 \times 10^{24}$ kg is the mass of the Earth, $R \simeq 6.4 \times 10^6$ m is the radius of the Earth and $G \simeq 6.7 \times 10^{-11}$ m³kg⁻¹s⁻² is Newton's constant. Thus

$$v_e \simeq 11.2 \text{ kms}^{-1} .$$

At room temperature the typical vertical speed of ¹⁴N₂ molecules is

$$\langle |v_z| \rangle = \sqrt{\frac{2}{3\pi}} \bar{c} \simeq 0.5 \times 500 \text{ ms}^{-1} = 250 \text{ ms}^{-1} \ll 11.2 \text{ kms}^{-1} = v_e$$

from lectures. Thus we are in the first limit and may use the approximation Eq. (5.1).

We find that for the nitrogen molecule, mass m , using Eq. (5.1):

$$\begin{aligned} p(v_z \geq v_e) &= \sqrt{\frac{m}{2\pi k_B T}} \int_{v_e}^{\infty} dv_z \exp\left(-\frac{mv_z^2}{2k_B T}\right) \\ &\simeq \sqrt{\frac{m}{2\pi k_B T}} \frac{1}{2} \frac{2k_B T}{mv_e} \exp\left(-\frac{mv_e^2}{2k_B T}\right) \\ &= \sqrt{\frac{k_B T}{2\pi m}} \frac{1}{v_e} \exp\left(-\frac{mv_e^2}{2k_B T}\right) \\ &= \frac{1}{2} \frac{\langle |v_z| \rangle}{v_e} e^{-(v_e/\langle |v_z| \rangle)^2/\pi} \\ &\simeq 0.01 \times e^{-700} \sim 10^{-350} . \end{aligned}$$

Here we used the crude estimate of $e^2 \sim 10$. It really does not matter; the number is minuscule. ¹⁶O₂ has an even smaller probability. How to turn this into a rate is more

complicated. We would need to admit the molecules interact and discuss how the velocity distribution is re-filled. There are several contributions in the high atmosphere for this, see [this article](#). But the estimate for hydrogen is around 3 kgs^{-1} . (where the counterpart to the probability we calculated is much higher)

For the difference between ^4He and ^3He , it is implausible that the origin is thermal – the natural abundance of ^4He is 99.9998% and ^3He is 0.0002%, whereas the concentration of H_2 in the atmosphere is 10% of ^4He . The reason for the disparity in the two helium isotopes appears to be the complicated reactions in the production of nuclei in the first twenty minutes after the Big Bang, but [hard to isolate a particular aspect](#).

Problem 5.8 Counterpart to equipartition for different potential shapes

The Boltzmann factor for $V_n(x)$ is

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

So the *normalised* probability for the particle being $x_0 \leq x \leq x_0 + dx$, $p(x)dx$, is

$$p(x) dx = \frac{\exp\left(-\frac{V_0|x|^n}{k_B T}\right) dx}{\int_{-\infty}^{\infty} dx \exp\left(-\frac{V_0|x|^n}{k_B T}\right) dx} .$$

It is convenient to define the quantity Z_n :

$$Z_n = \int_{-\infty}^{\infty} dx \exp\left(-\frac{V_0|x|^n}{k_B T}\right) .$$

And the average value for the potential energy is

$$\langle V_n \rangle = \int_{-\infty}^{\infty} dx V_0|x|^n p(x) = \frac{\int_{-\infty}^{\infty} dx V_0|x|^n \exp\left(-\frac{V_0|x|^n}{k_B T}\right) dx}{\int_{-\infty}^{\infty} dx \exp\left(-\frac{V_0|x|^n}{k_B T}\right) dx} .$$

(i)

$$\begin{aligned} -\frac{\partial \ln Z_n}{\partial \beta} &= -\frac{1}{Z_n} \frac{\partial Z_n}{\partial \beta} \\ &= -\frac{1}{Z_n} \frac{\partial}{\partial \beta} \int_{-\infty}^{\infty} dx \exp(-\beta V_0|x|^n) dx \\ &= -\frac{1}{Z_n} \int_{-\infty}^{\infty} dx [-V_0|x|^n] \exp(-\beta V_0|x|^n) dx \\ &= \langle V_n \rangle \end{aligned}$$

(ii) If

$$y = (\beta V_0)^{1/n} x \quad \Rightarrow \quad dx = dy (\beta V_0)^{-1/n} .$$

Then:

$$\begin{aligned} Z_n &= \int_{-\infty}^{\infty} dx \exp\left(-\frac{V_0|x|^n}{k_B T}\right) dx \\ &= (\beta V_0)^{-1/n} \int_{-\infty}^{\infty} dy e^{-|y|^n} = (\beta V_0)^{-1/n} I_0 \end{aligned} \quad (5.3)$$

Note I_0 is a pure number.

(iii) Now we use Eq. (5.3)

$$\begin{aligned} \ln Z_n &= -\frac{1}{n} \ln(\beta V_0) + \ln I_0 \\ \Rightarrow -\frac{\partial \ln Z_n}{\partial \beta} &= \frac{1}{n} \frac{1}{\beta V_0} V_0 = \frac{1}{n} k_B T . \end{aligned}$$

For $n = 2$ we obtain the harmonic oscillator and get the usual Equipartition theorem.

(iv) For the "flat Earth" gravitational potential $V(z) = mgz$, we use $z \geq 0$ and get the same answer ie

$$\langle V_1 \rangle = k_B T .$$

Problem 5.9 A two-level heat engine – magnetic cooling

The probabilities for the energy levels $E_{\pm} = \pm \mu H$ are (defining $\beta = 1/(k_B T)$):

$$p(E_{\pm}) = \frac{e^{\mp \beta \mu H}}{e^{-\beta \mu H} + e^{\beta \mu H}} .$$

This implies the magnetisation is

$$\begin{aligned} M(T, H) &= \mu p(E_-) - \mu p(E_+) \\ &= \mu \frac{\sinh(\beta \mu H)}{\cosh(\beta \mu H)} \\ &= \mu \tanh(\beta \mu H) . \end{aligned} \quad (5.4)$$

This plays the role of the equation of state with the correspondence $M \leftrightarrow p$ and $H \leftrightarrow V$, where H and V are the external variables which are controlled and M and p are the responses of the system.

The internal energy, $U(T, H)$ is similarly

$$\begin{aligned} U(T, H) &= E_+ p(E_+) + E_- p(E_-) \\ &= \mu H p(E_+) - \mu H p(E_-) \\ &= -M(T, H) H \end{aligned} \quad (5.5)$$

Turning now to the thermodynamic cycle in Fig. (5.2)

1. Since we know $M(T, H)$ from Eq. (5.4), we may invert to obtain:

$$\beta_1 \mu H_1 = \tanh^{-1}(M_1/\mu) \quad \Rightarrow \quad k_B T_1 = \frac{\mu H_1}{\tanh^{-1}(M_1/\mu)} . \quad (5.6)$$

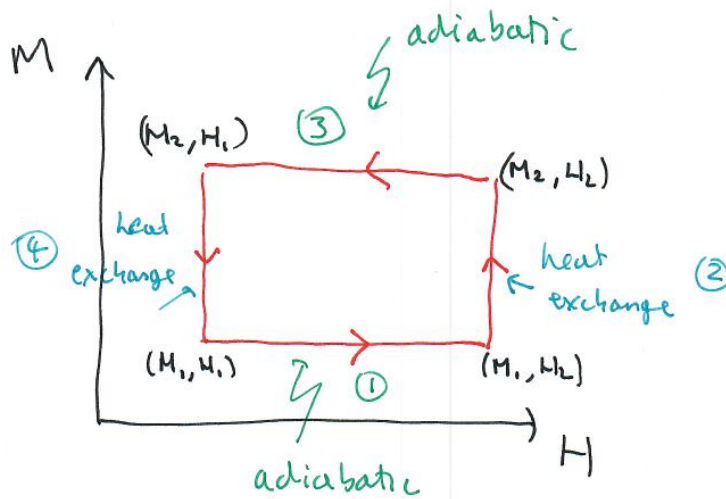


Figure 5.2: A magnetic refrigeration cycle.

2. The internal energy is

$$\Delta U(T, H_2) = -H_2 M(T_1, H_1) + H_1 M(T_1, H_1) = -(H_2 - H_1) M(T_1, H_1) .$$

3. The temperature may be deduced as before – the magnetisation has not changed, but the field has so

$$k_B T_2 = \frac{\mu H_2}{\tanh^{-1}(M_1/\mu)} > k_B T_1 .$$

(So this is like the adiabatic compression of a gas in the refrigeration cycle.)

4. Letting the two-level system come into equilibrium at T_3 , we see:

$$M_2(T_3, H_2) = \mu \tanh(\beta_3 \mu H_2) .$$

The change in $U(T, H)$ on stage ② is:

$$\Delta U = -M_2 H_2 + M_1 H_2 = -(M_2 - M_1) H_2 < 0 .$$

5. Reducing the field adiabatically to H_1 , we find that the temperature is:

$$\begin{aligned} k_B T_4 &= \frac{\mu H_1}{\tanh^{-1}(M_2/\mu)} \\ &= \frac{\mu H_1}{\tanh^{-1} \left[\tanh \left\{ \frac{\mu H_2}{k_B T_3} \right\} \right]} \\ &= k_B T_3 \frac{H_1}{H_2} < k_B T_3 . \end{aligned}$$

6. And in turn since $M_2 > M_1$, $T_4 < T_1$ and so the two-level system will absorb heat from the system at T_1 .
7. The cycle is refrigerating as heat is absorbed from the system at T_1 and heat is deposited at T_3 after work has been done.
8. The isotherms are shown in Fig. (5.3) .

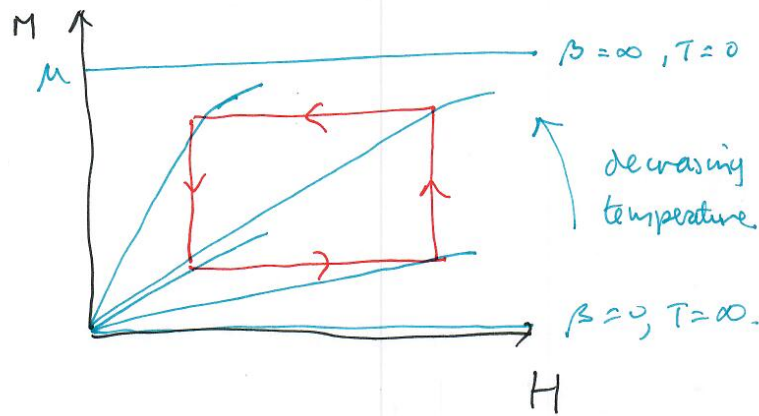


Figure 5.3: Magnetic isotherms.

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,

$$\frac{dN}{dt} = -D \frac{\partial n}{\partial y} A .$$

Then the concentrations on the different planes (see diagrams in section 10),

$$\text{For } P: \quad n(y + \lambda) \simeq n + \frac{\partial n}{\partial y} \lambda$$

$$\text{For } Q: \quad n(y - \lambda) \simeq n - \frac{\partial n}{\partial y} \lambda .$$

So the net flux of particles per unit time through the middle plane is (they are only "carrying themselves now, so no factor of mass, m , or specific heat:

$$\dot{N} = -2A \langle v_y^+ \rangle \lambda \frac{\partial n}{\partial y} , \quad (5.7)$$

So comparing with the equation defining D , we see that

$$D = 2\lambda \langle v_y^+ \rangle = \frac{2\langle v_y^+ \rangle}{\pi n r_0^2} .$$