

Kinetic Theory and Thermodynamics



Second year physics course

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Questions
MICHAELMAS 2009

Kinetic Theory and Thermodynamics: Problems

Problem sheet 1: Distributions and averages
Questions to be answered for the first problem class.

These first questions are all about finding the average of various quantities assuming particular probability distributions.

- 1.1 This question is about a **discrete** probability distribution known as the **Poisson distribution**. Let x be a discrete random variable which can take the values $0, 1, 2, \dots$. It is said to be Poisson distributed if it takes the value x with probability

$$p(x) = \frac{e^{-m} m^x}{x!},$$

where m is a number (which we will see later is the mean value of x).

- (a) Show that $p(x)$ is a well-behaved probability distribution in the sense that

$$\sum_{x=0}^{\infty} p(x) = 1.$$

(Why is this condition important?)

- (b) Show that the mean value of the probability distribution is $\langle x \rangle = \sum_{x=0}^{\infty} xp(x) = m$.

(c) The Poisson distribution is useful for describing very rare events which occur independently and whose average rate does not change over the period of interest. Examples include birth defects measured per year, traffic accidents at a particular junction per year, numbers of typographical errors on a page, and number of activations of a Geiger counter per minute. The first recorded example of a Poisson distribution, the one which in fact motivated Poisson, was connected with the rare event of someone being kicked to death by a horse in the Prussian army. The number of horse-kick deaths of Prussian military personnel was recorded for each of 10 corps in each of 20 years from 1875–1894 and the following data found:

Number of deaths per year per corps	0	1	2	3	4	≥ 5	Total
Observed frequency	109	65	22	3	1	0	200

Calculate the mean number of deaths per year per corps. Compare the observed frequency with a calculated frequency assuming the number of deaths per year per corps are Poisson distributed with this mean.

- 1.2 This question is about a **continuous** probability distribution known as the **exponential distribution**. Let x be a continuous random variable which can take any value $x \geq 0$. It is said to be exponentially distributed if it takes values between x and $x + dx$ with probability

$$p(x) dx = Ae^{-x/\lambda} dx$$

where λ and A are constants.

(a) Find the value of A that makes $p(x)$ a well-defined continuous probability distribution so that

$$\int_0^{\infty} p(x) dx = 1.$$

(b) Show that the mean value of the probability distribution is $\langle x \rangle = \int_0^{\infty} xp(x) dx = \lambda$.

(c) Find the variance and standard deviation of this probability distribution.

Both the exponential distribution and the Poisson distribution are used to describe similar processes, but for the exponential distribution x is the *actual time* between successive radioactive decays, successive molecular collisions, or successive horse-kicking incidents (rather than x being simply *the number* of such events in a specified interval).

1.3 If θ is a continuous random variable which is uniformly distributed between 0 and π , write down an expression for $p(\theta)$. Hence find the value of the following averages:

- | | |
|--|---|
| (i) $\langle \theta \rangle$ | (vi) $\langle \sin \theta \rangle$ |
| (ii) $\langle \theta - \frac{\pi}{2} \rangle$ | (vii) $\langle \cos \theta \rangle$ |
| (iii) $\langle \theta^2 \rangle$ | (viii) $\langle \cos^2 \theta \rangle$ |
| (iv) $\langle \theta^n \rangle$ (for the case $n \geq 0$) | (ix) $\langle \sin^2 \theta \rangle$ |
| (v) $\langle \cos \theta \rangle$ | (x) $\langle \cos^2 \theta + \sin^2 \theta \rangle$ |

Check that your answers are what you expect.

1.4 A Maxwellian distribution (also known as a Maxwell-Boltzmann distribution) is a probability distribution which describes the probability distribution of molecular speeds in a gas. It implies that a given molecule (mass m) will have a speed between v and $v + dv$ with probability equal to $f(v) dv$ where

$$f(v) \propto v^2 e^{-mv^2/2k_B T},$$

where k_B is Boltzmann's constant and I have used a proportional sign (\propto) because a normalization constant has been omitted. (You can correct for this by dividing any averages you work out by $\int_0^{\infty} f(v) dv$.)

For this Maxwellian distribution, calculate the mean speed $\langle v \rangle$ and the mean inverse speed $\langle 1/v \rangle$. Show that

$$\langle v \rangle \langle 1/v \rangle = \frac{4}{\pi}.$$

1.5 The molecules in a gas travel with different velocities. A particular molecule will have velocity \mathbf{v} and speed $v = |\mathbf{v}|$ and will move at an angle θ to some chosen fixed axis. We have shown that the number of molecules in a gas with speeds between v and $v + dv$, and moving at angles between θ and $\theta + d\theta$ to any chosen axis is given by

$$\frac{1}{2} n f(v) dv \sin \theta d\theta,$$

where n is the number of molecules per unit volume and $f(v)$ is some function of v only. [$f(v)$ could be the Maxwellian distribution given above; however you should not assume this but rather calculate the general case.] Hence show by integration that:

- (a) $\langle u \rangle = 0$
- (b) $\langle u^2 \rangle = \frac{1}{3} \langle v^2 \rangle$
- (c) $\langle |u| \rangle = \frac{1}{2} \langle v \rangle$

where u is any one Cartesian component of v , i.e. v_x , v_y or v_z .

[Hint: You can take u as the z -component of \mathbf{v} without loss of generality. Why? Then express u in terms of v and θ and average over v and θ . You can use expressions such as

$$\langle v \rangle = \frac{\int_0^\infty v f(v) dv}{\int_0^\infty f(v) dv}$$

and similarly for $\langle v^2 \rangle$. Make sure you understand why.]

- 1.6 If v_1, v_2, v_3 are three Cartesian components of \mathbf{v} , what value do you expect for $\langle v_1 v_2 \rangle$, $\langle v_1 v_3 \rangle$ and $\langle v_2 v_3 \rangle$? Evaluate one of them by integration to check your deduction.

The following 2 questions look slightly harder, but are actually quite straightforward. Do them if you have time.

- 1.7 In a simple model of a metal at low temperatures (which you will cover next year), the number of electrons with energy between E and $E + dE$ is given by $A E^{1/2} dE$ for values of E less than a maximum value E_F , and zero for $E > E_F$. A is a constant.

(a) What is the speed distribution? (Treat the electrons as classical particles with speed c so that $E = \frac{1}{2} m v^2$.)

(b) Show that $\frac{\langle v^2 \rangle}{\langle v \rangle^2} = \frac{16}{15}$.

- 1.8 Black-body radiation inside a cavity at temperature T may be thought of as a gas of photons with an energy distribution given by a function $n(E)$ given by

$$n(E) dE = A \frac{E^2}{e^{E/k_B T} - 1} dE,$$

where A is independent of E and T . The function $n(E)$ describes the number of photons with energy between E and $E + dE$. There is no upper limit on E (although a sketch of $n(E)$ will convince you that $n(E) \rightarrow 0$ as $E \rightarrow 0$). Show that

- (a) the total number of photons is proportional to T^3 , and
- (b) the total energy is proportional to T^4 .

Kinetic Theory and Thermodynamics: Problems

Problem sheet 2: Effusion and mean free path
Questions to be answered for the first tutorial.

The following questions concern the effusion of molecules through small holes and the mean free path, the average distance that a molecule will travel before a collision.

- 2.1 (a) Given that the number of molecules hitting unit area of a surface per second with speeds between v and $v + dv$ and angles between θ and $\theta + d\theta$ to the normal is

$$\frac{1}{2} v n f(v) dv \sin \theta \cos \theta d\theta,$$

show that the average value of $\cos \theta$ for these molecules is $\frac{2}{3}$.

(b) Using the results above, show that for a gas obeying the Maxwellian distribution (i.e. $f(v) \sim v^2 e^{-mv^2/2k_B T}$) the average energy of all the molecules is $\frac{3}{2} k_B T$, but the average energy of those which hit the surface is $2k_B T$.

- 2.2 A Maxwellian gas effuses through a small hole to form a beam. What is the most probable speed
- (a) in the gas?
- (b) in the beam?

Show that the ratio of (b) to (a) is $\sqrt{3/2}$.

- 2.3 A vessel contains a monatomic gas at temperature T . Use Maxwell's distribution of speeds to calculate the mean kinetic energy of the molecules.

Molecules of the gas stream through a small hole into a vacuum. A box is opened for a short time and catches some of the molecules. Neglecting the thermal capacity of the box, calculate the final temperature of the gas trapped in the box.

- 2.4 A gas is a mixture of H_2 and HD in the proportion 7000:1. As the gas effuses through a small hole from a vessel at constant temperature into a vacuum the composition of the remaining mixture changes. By what factor will the pressure in the vessel have fallen when the remaining mixture consists of H_2 and HD in the proportion 700:1. (H=hydrogen, D=deuterium)

- 2.5 A closed vessel is partially filled with liquid mercury; there is a hole of area 10^{-7} m^2 above the liquid level. The vessel is placed in a region of high vacuum at 273 K and after 30 days is found to be lighter by $2.4 \times 10^{-5} \text{ kg}$. Estimate the vapour pressure of mercury at 273 K. (The relative molecular mass of mercury is 200.59.)

- 2.6 Calculate the mean speed and most probable speed for a molecule of mass m which has effused out of an enclosure at temperature T . Which is the larger?

- 2.7 (a) Show that the root mean square free path is given by $\sqrt{2}\lambda$ where λ is the mean free path.
- (b) What is the most probable free path length?
- (c) What percentage of molecules travel a distance greater (i) than λ , (ii) than 2λ , (iii) than 5λ ?
- 2.8 Given that the mean free path in a gas at standard temperature and pressure (S.T.P.) is about 10^3 atomic radii, *estimate* the highest allowable pressure in the chamber of an atomic beam apparatus 10^{-1} m long (if one does not want to lose an appreciable fraction of atoms through collisions).
- 2.9 A beam of silver atoms passing through air at a temperature of 0°C and a pressure of 1 Nm^{-2} is attenuated by a factor 2.72 in a distance of 10^{-2} m. Find the mean free path of the silver atoms and estimate the effective collision radius.

The following question uses concepts from above and requires you to think geometrically.

- 2.10 A gas effuses into a vacuum through a small hole of area A . The particles are then collimated by passing through a very small circular hole of radius a , in a screen a distance d from the first hole. Show that the rate at which particles emerge from the circular hole is $\frac{1}{4}nA\langle u\rangle(a^2/d^2)$, where n is the particle density and $\langle u\rangle$ is the average speed. (Assume no collisions take place after the gas effuses, and that $d \gg a$.)

Show that if a gas were allowed to leak into an evacuate sphere and the particles condensed where they first hit the surface they would form a uniform coating.

Useful constants which you may need

Boltzmann's constant	k_{B}	$1.3807 \times 10^{-23} \text{ J K}^{-1}$
Proton rest mass	m_{p}	$1.6726 \times 10^{-27} \text{ kg}$
Avogadro's number	N_{A}	$6.022 \times 10^{23} \text{ mol}^{-1}$
Standard molar volume		$22.414 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$
Molar gas constant	R	$8.315 \text{ J mol}^{-1} \text{ K}^{-1}$

Kinetic Theory and Thermodynamics: Problems

Problem sheet 3: Transport properties

Questions to be answered for the second tutorial.

These questions are about the transport of momentum (viscosity), heat (thermal conductivity) and particles (diffusion); these properties are intimately connected with the mean free path and the way in which molecules scatter off one another. The questions finish with a problem on the thermal diffusion equation and a brief mention of partial differentials which are used in thermodynamics.

- 3.1 Show that particles hitting a plane boundary have travelled a distance $2\lambda/3$ perpendicular to the plane since their last collision, on average.
- 3.2 Obtain an expression for the thermal conductivity of a gas at ordinary pressures. The thermal conductivity of argon (atomic weight 40) at S.T.P. is $1.6 \times 10^{-2} \text{ Wm}^{-1}\text{K}^{-1}$. Use this to calculate the mean free path in argon at S.T.P. Express the mean free path in terms of an effective atomic radius for collisions and find the value of this radius. Solid argon has a close packed cubic structure, in which, if the atoms are regarded as hard spheres, 0.74 of the volume of the structure is filled. The density of solid argon is 1.6 g cm^{-3} . Compare the effective atomic radius obtained from this information with the effective collision radius. Comment on the result.
- 3.3 Define the coefficient of viscosity. Use kinetic theory to show that the coefficient of viscosity of a gas is given, with suitable approximations, by

$$\eta = K\rho\langle v \rangle\lambda$$

where ρ is the density of the gas, λ is the mean free path of the gas molecules, $\langle v \rangle$ is their mean speed, and K is a number which depends on the approximations you make.

In 1660 Boyle set up a pendulum inside a vessel which was attached to a pump which could remove air from the vessel. He was surprised to find that there was no observable change in the rate of damping of the swings of the pendulum when the pump was set going. Explain the observation in terms of the above formula.

Make a rough order of magnitude estimate of the lower limit to the pressure which Boyle obtained; use reasonable assumptions concerning the apparatus which Boyle might have used. [The viscosity of air at atmospheric pressure and at 293 K is $18.2 \mu\text{N s m}^{-2}$.]

Explain why the damping is nearly independent of pressure despite the fact that fewer molecules collide with the pendulum as the pressure is reduced.

- 3.4 Two plane disks, each of radius 5 cm, are mounted coaxially with their adjacent surfaces 1 mm apart. They are in a chamber containing Ar gas at S.T.P. (viscosity $2.1 \times 10^{-5} \text{ N s m}^{-2}$) and are free to rotate about their common axis. One of them rotates with an angular velocity of 10 rad s^{-1} . Find the couple which must be applied to the other to keep it stationary.

3.5 Measurements of the viscosity, η , of argon gas (^{40}Ar) over a range of pressures yield the following results at two temperatures:

$$\begin{aligned} \text{at } 500 \text{ K} \quad \eta &\approx 3.5 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1} \\ \text{at } 2000 \text{ K} \quad \eta &\approx 8.0 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1} \end{aligned}$$

The viscosity is found to be approximately independent of pressure. Discuss the extent to which these data are consistent with (i) simple kinetic theory, and (ii) the diameter of the argon atom (0.34 nm) deduced from the density of solid argon at low temperatures.

3.6 Show that according to elementary kinetic theory, the thermal conductivity κ and the coefficient of self-diffusion D of a gas are related by the expression

$$\kappa = D\rho C_v$$

where C_v is the specific heat per unit mass and ρ is the density of the gas.

3.7 One face of a thick uniform layer is subject to a sinusoidal temperature variation of angular frequency ω . Show that damped sinusoidal temperature oscillations propagate into the layer and give an expression for the decay length of the oscillation amplitude.

A cellar is built underground covered by a ceiling which is 3 m thick made of limestone. The outside temperature is subject to daily fluctuations of amplitude 10°C and annual fluctuations of 20°C . Estimate the magnitude of the daily and annual temperature variations within the cellar. Assuming that January is the coldest month of the year, when will the cellar's temperature be at its lowest?

[The thermal conductivity of limestone is $1.6 \text{ Wm}^{-1} \text{ K}^{-1}$, and the heat capacity of limestone is $2.5 \times 10^6 \text{ J K}^{-1} \text{ m}^{-3}$.]

3.8 In polar coordinates, $x = r \cos \theta$ and $y = r \sin \theta$. The definition of x implies that

$$\frac{\partial x}{\partial r} = \cos \theta = \frac{x}{r}. \quad (1)$$

But we also have $x^2 + y^2 = r^2$, so differentiating with respect to r gives

$$2x \frac{\partial x}{\partial r} = 2r \quad \implies \quad \frac{\partial x}{\partial r} = \frac{r}{x}. \quad (2)$$

But equations 1 and 2 imply that $\frac{\partial x}{\partial r} = \frac{\partial r}{\partial x}$. What's gone wrong?

3.9 w is a function of three variables x , y and z . Prove that

$$(a) \quad \left(\frac{\partial w}{\partial x} \right)_{y,z} = \frac{1}{\left(\frac{\partial x}{\partial w} \right)_{y,z}} \quad (b) \quad \left(\frac{\partial w}{\partial x} \right)_{y,z} \left(\frac{\partial x}{\partial z} \right)_{w,y} \left(\frac{\partial z}{\partial w} \right)_{x,y} = -1$$

which are the reciprocal and reciprocity relations for functions of three variables.

Kinetic Theory and Thermodynamics: Problems

Problem sheet 4: Basic thermodynamics
Questions to be answered for the second class.

These questions are about use of the first law (Q1), the thermal diffusion equation (Q2), various types of expansions (Q3,4) and entropy (Q5,6).

4.1 Use the first law to show that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_V}{V\beta_p} - p$$

where β_p is the coefficient of volume expansivity and the other symbols have their usual meanings.

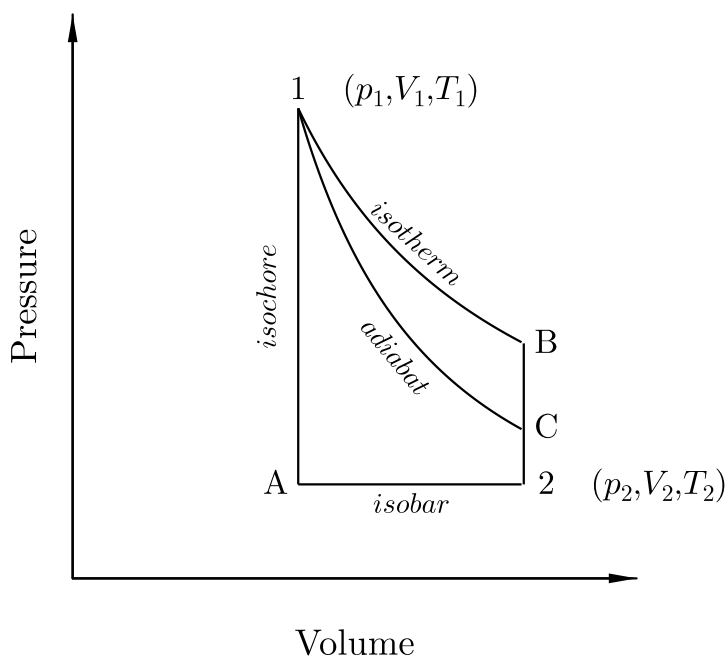
4.2 (a) A cylindrical wire of thermal conductivity κ , radius a and resistivity ρ uniformly carries a current I . The temperature of its surface is fixed at T_0 using water cooling. Show that the temperature $T(r)$ inside the wire at radius r is given by

$$T(r) = T_0 + \frac{\rho I^2}{4\pi^2 a^4 \kappa} (a^2 - r^2).$$

(b) The wire is now placed in air at temperature T_{air} and the wire loses heat from its surface according to Newton's law of cooling (so that the heat flux from the surface of the wire is given by $\alpha(T(a) - T_{\text{air}})$ where α is a constant. Find the temperature $T(r)$.

4.3 Two thermally insulated cylinders, A and B, of equal volume, both equipped with pistons, are connected by a valve. When open, the valve allows unrestricted flow. Initially A has its piston fully withdrawn and contains a perfect monatomic gas at temperature T_i , while B has its piston fully inserted, and the valve is closed. The thermal capacity of the cylinders is to be ignored. The valve is fully opened and the gas slowly drawn into B by pulling out the piston B; piston A remains stationary. Show that the final temperature of the gas is $T_f = T_i/2^{2/3}$.

- 4.4 An ideal gas is changed from an initial state (p_1, V_1, T_1) to a final state (p_2, V_2, T_2) by the following quasi-static process shown in the figure: (I) 1A2 (ii) 1B2 and (iii) 1C2. What is the increase in internal energy for $1 \rightarrow 2$? Also obtain the work that must be done on the system and the heat that must be added in each process. (Assume that the heat capacity is constant.)



- 4.5 A mug of tea has been left to cool from 90°C to 18°C . If there is 0.2 kg of tea in the mug, and the tea has specific heat capacity $4200\text{ J K}^{-1}\text{ kg}^{-1}$, show that the entropy of the tea has decreased by 185.7 J K^{-1} . Comment on the sign of this result.
- 4.6 Calculate the changes in entropy of the universe as a result of the following processes:
- A copper block of mass 400 g and thermal capacity 150 J K^{-1} at 100°C is placed in a lake at 10°C
 - The same block, now at 10°C , is dropped from a height 100 m into the lake.
 - Two similar blocks at 100°C and 10°C are joined together (hint: save time by first realising what the final temperature must be, given that all the heat lost by one block is received by the other, and then reuse previous calculations)
 - A capacitor of capacitance $1\ \mu\text{F}$ is connected to a battery of e.m.f. 100 V at 0°C . (NB think carefully about what happens when a capacitor is charged from a battery.)
 - The same capacitor, after being charged to 100 V , is discharged through a resistor at 0°C .
 - One mole of gas at 0°C is expanded reversibly and isothermally to twice its initial volume.
 - One mole of gas at 0°C is expanded reversibly and adiabatically to twice its initial volume.
 - The same expansion as in (f) is carried out by opening a valve to an evacuated container of equal volume.

Kinetic Theory and Thermodynamics: Problems

Problem sheet 5: Entropy and heat engines.
Questions to be answered for the third tutorial.

These questions give you some more practice on the concept of entropy, and also introduce efficiencies of standard engine cycles, heat-engines and the expansion of real gases.

- 5.1 A block of lead of heat capacity 1 kJ K^{-1} is cooled from 200 K to 100 K in two ways.
- It is plunged into a large liquid bath at 100 K .
 - The block is first cooled to 150 K in one liquid bath and then to 100 K in another bath.

Calculate the entropy changes in the system consisting of block plus baths in cooling from 200 K to 100 K in these two cases. Prove that in the limit of an infinite number of intermediate baths the total entropy change is zero.

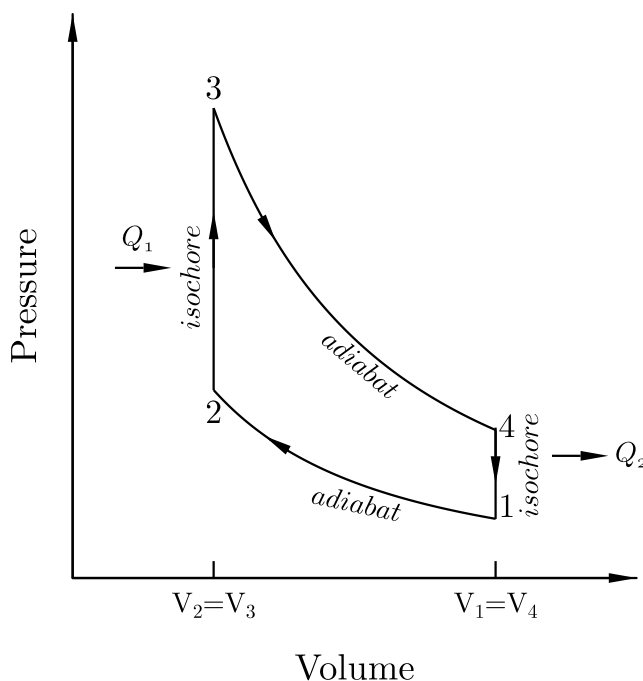
- 5.2 A possible ideal-gas cycle operates as follows.
- from an initial state (p_1, V_1) the gas is cooled at constant pressure to (p_1, V_2) .
 - the gas is heated at constant volume to (p_2, V_2) .
 - the gas expands adiabatically back to (p_1, V_1) .

Assuming constant heat capacities, show that the thermal efficiency is

$$1 - \gamma \frac{(V_1/V_2) - 1}{(p_2/p_1) - 1}$$

(You may quote the fact that in an adiabatic change of an ideal gas, pV^γ stays constant, where $\gamma = c_p/c_v$.)

- 5.3 Show that the efficiency of the standard Otto cycle (shown below) is $1 - r^{1-\gamma}$ where $r = V_1/V_2$ is the compression ratio.



- 5.4 Two identical bodies of constant heat capacity C_p at temperatures T_1 and T_2 respectively are used as reservoirs for a heat engine. If the bodies remain at constant pressure, show that the amount of work obtainable is

$$W = C_p(T_1 + T_2 - 2T_f)$$

where T_f is the final temperature attained by both bodies. Show that if the most efficient engine is used, then $T_f^2 = T_1 T_2$.

- 5.5 A building is maintained at a temperature T by means of an ideal heat pump which uses a river at temperature T_0 as a source of heat. The heat pump consumes power W , and the building loses heat to its surroundings at a rate $\alpha(T - T_0)$. Show that T is given by

$$T = T_0 + \frac{W}{2\alpha} \left(1 + \sqrt{1 + 4\alpha T_0/W} \right)$$

- 5.6 Three identical bodies of constant thermal capacity are at temperatures 300 K, 300 K and 100 K. If no work or heat is supplied from outside, what is the highest temperature to which any one of these bodies can be raised by the operation of heat engines?¹

- 5.7 [*This question is just some bookwork practice and should only take a couple of minutes.*]

- (a) Using the first law $dU = TdS - pdV$ to provide a reminder, write down the definitions of the four thermodynamic potentials U , H , F , G for a simple p - V system (in terms of U , S , T , p , V), and give dU , dH , dF , dG in terms of T , S , p , V and their derivatives.
 (b) Derive all the Maxwell relations.

- 5.8 (a) Derive the following general relations

$$\begin{aligned} \text{(a)} \quad \left(\frac{\partial T}{\partial V} \right)_U &= -\frac{1}{C_V} \left(T \left(\frac{\partial p}{\partial T} \right)_V - p \right) \\ \text{(b)} \quad \left(\frac{\partial T}{\partial V} \right)_S &= -\frac{1}{C_V} T \left(\frac{\partial p}{\partial T} \right)_V \\ \text{(c)} \quad \left(\frac{\partial T}{\partial p} \right)_H &= \frac{1}{C_p} \left(T \left(\frac{\partial V}{\partial T} \right)_p - V \right) \end{aligned}$$

In each case the quantity on the left hand side is the appropriate thing to consider for a particular type of expansion. State what type of expansion each refers to?

- (b) Using these relations, verify that for an ideal gas $\left(\frac{\partial T}{\partial V} \right)_U = 0$ and $\left(\frac{\partial T}{\partial p} \right)_H = 0$, and that $\left(\frac{\partial T}{\partial V} \right)_S$ leads to the familiar relation $pV^\gamma = \text{constant}$ along an isentrope.

- 5.9 A gas obeys the equation $p(V - b) = RT$ and has c_V independent of temperature. Show that (a) the internal energy is a function of temperature only, (b) the ratio $\gamma = c_p/c_V$ is independent of temperature and pressure, (c) the equation of an adiabatic change has the form $p(V - b)^\gamma = \text{constant}$.

¹If you set this problem up correctly you may have to solve a cubic equation. This looks hard to solve but in fact you can deduce one of the roots [hint: what is the highest temperature of the bodies if you do nothing to connect them?]

Kinetic Theory and Thermodynamics: Problems

Problem sheet 6: Further thermodynamics
Questions to be answered for the fourth tutorial.

These questions are about Joule and Joule-Kelvin expansions, thermal radiation, non p - V systems, and the Clausius Clapeyron equation.

- 6.1 In a free expansion of a perfect gas (also called Joule expansion), we know U does not change, and no work is done. However, the entropy must increase because the process is irreversible. Are these statements compatible with the 1st law $dU = TdS - pdV$?
- 6.2 In a Joule-Kelvin liquefier, gas is cooled by expansion through an insulated throttle – a simple but inefficient process with no moving parts at low temperature. Explain why enthalpy is conserved in this process. Deduce that

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right].$$

Estimate the highest starting temperature at which the process will work for helium at low densities, on the following assumptions:

- (i) the pressure is given at low densities by a virial expansion of the form

$$\frac{PV}{RT} = 1 + \left(b - \frac{a}{RT}\right) \left(\frac{1}{V}\right) + \dots$$

and

- (ii) the Boyle temperature a/bR (the temperature at which the second virial coefficient vanishes) is known from experiment to be 19 K for helium.

[Hint: One method of solving this problem is to remember that p is easily made the subject of the equation of state and one can then use $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_V / \left(\frac{\partial p}{\partial V}\right)_T$.]

- 6.3 For a gas obeying Dieterici's equation of state

$$p(V - b) = RTe^{-a/RTV}$$

for 1 mole, prove that the equation of the inversion curve is

$$p = \left(\frac{2a}{b^2} - \frac{RT}{b}\right) \exp\left(\frac{1}{2} - \frac{a}{RTb}\right)$$

and hence find the maximum inversion temperature T_{\max} .

- 6.4 Thermal radiation can be treated thermodynamically as a gas of photons with internal energy $U = u(T)V$ and pressure $p = u(T)/3$ where $u(T)$ is the energy density. Show that:
- the entropy density s is given by $s = 4p/T$;
 - the Gibbs function $G = 0$;
 - the heat capacity at constant volume $C_v = 3s$ per unit volume;
 - the heat capacity at constant pressure, C_p , is infinite. (What on earth does that mean?)
- 6.5 For a stretched rubber band, it is observed experimentally that the tension f is proportional to the temperature T if the length L is held constant. Prove that:
- the internal energy U is a function of temperature only;
 - adiabatic stretching of the band results in an increase in temperature;
 - the band will contract if warmed while kept under constant tension.
- 6.6 When lead is melted at atmospheric pressure the melting point is 327.0°C , the density decreases from 1.101×10^4 to $1.065 \times 10^4 \text{ kg m}^{-3}$ and the latent heat is 24.5 kJ kg^{-1} . Estimate the melting point of lead at a pressure of 100 atm?

Useful constants

Boltzmann's constant	k_B	$1.3807 \times 10^{-23} \text{ J K}^{-1}$
Proton rest mass	m_p	$1.6726 \times 10^{-27} \text{ kg}$
Avogadro's number	N_A	$6.022 \times 10^{23} \text{ mol}^{-1}$
Standard molar volume		$22.414 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$
Molar gas constant	R	$8.315 \text{ J mol}^{-1} \text{ K}^{-1}$

Other data and conversion factors

1 pascal (Pa)	1 N m^{-2}
1 standard atmosphere	$1.0132 \times 10^5 \text{ Pa (N m}^{-2}\text{)}$

Kinetic Theory and Thermodynamics: Problems

Problem sheet 7: Vacation problems
Questions to be answered during the vacation.

The first question revises some concepts concerning the thermal diffusion equation. The second and third concern inversion curves. The final questions are about the Clausius-Clapeyron equation and phase changes.

- 7.1 A microprocessor has an array of metal fins attached to it, whose purpose is to remove heat generated within the processor. Each fin may be represented by a long thin cylindrical copper rod with one end attached to the processor; heat received by the rod through this end is lost to the surroundings through its sides.

Show that the temperature $T(x, t)$ at location x along the rod at time t obeys the equation

$$\rho C_p \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} - \frac{2}{a} R(T),$$

where a is the radius of the rod, and $R(T)$ is the rate of heat loss per unit area of surface at temperature T .

The surroundings of the rod are at temperature T_0 . Assume that $R(T)$ has the form (Newton's law of cooling)

$$R(T) = A(T - T_0).$$

In the steady state:

- (a) obtain an expression for T as a function of x for the case of an infinitely long rod whose hot end has temperature T_m ;
- (b) show that the heat that can be transported away by a long rod of radius a is proportional to $a^{3/2}$, provided that A is independent of a .

In practice the rod is not infinitely long. What length does it need to have for the results above to be approximately valid? The radius of the rod is 1.5 mm.

[The thermal conductivity of copper is $380 \text{ W m}^{-1} \text{ K}^{-1}$. The cooling constant $A = 250 \text{ W m}^{-2} \text{ K}^{-1}$.]

- 7.2 Show that Dieterici's equation of state,

$$p(V - b) = RTe^{-a/RTV},$$

can be written in reduced units as

$$\tilde{P}(2\tilde{V} - 1) = \tilde{T} \exp \left[2 \left(1 - \frac{1}{\tilde{T}\tilde{V}} \right) \right],$$

where $\tilde{P} = P/P_c$, $\tilde{T} = T/T_c$, $\tilde{V} = V/V_c$, and (P_c, T_c, V_c) is the critical point. Show further that the equation for the inversion curve is

$$\tilde{P} = (8 - \tilde{T}) \exp \left[\frac{5}{2} - \frac{4}{\tilde{T}} \right]$$

and sketch it in the \tilde{T} - \tilde{P} plane.

7.3 Why is enthalpy conserved in steady flow processes? A helium liquefier in its final stage of liquefaction takes in compressed helium gas at 14 K, liquefies a fraction α , and rejects the rest at 14 K and atmospheric pressure. Use the value below to determine the input pressure which allows α to take its maximum value, and determine what this value is.

Enthalpy of liquid helium at atmospheric pressure = 10.1 kJ kg⁻¹.

Pressure (atm)	0	10	20	30	40
Enthalpy of He gas at 14 K (kJ kg ⁻¹)	87.4	78.5	73.1	71.8	72.6

7.4 Some tea connoisseurs claim that a good cup of tea cannot be brewed with water at a temperature less than 97°C. Assuming this to be the case, is it possible for an astronomer, working on the summit of Mauna Kea in Hawaii (elevation 4194 m) where the air pressure is 615 mbar, to make a good cup of tea without the aid of a pressure vessel?

7.5 (a) Show that the temperature dependence of the latent heat of vapourization L is given by the following expression:

$$\frac{d}{dT} \left(\frac{L}{T} \right) = \frac{C_{pv} - C_{pl}}{T} + \left[\left(\frac{\partial S_v}{\partial p} \right)_T - \left(\frac{\partial S_l}{\partial p} \right)_T \right] \frac{dp}{dT}.$$

In this equation, S_v and S_l are the entropies of the vapour and liquid and C_{pv} and C_{pl} are the heat capacities of the vapour and liquid. Hence show that $L = L_0 + L_1 T$ where L_0 and L_1 are constants.

(b) Show further that when the saturated vapour of an incompressible liquid is expanded adiabatically, some liquid condenses out if

$$C_{pl} + T \frac{d}{dT} \left(\frac{L}{T} \right) < 0$$

where C_{pl} is the heat capacity of the liquid (which is assumed constant) and L is the latent heat of vapourization.

(Hint: consider the gradient of the phase boundary in the p - T plane and the corresponding curve for adiabatic expansion.)

Useful constants

Boltzmann's constant	k_B	$1.3807 \times 10^{-23} \text{ J K}^{-1}$
Proton rest mass	m_p	$1.6726 \times 10^{-27} \text{ kg}$
Avogadro's number	N_A	$6.022 \times 10^{23} \text{ mol}^{-1}$
Standard molar volume		$22.414 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$
Molar gas constant	R	$8.315 \text{ J mol}^{-1} \text{ K}^{-1}$

Other data and conversion factors

1 pascal (Pa)	1 N m^{-2}
1 standard atmosphere	$1.0132 \times 10^5 \text{ N m}^{-2}$
1 bar (= 1000 mbar)	10^5 N m^{-2}