Thermodynamics: Example Sheet 2

1

(a) By considering some small numbers N and m, verify that the number of ways (degeneracy Ω) of sharing m quanta, each of energy ϵ, amongst N oscillators is:

$$g(N, m) = (N + m - 1)!/[(N - 1)!m!].$$

(b) Enumerate the degeneracy of a system of 4 oscillators and a system of 2 oscillators for up to 5 quanta each. *For this and the following section it may be worth writing a short MATLAB script!*

(c) Consider 3 systems, A, B and C in thermal contact *i.e.* able to exchange energy with one another. The sytems A and B each consist of 4 oscillators and system C consists of 2 oscillators. What are the most likely ways in which 5 quanta will be shared when the three systems are in equilibrium? Comment on your answer.

(d) Two systems containing large numbers (N_1 and N_2) of weakly interacting oscillators are in thermal contact. If the total energy available to be shared amongst the $N_1 + N_2$ oscillators is fixed at $m\epsilon$, obtain an expressions for $\Omega(m_1)$, the number of ways in which system 1 has energy $m_1\epsilon$ and system 2 has energy $m_2\epsilon$ where $m_1 + m_2 = m$.

By evaluating the first and second derivatives of Ω w.r.t. m_1, show that the most probably value of m_1 satisfies the relation $m_1/N_1{=}m_2/N_2$ and that the sharing of energy between the two systems will be very sharply peaked at this value.

2 *Counting configurations.* A box with adiabatic walls contains a partition that divides its volume in the ratio 3:1. Initially the smaller region contains N molecules of an ideal gas at low density, and the larger is empty. A small hole is then made in the partition, so that the two regions come into equilibrium. Determine the number of configurations for the system as a function of n, the number of molecules in the smaller region, and hence find the most likely value for n. Compare the probability for this arrangement with that for a recurrence of the original configuration for the case $N = 100$. Consider small fluctuations δn about the most probable configuration. Using a Taylor expansion, or otherwise, find the distribution of δn and show that its standard deviation is $\sqrt{3N}/4$. Hence, for one mole of gas, compute the fractional fluctuation in n.

3 *The two state system.* Consider a system with two energy levels, 0 and $\epsilon > 0$. Write down the probabilities for each energy level (see lecture notes). Then derive an expression for the average energy $\langle E\rangle$ and the variance of the energy.

4 *A system of N states.* Consider a system containing N two-level systems that can have an energy 0 or Δ. Show that the number of ways $\Omega(E)$ of arranging the total system to have energy $E = r\Delta$ (where r is an integer) is given by

$$\Omega(E) = \frac{N!}{r!(N-r)!}.$$

Subsequently, remove a small amount of energy $s\Delta$ from the system (assuming $s << r$). Show that

$$\Omega(E-\epsilon) \approx \Omega(E)\frac{r^s}{(N-r)^s}.$$

Finally, show that the temperature T of the system is given by

$$\frac{1}{k_B T} = \frac{1}{\Delta}\ln\left(\frac{N-r}{r}\right).$$

Sketch $k_B T$ as a function of r from $r = 0$ to $r = N$, and explain the result.

5 In thermal equilibrium at temperature T, a crystal with N atoms can have a certain number n of lattice sites vacant, giving a structure with $N + n$ sites in total. Obtain an expression for the number of ways, Ω, in which this situation can arise by considering the different arrangements of the n vacant sites chosen from $N + n$ possibilities.

Assuming that $S = kln\Omega$ and that the internal energy $U = n\epsilon$, find an expression for the vacancy concentration n/N by minimising the Helmholtz free energy $F = U - TS$. Estimate the vacancy concentration in copper at 1300K if $\epsilon = 1\,\text{eV}$. (*In this estimation we are assuming that the volume does not change, and provided the pressure is small (atmospheric) this is not a major approximation.*) Why has it been suggested that you use the Boltmann rather than the Gibbs expression for entropy when formally the latter is set up specifically for this 'canonical' case?

6 *Average energy of an n-state system and a harmonic oscillator.* Given that the temperature of the system is T, find the partition function and hence the average energy $\langle E\rangle$ for:

(a) An n-state system, in which a given state can have energy 0, ϵ, 2ϵ, ..., $n\epsilon$.

(b) A harmonic oscillator, in which a given state can have energy 0,ϵ, 2ϵ, ..., $n\epsilon$,... (i.e. with no upper limit).

7 *A question about radiation.* By treating radiation in a cavity as a gas of photons whose energy E and momentum p are related by $E = pc$ where c is the speed of light, show that the pressure exerted on the walls of the cavity is one-third of the energy density, *i.e.* $p = \frac{1}{3}u(T)$.

(a) Show that when radiation contained in a vessel wth perfectly reflecting walls is compressed adiabatically it obeys the equation of state $pV^{\frac{4}{3}} = \text{constant}$.

(b) Show that the entropy density $s = \frac{S}{V}$ is given by $s = \frac{4p}{T}$. *Note that s cannot depend on V.*

(c) Show that $p \propto T^4$ and hence that $u(T) \propto T^4$

(d) Show that the Gibbs free energy G is zero.

(e) Show that the heat capacity per unit volume, at constant volume, is given by $C_V = 3s$.

(f) Show that the heat capacity at constant pressure is infinite.

8 *A question about the kinetic theory of gases.* In the lectures, we worked out the properties of a gas by considering the three-dimensional distribution of velocities. This example changes the problem from three to two dimensions. Particles are sometimes bound to a flat solid surface at low density, but free to move parallel to the surface. What is the analogue of the pressure for such a 2D gas? Develop a 2D kinetic theory for such a gas, and in particular find 2D analogues of the 3D equations for $\phi = \frac{1}{4}n\langle v\rangle$, $p = \frac{1}{3}nm\langle v^2\rangle$, $\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_BT$, and $pV = RT$.

9 *A question about molecular speeds in a gas.* Here is an example of the type of question that might appear in an examination paper. Use it as an example to be tried without your notes.

(a) The distribution of molecular speeds v in an ideal gas in thermal equilibrium has the form

$$f(v)\mathrm{d}v = Av^2\mathrm{e}^{-mv^2/2k_BT}\mathrm{d}v$$

where A is a constant, m is the mass of a molecule, k_B is Boltzmann s constant, and T is the temperature. Explain what is meant by $f(v)$, and how the factors v^2 and $\exp(-mv^2/2k_BT)$ arise. Explain how the constant A is determined and find its value.

(b) Show that the average kinetic energy (averaged over all molecules in the body of the gas) is $\frac{3}{2}k_BT$, exactly as predicted by the equipartition theorem.

(c) Show that the mean speed is given by

$$\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}}.$$

(d) Consider now the kinetic energy averaged over all the molecules hitting the sides of the container. Would you expect this to be less than, equal to, or greater than $\frac{3}{2}k_BT$? Argue your case clearly in a few lines.

10 *Chemical reactions and the Boltzmann equation.* A chemical reaction is observed to proceed at different rates depending on the temperature as shown in the following table:

T (° C)	0	6	12	18	24	30
Rate (arbitrary units)	5.5	10.9	23.5	48.0	98.0	206.0

The probability that a particular reaction occurs is proportional to $\exp(-E_{act}/k_BT)$, where E_{act} is the activation energy.

(a) Explain in a few lines why the rate of reaction depends upon the temperature. Explain what is meant by the activation energy.

(b) Write down an expression showing the form of the dependence of the rate on temperature. Hence, by re-expressing the figures in the table, fit a straight line to the points. By drawing a graph, or by using your calculator, find the best-fitting slope.

(c) Hence, find the characteristic energy for this reaction that is the activation energy of the reaction.

11 *The flux density expression* $\phi = \frac{1}{4}n\langle v\rangle$. A vessel partly filled with mercury is closed except for a hole of area 0.1 mm^2 above the liquid level and is kept at 0°C. The vessel is contained within a very much larger vessel in which a very high vacuum is maintained. After 30 days, it is found that 24 mg of mercury have been lost from the inner vessel. The relative atomic mass of mercury is 201.

(a) Draw a diagram, and explain why mercury is lost.

(b) What is the average speed $\langle v\rangle$ of the mercury atoms in the vapour above the liquid? You will need to use the relationship

$$\langle v\rangle^2 = \frac{8}{3\pi}\langle v^2\rangle.$$

(c) What is the mean rate of flow of mercury atoms through the hole?

(d) Calculate the vapour pressure of mercury at 0°C.

12 *Thermal conductivity of a gas.* The thermal conductivity of argon (atomic weight 40) at standard atmospheric pressure p_0 is 1.6×10^{-2} W $\mathrm{m}^{-1}\mathrm{K}^{-1}$.

(a) Calculate the mean free path of the argon atoms at p_0.

(b) Express the mean free path in terms of an effective atomic radius for collisions and find a value for this radius.

(c) Solid argon has a close-packed cubic structure with density $\rho = 1.6\times10^3$ kg m^{-3}. Assuming that the argon atoms behave like hard spheres, 74% of the total volume will be occupied by them. Compare the effective atomic radius obtained from this information with your effective collision radius. Comment on your result.

13 *Scaling relations for transport properties of gasses* Why are 'halogen' light bulbs filled with Xenon gas at high pressure.

14 *Heat loss under steady state condition.* The surface of a spherical chicken of radius a is maintained at temperature T_0 by its internal metabolism. It sits in a medium of thermal conductivity κ, which is at a lower temperature T_1 (measured a large distance away from the chicken). Assuming steady-state conditions, find the rate at which the animal loses heat.

15 *Sinusoidal temperature variations.* One face of a thick uniform layer is subject to sinusoidal temperature variations of angular frequency ω.

(a) Show that damped sinusoidal temperature oscillations propagate into the layer, and give an expression for the decay length of the oscillation amplitude.

(b) A cellar is built underground and is covered by a ceiling, which is 3 m thick and 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.

(c) 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 W $\mathrm{m}^{-1}\mathrm{K}^{-1}$, and the heat capacity of limestone is 2.5×10^6 J $\mathrm{K}^{-1}\mathrm{m}^{-3}$.]