Michaelmas 2010 **Thermal and Statistical Physics** (Part II)

Examples Sheet 1

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1. Show that, for a van der Waals gas, the specific heat at constant volume, C_V, obeys

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0.$$

2. The Gibbs free energy of an imperfect gas containing N molecules is given, in terms of its natural variables T, p and N, by

$$G = Nk_BT\ln\left(\frac{p}{p_0}\right) - NA(T)\,p,$$

where p_0 is a constant and A is a function of T only. Derive expressions in terms of T, p, V, and N for:
(a) the equation of state of the gas;
(b) the entropy, S;
(c) the enthalpy, H;
(d) the internal energy, U;
(e) the Helmholtz free energy, F.
Can all equilibrium thermodynamic information about the gas be obtained from a knowledge of: (i) $F(T,V,N)$; (ii) the equation of state and $U(T,p,N)$?

3. The entropy of a monatomic ideal gas is given by the Sackur-Tetrode equation which can be written in the form:

$$S(U,V,N) = Nk_B\ln\left\{\alpha\frac{V}{N}\left(\frac{U}{N}\right)^{3/2}\right\},$$

where α is a constant to be derived later in the course.

Invert this expression to get $U(S,V,N)$. From this, obtain the equation of state expressing p as a function of V, N and T.

4. Use a Maxwell relation and the chain rule to show that for any substance the rate of change of T with p in a reversible adiabatic compression is given by

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{T}{C_p}\right)\left(\frac{\partial V}{\partial T}\right)_p.$$

Find an equivalent expression for the adiabatic rate of change of T with V, and check that both results are valid for an ideal monatomic gas.

5. Write brief notes on thermodynamic equilibrium in closed and open systems.

6. Under what conditions is the Helmholtz free energy F a minimum for a system in equilibrium? The work corresponding to an increase in the surface area of a liquid is

$$dW = \Gamma \, dA$$

where Γ is the surface tension, and A is the area of the surface.

Consider a bubble of air in a large container of liquid in equilibrium. Write the total Helmholtz free energy of the system as the sum of contributions from the air in the bubble, F_a, the surface of the bubble, F_s, and the surrounding liquid, F_l. Show that the pressure of the air inside the bubble is equal to $p_l + 2\Gamma/r$, where p_l is the pressure of the liquid.

7. What is the minimum work required to extract 1 mole of pure O_2 from a large volume of air at the same temperature and pressure, if air is regarded as being composed of 1 volume of O_2 mixed with 4 volumes of N_2. [Ans. 13.4 J $K^{-1} \times T$, where T is the temperature in Kelvin.]

8. The heat capacities of the superconducting and normal phases of a metal at low temperatures are given approximately by

$$\begin{aligned} C_s(T) &= V\alpha T^3 && \text{superconducting phase} \\ C_n(T) &= V\beta T^3 + V\gamma T && \text{normal phase,} \end{aligned}$$

where V is the volume and α, β, and γ are constants. At low temperatures the superconducting phase is stable while above a temperature T_c the normal phase is stable.

Experiments indicate that the latent heat for the transition is zero. Find an expression for T_c.

9. The partition function of a system is

$$Z = \exp\left[aT^3 V\right],$$

where a is a positive constant. Obtain expressions for the Helmholtz free energy, the equation of state, the internal energy, the heat capacity at constant volume, and the chemical potential.

Write the pressure as a function of the internal energy per unit volume. Can you identify the physical system that corresponds to such a partition function?

10. A crystalline solid contains N identical atoms on N lattice sites, and N interstitial sites to which atoms may be transferred at the energy cost ε_c. If n atoms are on interstitial sites, show that the configurational entropy is $2k_B \ln(N!/n!\,(N-n)!)$.

Assuming n/N is small, and that vacancies are very rare, show by minimising the total free energy that the equilibrium proportion of atoms on interstitial sites n/N is

$$\left\langle \frac{n}{N} \right\rangle = \frac{1}{1+\exp(\varepsilon_c/2k_BT)}.$$

11. A zipper has N links; each link has a state in which it is closed with energy 0 and open with energy ϵ. We require, however, that the zipper can only unzip from the left end, and that the link number s can only open if all links to the left $(1, 2, \ldots, s-1)$ are already open.
(a) Show that the partition function is

$$Z = \frac{1-\exp\left(-(N+1)\epsilon/k_BT\right)}{1-\exp\left(-\epsilon/k_BT\right)}.$$

(b) Find the average number of open links in the low-temperature limit. The model is a very simplified model of the unwinding of two-stranded DNA molecules.

Examples Sheet 2

1. Calculate the classical partition functions, and discuss the high- and low-temperature limits of:
(a) a one-dimensional simple harmonic oscillator, for which

$$E(p,x) = \frac{p^2}{2m} + \frac{1}{2}kx^2 \ ;$$

(b) a particle moving in three dimensions in a uniform gravitational field, for which

$$E(p,z) = \frac{p^2}{2m} + mgz \ .$$

2. Consider an ideal classical gas of volume V and temperature T, consisting of N indistinguishable particles in the extreme relativistic limit where the energy ϵ and momentum p of a particle are related by $\epsilon = cp$, where c is the speed of light.
(a) Calculate the partition function of the system Z, the equation of state, the entropy S, internal energy U, and the heat capacity C_V.
(b) Suppose that, in addition to its translational motion, each of the particles can exist in one of two states of energy Δ and $-\Delta$. Calculate Z, the equation of state, S, U, and C_V.

3. Helium atoms of mass m may be adsorbed from the vapour phase at pressure p onto a solid surface where they can move freely without interaction, behaving as a two-dimensional perfect gas. If the adsorption energy is Δ, then by treating the vapour as a particle reservoir for the helium atoms on the solid surface, and treating both sets of atoms as ideal classical gases, show that the number density per unit area of helium atoms on the surface is

$$n_{\rm ads} = \left(\frac{p}{k_BT}\right)\left(\frac{2\pi\hbar^2}{mk_BT}\right)^{1/2} \exp\left(\frac{\Delta}{k_BT}\right) .$$

4. A point defect in a solid may be occupied by 0, 1 (spin up or down) or 2 electrons, and the solid provides a reservoir of electrons at chemical potential μ. The energy for occupation by a single electron is ϵ, and that for 2 electrons is $2\epsilon + U$, where U is the Coulomb repulsion energy between

the electrons. Obtain an expression for the average electron occupancy of the defect.

5. Show that the equilibrium constant K_N for the ionisation reaction He $\rightleftharpoons$ $\mathrm{He}^+ + \mathrm{e}^-$ is to a good approximation

$$K_N = \frac{1}{4V}\left(\frac{2\pi\hbar^2}{m_e k_B T}\right)^{3/2} \mathrm{e}^{e\phi/k_B T}$$

where ϕ is the first ionisation potential of He, which is 24.6 V.

Find the proportion of He that is ionised at 10^4 K (i) at atmospheric pressure, and (ii) at 10^{-2} Nm^{-2}. What is the cause of the change in the equilibrium constant? This effect is important for spectral lines from interstellar gases, one finds a surprisingly large intensity corresponding to spectral lines of ionised atoms.

6. A system contains 2 particles, each of which can occupy either a level of energy 0, or one of energy ϵ. Calculate the partition function of the system if the particles obey:
(a) Fermi-Dirac statistics;
(b) Bose-Einstein statistics;
(c) Classical statistics and are indistinguishable;
(d) Classical statistics and are distinguishable.

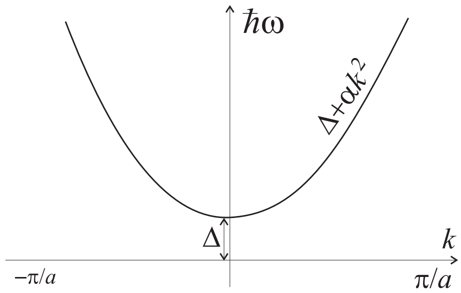
In the high-temperature limit the partition functions for cases (a), (b), and (c) tend to different values. Why is this?

7. The temperature at the centre of the sun is $T = 1.6 \times 10^7$ K, and plasma at the centre of the sun consists of hydrogen at a density of $\rho_{\mathrm{H}} = 6 \times 10^4$ kg m^{-3} and helium at a density of $\rho_{\mathrm{He}} = 1 \times 10^5$ kg m^{-3}.
(a) Calculate the thermal wavelengths of the electrons, protons and He nuclei.
(b) Determine whether the electrons, protons and He nuclei are degenerate or non-degenerate under these conditions.
(c) Estimate the pressure at the centre of the sun due to these particles and that due to the radiation pressure.
(d) Is it the pressure due to the particles or the radiation which prevents gravitational collapse of the sun?

8. At temperatures below 0.4 K, a dilute solution of ^{3}He in liquid ^{4}He behaves like a gas of ^{3}He atoms moving freely *in vacuo* except that the effective mass of each ^{3}He atom is enhanced by a factor of about 2.4. The concentration of ^{3}He is 5 atomic percent and the density of the solution is 140 kg/m^3. Sketch the temperature dependence of the heat capacity per

^{3}He atom at low temperatures. Calculate the Fermi temperature, T_F, and the coefficient γ of the specific heat at low temperatures, $c_V = \gamma T$.
[Answer: $T_F = \varepsilon_F / k_B = 0.33$ K, $\gamma = 2.0 \times 10^{-22}$ J atom^{-1}K^{-2}.]

9. Spin waves in many ferromagnets show a gap at low energy, due to coupling of the orbital moments to the crystalline lattice. The resulting dispersion relation curves are typically as shown below.



By first carrying out an approximate calculation sufficient to show the qualitative temperature dependence of the internal energy U (or otherwise), sketch the expected temperature dependence of the specific heat at low temperatures, assuming that the dispersion relation is isotropic.

10. A long air-filled coaxial transmission line, of length L and small diameter, is short circuited at each end. Show that, at room temperature and at a cyclic frequency $\nu = 10^9$Hz ($\nu = \omega/2\pi$), the mean energy of black body radiation between the conductors in a small frequency range $d\omega$ will be approximately

$$k_B T \frac{L}{\pi c} d\omega \; .$$

If the outer diameter is 1cm and the inner diameter 2mm, explain why it would be reasonable at 10^{12}Hz to replace this expression by one proportional to

$$k_B T \frac{V}{(2\pi c)^3} \omega^2 d\omega$$

where V is the volume between the conductors.

11. Write brief notes describing the chemical potential and examples of its use in thermodynamics and statistical mechanics. In your essay, include a sketch of μ as a function of the number of particles per unit volume in both the classical and quantum regimes.

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Examples Sheet 3

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1. The partition function of a system is

$$Z = \frac{A^N}{N!}\, T^{3N/2}\, V^N \exp\left[\frac{-B(T)N^2}{V}\right],$$

where A is a positive constant and $B(T)$ is a function of temperature. Obtain expressions for the Helmholtz free energy, the equation of state, the internal energy, the heat capacity at constant volume, and the chemical potential.

What physical system corresponds to such a partition function?

2. An inter-molecular potential takes the form

$$\begin{aligned} \phi(r) &= \infty \qquad r < a \\ &\quad -\epsilon \qquad a < r < 2a \\ &\quad 0 \qquad r > 2a. \end{aligned}$$

Within the virial expansion the radial distribution function is expanded in powers of the density.
(a) Sketch the form of the density-independent part of the radial distribution function versus r for $k_BT \gg \epsilon$ and $k_BT \ll \epsilon$.
(b) Evaluate the 2nd virial coefficient, $B_2(T)$, and the Boyle temperature of the gas.
(c) Identify a set of reduced units, v_0^* and T^*, for which $B_2(T^*)/v_0^*$ is independent of a and ϵ. Sketch $B_2(T^*)/v_0^*$ versus T^*.

3. The order parameter for a fluid of rod shaped molecules is their degree of alignment, Q, with $Q = 0$ corresponding to a disordered fluid, and $Q \neq 0$ corresponding to a nematic liquid crystal. The free energy can be written as

$$F(Q,T) \;=\; a(T - T_c)Q^2 - bQ^3 + cQ^4,$$

where a, b, c and T_c are positive constants. This system shows a first order phase transition, at a temperature T^*, between two states with $Q = 0$ and $Q = Q^*$.
(a) Calculate Q^* and T^*, using the conditions that the free energies of the two states are equal at the transition and that the free energies are stationary

in equilibrium.
(b) Calculate the latent heat of the transition.

4. (i) Suppose the free energy of a system can be written as

$$F = \alpha(T - T_c)P^2 + bP^4 + cP^6,$$

where $c > 0$. Show that the system can undergo a first order phase transition at temperature $T = T_c + b^2/4ac$ if $b < 0$.
(ii) The free energy of a ferroelectric crystal can be written as

$$F = \alpha(T - T_c)P^2 + bP^4 + cP^6 + D\varepsilon P^2 + E\varepsilon^2,$$

where P is the polarisation of the crystal and ε is the elastic strain. Show that the crystal will undergo a first order phase transition when $D^2/4E > b$.

5. Show that the fluctuations in particle number, N, at constant temperature, T, and volume, V, are given by

$$\langle \Delta N^2 \rangle = k_B T \left(\frac{\partial N}{\partial \mu} \right)_{T,V} .$$

6. For a system of N free electrons the statistical weight, $\Omega(U)$, is proportional to $\exp[(NU/\epsilon_0)^{1/2}]$, where ϵ_0 is about 10^{-19} J. Calculate the heat capacity, C, of the system at room temperature. Show that the probability distribution of the energy of the system is approximately Gaussian and find the root mean square fractional energy fluctuation, $\sqrt{\langle \Delta U^2 \rangle / \langle U^2 \rangle}$, for a system with $N = 10^{23}$ at room temperature.
[Answer: $C = 2.8 \times 10^{-25}$ J K^{-1} per electron; $\sqrt{\langle \Delta U^2 \rangle / \langle U^2 \rangle} = 4.5 \times 10^{-11}$.]

7. Find the mean square fluctuation of magnetisation, $\langle \Delta M^2 \rangle$, as a function of temperature on both sides of the critical point T_c of the ferromagnetic phase transition, which can be described by the Landau free energy expansion

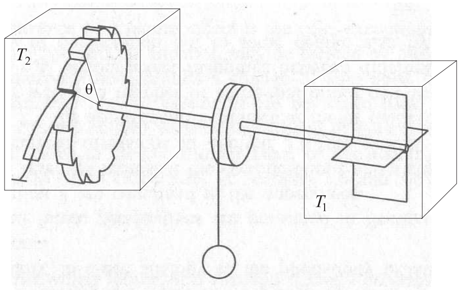
$$F = a(T - T_c)M^2 + bM^4 .$$

8. Derive the Stokes-Einstein relationship for the diffusion constant of particles of radius R in a fluid of viscosity η

$$D = \frac{k_B T}{6\pi\eta R} .$$

In 1928 Pospisil observed the Brownian motion of soot particles of radius 0.4×10^{-7} m immersed in a water-glycerine solution of viscosity 2.78×10^{-3} kg m^{-1} s^{-1}, at a temperature of 292 K. The observed value of $\langle x^2\rangle$ was 3.3×10^{-12} m^2 in a 10-second interval. Use these data to determine a value of the Boltzmann constant, k_B, and compare it with the modern value.

9. The famous ratchet and pawl machine, originally suggested by Smoluchowski in 1912 to be able to extract useful work from a thermal reservoir (against the Laws of Thermodynamics) is shown below. The pawl preventing the backward rotation of the wheel allows the energy transferred to the flaps from the thermal motion of surrounding gas to be *rectified*, i.e. only channelled in one direction.



If the energy required to lift the pawl and make one step of forward motion is ε and the work against the external torque L (e.g. from the lifted mass in the sketch) is $L\theta$, with θ the angle of single-step turn, show that the system is reversible if

$$\frac{\varepsilon + L\theta}{T_1} = \frac{\varepsilon}{T_2}$$

where T_1 and T_2 are the temperatures of the gas and the vanes, and of the ratchet wheel, respectively. As a result, prove that the Carnot condition for a reversible cycle holds, $Q_1/Q_2 = T_1/T_2$, where Q_1 is the energy taken from the vanes and Q_2 the energy delivered to the wheel.

[see Feynman Lectures on Physics, chapter 46-2, for detail]

10. Consider free Brownian particles diffusing along the axis $x \geq 0$, so that there is a reflecting wall at $x = 0$. Also there is a "sink" at $x = L$ where the particles can escape from the system, so that the probability at that point is $P(L, t) = 0$ at any time.

If the diffusion constant is D, estimate how long on average would it take for all the particles to escape from the system?