School of Physics & Astronomy

THE UNIVERSITY *of* EDINBURGH

Thermal Physics

PHYS09061 (SCQF Level 9)

Monday 13th May, 2019 14:30 - 17:30
(May Diet)

Please read full instructions before commencing writing.

Examination Paper Information

Answer **ALL** questions from Section A,
ONE question from Section B and **ONE** question from Section C.

Special Instructions

- Only authorised Electronic Calculators may be used during this examination.
- A sheet of physical constants is supplied for use in this examination.
- Attach supplied anonymous bar codes to *each* script book used.

Special Items

- School supplied Constant Sheets
- School supplied barcodes

Chairman of Examiners: Prof A Trew
External Examiner: Prof S J Clark

Anonymity of the candidate will be maintained during the marking of this examination.

Section A: Answer ALL the questions in this Section

A.1 Write down the central equation of Thermodynamics in differential form. Use the definition of Enthalpy to derive the expression for dH and the associated Maxwell relation. **[5]**

A.2 The Clausius inequality can be written:

$$\oint \frac{dQ}{T} \leq 0$$

Explain carefully with respect to system and surroundings the thermodynamic meanings of $\oint$, dQ, and T. State which thermodynamic variable the integrand represents, and the conditions under which the equality applies. **[5]**

A.3 According to the Schottky equation, the heat capacity is given by $c_v = b/(T - T_c)^2$ with constant b. Describe the physical process occurring at T_c to which the equation may apply, and whether this formula is consistent with the Third Law. **[5]**

A.4 A particle's position is specified by a random variable x that lies in the range $0 \leq x < \infty$. The probability that it is found in the range $[x, x + \mathrm{d}x]$ is given by $p(x)\mathrm{d}x$ where $p(x) = \lambda \mathrm{e}^{-\lambda x}$ and $\lambda > 0$ is a constant.

(a) Show that the distribution $p(x)$ is correctly normalised. **[2]**

(b) Determine the mean position of the particle. **[3]**

A.5 A model magnet comprises $N = 3$ weakly-interacting dipoles. Each has a dipole moment m, and may be aligned or anti-aligned with an external field with magnitude H. The energy of a dipole that is aligned with the field is $-mH$ and that of a dipole that is anti-aligned with the field is $+mH$.

(a) Specify the distinct energy macrostates that this system has. **[2]**

(b) Specify the weight of each of the energy macrostates. **[3]**

A.6 This question concerns a system of interest in the grand canonical ensemble where the temperature is T and the chemical potential is μ.

(a) Draw a diagram that illustrates the physical setup of the grand canonical ensemble, noting which quantities can fluctuate in the system of interest. **[3]**

(b) Under the assumption that the system of interest comprises weakly-interacting bosons, state the mean number of particles that occupy a non-degenerate quantum state with energy ϵ. **[2]**

Section B: Answer ONE of the questions in this Section

B.1 This question concerns the use of different working substances in an engine

(a) Carbon monoxide (CO) and ethene (C_2H_4) are gases with the same molecular mass: how do you expect their heat capacities to compare, and why? **[3]**

A reversible heat engine involves one mole of diatomic ideal gas cycling around four states labelled a,b,c & d where a is the state of highest pressure. The cycle comprises two isotherms (a-b, c-d) and two isochores (b-c, d-a). [Note: 'isochore' means constant volume.]

(b) Sketch the cycle on a PV indicator diagram, showing the direction around the cycle required to generate work. **[5]**

(c) Calculate the heat and work inputs and outputs in each part of the cycle, in terms of temperatures T_a, T_c and volumes V_a, V_c. **[5]**

(d) Identify the waste heat, and write an expression for the efficiency of the engine. **[4]**

(e) Use your expression for efficiency to predict whether using a triatomic ideal gas as the working fluid would improve the efficiency. **[3]**

(f) By comparing the ideal efficiency of this engine with the efficiency of a Carnot engine running between heat reservoirs at T_a and T_c, show that a working fluid with a negative heat capacity would violate the Second Law. **[5]**

B.2 This question concerns the relationship between free energy and measurable quantities.

(a) Write down the general definition of the specific molar Helmholtz free energy. **[2]**

The specific molar Helmholtz Free Energy of a particular fluid is given by

$$f(T,v) = cRT\,(1 - \ln(RT)) - RT\ln(v-b) - \frac{a}{v} + Td$$

(b) Identify the dimensions of the constants a, b, c and d. **[2]**

(c) Write down expressions for the pressure and entropy in terms of $f(T,v)$, and evaluate them for the fluid above. **[6]**

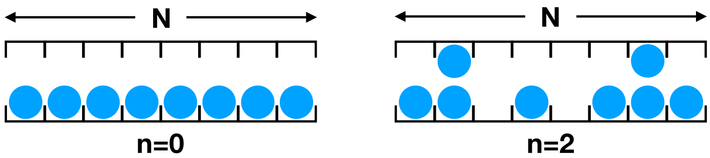
(d) Define the heat capacity at constant volume (c_v) and the isothermal bulk modulus (K_T) in terms of partial derivatives of f, and evaluate them for the fluid above. **[6]**

(e) Sketch the value of K_T as a function of v. Hint: identify the zeroes and the limits at large and small v. **[4]**

(f) You should find that there are densities for which $K_T(v)$ is negative. Explain what this would imply for the behaviour of a real system described by this free energy. **[5]**

Section C: Answer ONE of the questions in this Section

C.1 This question concerns a system with two parallel surfaces, each comprising a lattice of N sites. Each of these sites may be vacant or accommodate a single atom. The ground state is one in which all sites on the lower surface are occupied by an atom, and all sites on the upper surface are vacant. Excited states are created by moving n atoms from the lower surface to the upper surface. Any atom that is excited from the lower surface can move to any site on the upper surface, as shown in the figure.



The energy of an excited state, relative to that of the ground state, is $n\epsilon$, where $\epsilon > 0$. This system is in equilibrium with a heat bath at temperature T.

(a) Show that the weight function $\Omega(n)$ for the state with n excited atoms is given by the binomial coefficient $\binom{N}{n}$ raised to the power ν, specifying the numerical value of the exponent ν. **[3]**

(b) Under the assumption that both n and N are large, show that the Helmholtz free energy as a function of n satisfies

$$\frac{F(n)}{N} = x\epsilon + \nu k_B T \left[x \ln x + (1-x)\ln(1-x)\right] \ ,$$

where $x = n/N$ is the fraction of excited atoms. **[4]**

(c) Hence, or otherwise, show that the equilibrium value of x, as a function of temperature, is

$$\bar{x}(T) = \frac{1}{1 + \exp\left(\frac{\epsilon}{\nu k_B T}\right)} \ .$$ **[4]**

(d) Sketch the form of the equilibrium fraction of excited atoms, $\bar{x}(T)$, as a function of T, noting the limiting values as $T \to 0$ and $T \to \infty$. **[4]**

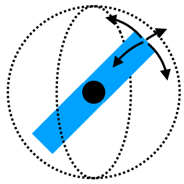
(e) By appealing to energy-entropy competition, explain why a state with $\bar{x}(T) > \frac{1}{2}$ is not an equilibrium state. **[3]**

We now consider two systems of the same size that are both prepared at the same temperature, but are not initially in contact with each other. They are then placed in thermal contact, and allowed to exchange energy (in the form of heat) and particles between them until they reach equilibrium.

(f) Calculate the change in the entropy of the two systems when they are brought into in contact. **[4]**

(g) Explain this entropy change by appealing to an argument based on whether or not the atoms are distinguishable. **[3]**

C.2 The rotational degrees of freedom of a diatomic molecule can be modelled as a thin rigid rod that is free to rotate about its centre of mass whilst the position of the centre of mass remains fixed.
The quantum mechanical state of the system is determined by two quantum numbers, ℓ and m, which satisfy $\ell = 0, 1, 2, \ldots$ and $m = -\ell, -\ell+1, \ldots, \ell-1, \ell$.



The energy of the state (ℓ, m) is

$$\epsilon(\ell, m) = \frac{\hbar^2}{2I}\ell(\ell+1) ,$$

where I is the moment of inertia of the rod. The rod is in thermal equilibrium with a heat bath at temperature T.

(a) State the general definition of the canonical partition function Z. **[2]**

(b) Show that for the rigid rod, we have that

$$Z = \sum_{\ell=0}^{\infty}(2\ell+1)\mathrm{e}^{-\frac{\beta\hbar^2}{2I}\ell(\ell+1)} ,$$

where $\beta = \frac{1}{k_B T}$. **[3]**

(c) By replacing the sum over ℓ with an integral over the range $0 \leq \ell < \infty$, show that Z can be approximated as

$$Z \approx A k_B T ,$$

specifying the value of the constant A. **[4]**

(d) Hence, or otherwise, determine the equilibrium value of the mean energy of the rod. **[3]**

(e) Show that the result obtained in part (d) is compatible with the equipartition theorem at high temperatures, but incompatible with the third law of thermodynamics at low temperatures. **[4]**

(f) Explain why, at low temperatures, we can justify truncating the sum in part (b) at $\ell = 1$. **[3]**

(g) Show that this manipulation leads to a result that is compatible with the third law of thermodynamics. **[6]**