UNIVERSITY OF LONDON

MSci EXAMINATION 2003

For Internal Students of

Royal Holloway

<u>DO NOT TURN OVER UNTIL TOLD TO BEGIN</u>

PH4211A: STATISTICAL MECHANICS

Time Allowed: TWO AND A HALF hours

Answer THREE QUESTIONS only

No credit will be given for attempting any further questions

Approximate part-marks for questions are given in the right-hand margin

Only CASIO fx85WA Calculators are permitted

GENERAL PHYSICAL CONSTANTS

Permeability of vacuum	μ_0	=	$4\pi \times 10^{-7}$	H m^{-1}
Permittivity of vacuum	ε_0	=	8.85×10^{-12}	F m^{-1}
	$1/4\pi\varepsilon_0$	=	9.0×10^{9}	m F^{-1}
Speed of light in vacuum	c	=	3.00×10^{8}	m s^{-1}
Elementary charge	e	=	1.60×10^{-19}	C
Electron (rest) mass	m_e	=	9.11×10^{-31}	kg
Unified atomic mass constant	m_u	=	1.66×10^{-27}	kg
Proton rest mass	m_p	=	1.67×10^{-27}	kg
Neutron rest mass	m_n	=	1.67×10^{-27}	kg
Ratio of electronic charge to mass	e/m_e	=	1.76×10^{11}	C kg^{-1}
Planck constant	h	=	6.63×10^{-34}	J s
	$\eta = h/2\pi$	=	1.05×10^{-34}	J s
Boltzmann constant	k	=	1.38×10^{-23}	J K^{-1}
Stefan-Boltzmann constant	σ	=	5.67×10^{-8}	W m^{-2} K^{-4}
Gas constant	R	=	8.31	J mol^{-1} K^{-1}
Avogadro constant	N_A	=	6.02×10^{23}	mol^{-1}
Gravitational constant	G	=	6.67×10^{-11}	N m^2 kg^{-2}
Acceleration due to gravity	g	=	9.81	m s^{-2}
Volume of one mole of an ideal gas at STP		=	2.24×10^{-2}	m^3
One standard atmosphere	P_0	=	1.01×10^{5}	N m^{-2}

MATHEMATICAL CONSTANTS

$e \cong 2.718$ $\pi \cong 3.142$ $\log_e 10 \cong 2.303$

PART MARKS

1. (a) When the liquid and the gas phase of a fluid coexist in equilibrium the temperature, pressure and chemical potential are the same in both phases. Explain why this is the case. **[3]**

(b) Under what constraints is the equilibrium state of such a system determined by minimising the Helmholtz free energy $F = E - TS$? **[3]**

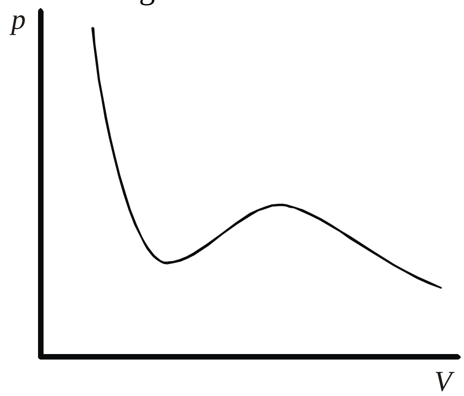
(c) Justify the double tangent construction on the $F(V)$ curve to determine the equilibrium state and show that the volume fractions α_1 and α_2 of the two coexisting phases may be written

$$\alpha_1 = \frac{V_2 - V_0}{V_2 - V_1}, \qquad \alpha_2 = \frac{V_0 - V_1}{V_2 - V_1}$$

[6]

where the symbols have their usual meaning.

(d) A van der Waals p-V isotherm, for a temperature less than the critical temperature, is shown in the figure.



The true coexistence behaviour should be a horizontal straight line. Using the result

$$p = -\left.\frac{\partial F}{\partial V}\right|_T$$

show how the coexistence pressure may be determined from the double tangent construction. **[5]**

(e) Explain the connection with Maxwell's 'equal area' construction. **[3]**

PART MARKS

2. (a) The ferromagnetic transition and the ferroelectric transition have similarities and differences. For each case:

   i) What is the order parameter?

   ii) Is the order parameter conserved or non-conserved?

   iii) What symmetry is broken at the transition?

   iv) Is the broken symmetry continuous or discrete?

   v) What is the order of the transition? **[10]**

   (b) Outline the arguments by which the Heisenberg Hamiltonian

$$H = -J\sum_{i,j}\mathbf{S}_i.\mathbf{S}_j$$

   is approximated, in mean field theory, by a local magnetic field

$$\mathbf{b} = \lambda\mathbf{M}$$

   where **M** is the magnetisation and λ is a constant. **[4]**

   (c) The magnetisation of a non-interacting assembly of N spin ½ magnetic moments μ is given by

$$\frac{M}{M_0} = \tanh\left(\frac{M_0}{N}\frac{B}{kT}\right)$$

   where the saturation magnetisation is $M_0 = N\mu$ and the directions of **M** and the applied magnetic field **B** are parallel.

   Show that in the presence of a Heisenberg interaction between the spins, in the mean field approximation, the spontaneous magnetisation is given by

$$\frac{M}{M_0} = \tanh\left(\frac{M}{M_0}\frac{T_c}{T}\right)$$

   where $T_c = \lambda M_0^2 / Nk$. What is the interpretation of T_c? **[4]**

   (d) Sketch the behaviour of the spontaneous magnetisation as a function of temperature and discuss the order of the transition. **[2]**

3. (a) Show that when two isolated systems are brought into thermal contact, they end up in the thermodynamic state for which

$$\frac{\partial \ln \Omega_1}{\partial E} = \frac{\partial \ln \Omega_2}{\partial E}$$

defining the terms Ω_1, Ω_2 and E in this expression. **[5]**

(b) Write down the Boltzmann expression for entropy in terms of Ω. How does the above equation imply the equalisation of the temperatures of the two systems? **[4]**

(c) Now consider a small sub-system of a large isolated system. The total energy of the isolated system is E_t. The sub-system can exchange thermal energy with the large system. When the sub-system is in a microstate of energy E the entropy of the combined system may be expressed as

$$S = S\left(E_\mathrm{t}\right) - E\frac{\partial S}{\partial E} + \frac{E^2}{2}\frac{\partial^2 S}{\partial E^2} - \ldots.$$

Justify the structure of this expression. **[3]**

(d) Show how the above result leads to the Boltzmann distribution function (otherwise known as the Boltzmann factor). **[4]**

(e) The equilibrium state of an isolated system corresponds to a maximum of the entropy. Discuss, in terms of the second derivative of *S*, how the existence of an entropy *maximum* implies that the heat capacity of the system is positive. **[4]**

PART MARKS

4. (a) The partition function for a single particle moving freely in a box of volume V may be written as

$$z = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2} = \frac{V}{\Lambda^3}$$

where the symbols have their usual meaning.

The quantity Λ is known as the *thermal de Broglie wavelength*. Explain the meaning of this quantity. **[3]**

(b) Show that the pressure of a gas of N indistinguishable such particles is related to z by

$$p = NkT \left.\frac{\partial \ln z}{\partial V}\right|_T .$$ **[4]**

(c) Evaluate the pressure for this system, hence deriving the equation of state of an ideal gas. **[3]**

(d) In the van der Waals approach to an *interacting* gas the single particle partition function may be approximated by

$$z = \frac{V - V_{\text{ex}}}{\Lambda^3} e^{-\langle E\rangle/kT}$$

Sketch the expected variation of the inter-particle interaction potential with separation. Discuss how the various features of the interaction are incorporated into the above expression for z through the quantities V_{ex} and $\langle E\rangle$. **[5]**

(e) Why is this approach referred to as a *mean field* approximation? **[2]**

(f) Discuss qualitatively how this approach to the interacting gas is connected with the law of corresponding states. **[3]**

PART MARKS

5. (a) The autocorrelation function of a random function of time $x(t)$ is defined by

$$G(t) = \langle x(0)x(t) \rangle$$

where the angled brackets indicate an average. Explain how $G(t)$ describes the mean decay of the fluctuations of $x(t)$. **[4]**

(b) The correlation time τ_c of the random function is defined by

$$\tau_c = \frac{1}{G(0)} \int_0^\infty G(t)\,\mathrm{d}t \,.$$

What feature of the fluctuating quantity $x(t)$ does the correlation time describe? **[3]**

(c) A fluctuating quantity is found to have an exponential correlation function

$$G(t) = G(0)e^{-t/\tau} \,.$$

What is the corresponding correlation time? **[2]**

(d) For an isolated system the probability $P(x)$ that a fluctuating quantity has the value x is given by the Einstein expression

$$P(x) \propto e^{S(x)/k}$$

where S is the entropy. Justify this formula. **[3]**

(e) Sketch and explain the functional form of $S(x)$ in the vicinity of the mean value $\langle x \rangle$. **[3]**

(f) Hence discuss qualitatively why the fluctuations in x may follow a normal distribution. **[3]**

(g) Discuss the way the diffusion coefficient of a particle is related to its velocity autocorrelation function. **[2]**