

UNIVERSITY OF LONDON

MSci EXAMINATION 2000

For Internal Students of
Royal Holloway

DO NOT TURN OVER UNTIL TOLD TO BEGIN

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

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}
	$1/4\pi\epsilon_0$	=	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
	$\hbar = h/2\pi$	=	1.05×10^{-34}	J s
Boltzmann constant	k	=	1.38×10^{-23}	J K^{-1}
Stefan-Boltzmann constant	σ	=	5.67×10^{-8}	$\text{W m}^{-2} \text{K}^{-4}$
Gas constant	R	=	8.31	$\text{J mol}^{-1} \text{K}^{-1}$
Avogadro constant	N_A	=	6.02×10^{23}	mol^{-1}
Gravitational constant	G	=	6.67×10^{-11}	$\text{N m}^2 \text{kg}^{-2}$
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

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

1. (a) The partition function Z for a system of N indistinguishable non-interacting particles is often approximated by

$$Z = \frac{1}{N!} z^N$$

where z is the partition function for a single particle.

Explain the arguments that lead to this approximation. [3]

- (b) Given that the Helmholtz free energy $F = E - TS$ is related to Z by

$$F = -kT \ln Z$$

where the symbols have their usual meanings, show that the pressure is given by

$$p = kT \left. \frac{\partial \ln Z}{\partial V} \right|_{T,N}. \quad [3]$$

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

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

By evaluating the pressure for system of N such indistinguishable particles, show that the equation of state corresponds to that for 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 with separation of the inter-particle interaction potential. 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) Sketch the general form for a van der Waals isotherm and identify the stable, metastable, and unstable regions. [4]

2. (a) Outline the sequence of arguments by which one finds that two isolated systems, when brought into thermal contact, end up in the thermodynamic state for which

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

and define the terms Ω_1 , Ω_2 and E in this expression. [4]

- (b) Write down an 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

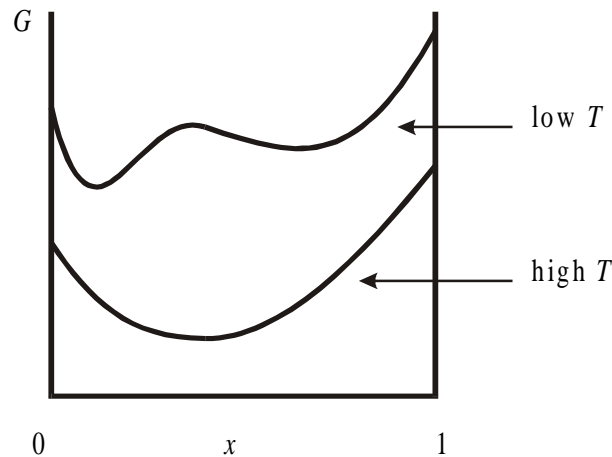
$$S = S(E_t) - E \frac{\partial S}{\partial E} + \frac{E^2}{2} \frac{\partial^2 S}{\partial E^2} - \dots$$

Justify the structure of this expression. [4]

- (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* has a consequence for the heat capacity of the system. [4]

3. (a) A binary alloy contains two atomic species A and B with relative proportions x and $1-x$. The Gibbs free energy for this system has the form shown in the figure:



In the low temperature case explain how, for some values of x , the system may lower its free energy by separating into two phases of different concentrations. [3]

- (b) If the fraction of the system at concentration x_1 is denoted by α then the fraction at the other concentration x_2 is $1-\alpha$. Show that the fractions α and $1-\alpha$ are given by the *lever rule*:

$$\alpha = \frac{x_2 - x_0}{x_2 - x_1}, \quad 1 - \alpha = \frac{x_0 - x_1}{x_2 - x_1}$$

where x_0 is the initial concentration of A atoms. [4]

- (c) Sketch, on a $T-x$ graph, the *phase separation curve* and the *spinodal curve*. How are these determined from the above figure? What is the meaning of the spinodal curve? [4]
- (d) Identify, on the phase separation curve, the *critical point*. [2]
- (e) It may be said that the first order transition becomes second order at the critical point. Explain this. [3]
- (f) Why are fluctuations important in the vicinity of the critical point? Describe the nature of the fluctuations in this system. [4]

4. (a) Explain what is meant by the *order parameter* in the context of phase transitions and describe the difference in the behaviour of the order parameter for *first order* and *second order* transitions. [3]

- (b) When the Landau theory of phase transitions is applied to the ferroelectric transition the free energy is expressed by a polynomial of the form

$$F = F_0 + F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6$$

What is the order parameter φ for this system? Give arguments for the absence of odd-order terms in the expression. [3]

- (c) By varying an external parameter, such as the strain, the ferroelectric transition can be either first order or second order. Sketch the possible variations of the free energy as a function of the order parameter that can account for the first order and the second order transitions respectively. [4]

- (d) Explain qualitatively how the order of the transition depends on the *sign* of the F_4 coefficient and why the F_6 term may be neglected when the transition is second order. [3]

- (e) When the transition is first order show that the discontinuity in the order parameter at the transition is given by

$$\Delta\varphi = \sqrt{\frac{-F_4}{2F_6}}$$

and discuss the behaviour of the discontinuity as the transition becomes second order. [3]

- (f) Within the spirit of the Landau theory it is conventional to approximate the temperature dependence of the F_2 coefficient by

$$F_2 = \alpha(T - T_c).$$

Explain this by reference to the second order case. Using this temperature dependence show that the latent heat at the first order transition is given by

$$L = \alpha T_c \frac{|F_4|}{2F_6} \quad [4]$$

and discuss the behaviour of L as the transition becomes second order.

5. (a) The velocity $v(t)$ of a Brownian particle is a randomly-varying function of time. Define $G_v(\tau)$, the autocorrelation function for the velocity and explain its physical significance. [4]
- (b) Show that the mean square displacement of the particle is given by [3]
- $$\langle x^2(t) \rangle = 2 \int_0^t (t-\tau) G_v(\tau) d\tau.$$
- (c) What is meant by the correlation time of $G_v(\tau)$? Discuss the limiting behaviour of the mean square displacement for times shorter than, and longer than the correlation time. In particular, show that in the long time limit the mean square displacement is proportional to time whereas in the short time limit the mean square displacement is proportional to time squared. [4]
- (d) Give a physical explanation of the behaviour in the short and long time limits. [4]
- (e) Using the above results, show that the diffusion coefficient of the Brownian particle may be expressed in terms of the area under $G_v(\tau)$. [3]
- (f) Why is this called a *fluctuation-dissipation* theorem? [2]