

UNIVERSITY OF LONDON

MSci EXAMINATION 2002

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

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
	$1/4\pi\epsilon_0$	=	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}	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

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

1. (a) Explain why a system in thermal equilibrium with a reservoir at a temperature T has fluctuations in its energy E . [3]

- (b) The quantity σ_E is given by

$$\sigma_E = \left\langle \left(E - \langle E \rangle \right)^2 \right\rangle^{1/2} .$$

[3]

Why is σ_E a measure of the energy fluctuations?

- (c) Show that

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 .$$

[2]

- (d) The mean energy of a system in thermal equilibrium at a temperature T may be written as

$$\langle E \rangle = \frac{1}{Z} \sum_j E_j e^{-E_j/kT} .$$

[3]

Explain the meaning of this expression, defining the quantity Z .

- (e) By considering the expression for the mean square energy $\langle E^2 \rangle$ show that the size of the energy fluctuations may be written as

$$\sigma_E = \sqrt{kT^2 C_V}$$

[6]

where C_V is the thermal capacity of the system.

- (f) Discuss how the energy fluctuations depend on the size (number of particles N) of the system and show that the fractional energy fluctuations tend to zero as $N^{-1/2}$. [3]

2. (a) What is Brownian motion? [2]
 (b) The force on a Brownian particle may be written as [4]

$$F(t) = f(t) - \frac{1}{\mu} v$$

where $f(t)$ is a randomly fluctuating force, v is the velocity and μ the mobility of the particle. Discuss the separation of the force into these two parts.

- (c) Show that the equation of motion for the Brownian particle may be written as [3]

$$\frac{dv(t)}{dt} + \gamma v(t) = A(t)$$

and identify the terms.

- (d) The solution to the equation of motion may be written [3]

$$v(t) = v(0)e^{-\gamma t} + \int_0^t e^{\gamma(u-t)} A(u) du .$$

Describe how this solution arises and explain its implications.

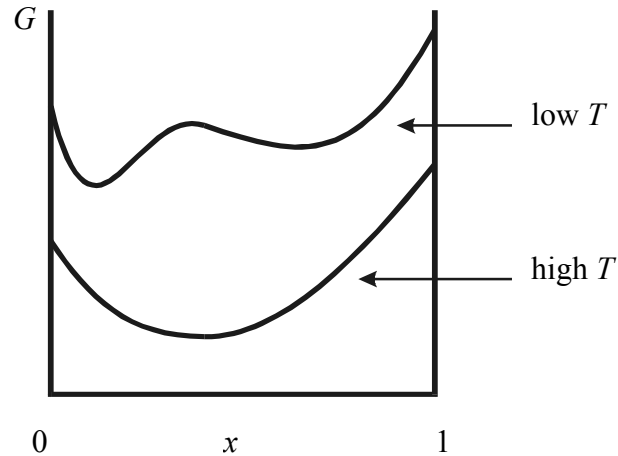
- (e) The autocorrelation function for the random force is defined by the average [3]

$$\langle A(t)A(t + \tau) \rangle .$$

Discuss the physical meaning of this expression and explain why it is independent of the time t .

- (f) Show how the motion of the Brownian particle depends on the autocorrelation function of the *velocity*, and show how this leads to diffusive behaviour. Give an expression for the diffusion coefficient in terms of the velocity autocorrelation function. [5]

3. (a) A binary alloy contains two atomic species A and B with relative proportions x and $1-x$ of different concentrations x_1 and x_2 . 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. [3]

- (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? [5]
- (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 structure of this free energy 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

$$L = \alpha T_c \frac{|F_4|}{2F_6}$$

and discuss the behaviour of L as the transition becomes second order. [4]

5. (a) Outline the sequence of arguments by which one shows 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]