

UNIVERSITY OF LONDON

MSci EXAMINATION 2004

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 or CASIO fx85MS 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 Boltzmann expression for entropy is written $S = k \ln \Omega$. Identify the terms in the equation, taking care to explain the meaning of Ω . [3]
- (b) By considering an isolated system containing a constraint, such as a dividing partition, explain clearly why the equilibrium state, upon removal of the constraint, corresponds to that of maximum entropy. [5]
- (c) Two systems are brought into contact so that they may exchange thermal energy, mechanical energy and particles. By using the appropriate definitions, show that the equilibrium state corresponds to that in which the temperatures, pressures and chemical potentials of the two systems are equalised [7]
- (d) Using the fact that the equilibrium state has maximum entropy, state what you can about the *second derivative* of the entropy with respect to energy of the composite system. Derive the implications for the heat capacity. [5]
2. (a) What is meant by the term *order parameter* in a phase transition ? [2]
- (b) Explain the difference between a *conserved* and a *non-conserved* order parameter. Give an example of each. [4]
- (c) In the Landau theory of phase transitions, the free energy is expanded in powers of the order parameter. A key feature of this approach is the *truncation* of the power series. Discuss what determines the power at which the series is terminated. [2]
- (d) Expansions (in even powers) up to fourth order can describe second order transitions while expansions up to sixth order can describe first order transitions. Explain *qualitatively* why this is. [4]
- (e) In the vicinity of the critical point of a ferromagnetic transition the free energy is expressed as a function of the order parameter φ as
- $$F = F_0 + F_2\varphi^2 + F_4\varphi^4 .$$
- Sketch the form of this function for temperatures above, equal to, and below the critical temperature. [4]
- (f) Show that the critical point corresponds to $F_2 = 0$. [2]
- (g) Show that below the critical temperature the order parameter has the form
- $$\varphi \sim \sqrt{T_c - T} . \quad [2]$$

3. The partition function Z for a gas of N interacting atoms is given by

$$Z = \frac{1}{N! h^{3N}} \int e^{-\left(\sum_i \frac{p_i^2}{2m} + \sum_{i < j} U(q_i, q_j)\right) / kT} d^{3N} p d^{3N} q$$

where the symbols have their usual meaning.

- (a) Show that Z may be expressed as

$$Z = Z_{id} \frac{1}{V^N} \int e^{-\sum_{i < j} U(q_i, q_j) / kT} d^{3N} q \quad \text{Eq. 3.1}$$

where Z_{id} is the partition function for an ideal (non-interacting) gas.

[4]

Be sure to explain the appearance of the V^N factor.

- (b) The interaction potential for a pair of *hard spheres* with centres a distance r apart is given by

$$\begin{aligned} U(r) &= \infty & r < \sigma \\ &= 0 & r > \sigma \end{aligned}$$

where σ is the hard core dimension.

Sketch and label this interaction potential and relate σ to the radius of an atom in the gas. [2]

- (c) The partition function for a gas of hard spheres might be approximated by

$$Z = Z_{id} \left(\frac{V - Nb}{V} \right)^N.$$

Give a justification for this from the structure of Eq. 3.1.

[3]

Question 3 continued overleaf

- (d) The above approximation for the partition function leads to the equation of state

$$p(V - Nb) = NkT .$$

Express this equation in terms of the *virial expansion*

$$\frac{p}{kT} = \frac{N}{V} + B_2(T) \left(\frac{N}{V} \right)^2 + B_3(T) \left(\frac{N}{V} \right)^3 + \dots .$$

Hence find expressions for B_2 and B_3 and write down the general B_n .

[4]

- (e) The virial coefficients for the hard sphere gas are independent of temperature. Why is this? [3]
- (f) Exact calculations of the first few virial coefficients for the hard sphere gas give:

$$B_2(T) = b, \quad B_3(T) = \frac{5}{8}b^2, \quad B_4(T) = 0.29b^3$$

where $b = 2\pi\sigma^3/3$.

What do you conclude, by comparing these values with those you obtained in part (d) above? [4]

You may find the expansion below useful in part (d).

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots$$

4. (a) Describe the essential features of the *Ising Model* for a ferromagnet. What is the order parameter for the Ising transition? To what extent is it a suitable model to describe the behaviour of real materials? [4]
- (b) In one dimension there is no transition at finite temperatures. By considering the free energy for this system in the thermodynamic limit, explain why this is so. [4]
- (c) In two dimensions the Ising model has a phase transition at finite temperatures. Sketch the temperature dependence of the order parameter and the heat capacity. Describe and explain how these differ from the results of mean field / Landau theory. [5]
- (d) When a transverse high magnetic field is applied to the system it exhibits a quantum phase transition. What is a quantum phase transition? Describe the nature of the ordered phase a) in the case of low magnetic field and b) high magnetic field. [3]
- (e) Sketch the temperature – transverse magnetic field phase diagram and label the phases. What would be the effect of a *parallel* field on the transition? [4]

5. The force on a Brownian particle may be written as

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

where $f(t)$ is a randomly fluctuating force, v is the velocity and μ the mobility of the particle.

- (a) What is Brownian motion? [2]

- (b) Discuss the separation of the force into the two parts. In particular, explain qualitatively how the friction force, proportional to the velocity, arises as a consequence of the random motion of the background fluid atoms. [5]

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

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

and identify the terms. [4]

- (d) The autocorrelation function for the velocity is defined by the average

$$G(\tau) = \langle v(t)v(t+\tau) \rangle$$

Discuss the physical meaning of this expression and explain why it is independent of the time t . Comment on the relative time scales of $G(\tau)$ and $v(t)$. [4]

- (e) Show how the mean square displacement of the Brownian particle depends on the velocity autocorrelation function. How does this lead to the description of the motion as diffusive? [5]