UNIVERSITY OF LONDON

MSci EXAMINATION 2007

For Students of the
University of London

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

PH4211A/100

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
	$\hbar = h/2\pi$	=	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) 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. **[2]**

(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. **[2]**

(c) Two systems are brought into contact so that they may exchange energy through a fixed impermeable diathermal wall. By using the appropriate definitions, show that the equilibrium state corresponds to that in which the temperatures of the two systems are equalised.

Explain why the equilibrium energy of each system is not fixed, but fluctuates. **[5]**

(d) The quantity σ_E is given by

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

Why is σ_E a measure of the energy fluctuations? **[2]**

(e) Show that

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 .$$ **[2]**

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

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

Explain the meaning of this expression, defining the quantity Z. **[2]**

(g) 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

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

where C_V is the thermal capacity of the system. **[3]**

(h) 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 $N^{-1/2}$. **[2]**

2. (a) The partition function Z for a classical gas of N interacting atoms is given by

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

where the symbols have their usual meaning. Explain the structure of this expression **[3]**

(b) Show that Z may be expressed as

$$Z = Z_{\mathrm{id}} Q_N$$

where Z_{id} is the partition function for an ideal (non-interacting) gas and the configuration integral Q_N is

$$Q_N = \frac{1}{V^N} \int e^{-\sum_{i<j} U(q_i, q_j)/kT} \mathrm{d}^{3N} q \,.$$

Be sure to explain the appearance of the V^N factor. **[4]**

(c) Show that the pressure of this gas may be expressed as

$$p = kT\left(\left.\frac{\partial \ln Z_{\mathrm{id}}}{\partial V}\right|_{T,N} + \left.\frac{\partial \ln Q_N}{\partial V}\right|_{T,N} \right) = kT\left(\frac{N}{V} + \left.\frac{\partial \ln Q_N}{\partial V}\right|_{T,N} \right).$$ **[4]**

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

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

where σ is the hard core diameter.

Explain why the configuration integral Q_N for a hard sphere gas is independent of temperature. Hence show that for such a gas p/kT is solely a function of the density N/V. **[3]**

(e) Argue that pV/NkT is a *universal* function of $N\sigma^3/V$ and discuss ways that this universal equation of state may be determined. **[3]**

(f) Would you expect this system to exhibit a transition to an ordered phase? Discuss. **[3]**

PART MARKS

3. (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. **[4]**

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

$$F_2 = \alpha\left(T - T_\mathrm{c}\right).$$

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

$$L = \alpha T_\mathrm{tr}\frac{|F_4|}{2F_6}$$

and discuss the behaviour of L as the transition becomes second-order. **[3]**

PART MARKS

4. (a) For the case of the ferromagnetic phase transition:
   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? **[5]**

(b) In the Weiss model of this transition it is assumed that the magnetic moments are subject to an additional 'mean' magnetic field

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

where **M** is the magnetisation and λ is a constant.

The magnetisation of a *non-interacting* assembly of N (per unit volume) spin ½ non-interacting 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 the Weiss model, in the absence of an external magnetic field, can lead to a spontaneous magnetisation 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? **[9]**

(c) Sketch the behaviour of the spontaneous magnetisation as a function of temperature and relate this to the order of the transition. **[2]**

(d) In iron the transition to the ferromagnetic phase occurs at a temperature of 1043 K. Estimate the value of the Weiss field that would be responsible for this. Could the electron dipole magnetic field be responsible? Discuss other possible mechanisms for this field. **[4]**

The Bohr magneton $\mu_B = 9.27 \times 10^{-24}$ A m^2.

5. (a) Write an essay on the logical structure of statistical mechanics and the connection between the microscopic and the macroscopic descriptions of matter. You should include a description of the micro-canonical, the canonical and the grand canonical approaches. **[20]**