Royal Holloway

UNIVERSITY OF LONDON

MSci EXAMINATION

STATISTICAL MECHANICS CP4211A

SUMMER 1999

Time Allowed: TWO AND A HALF HOURS

Answer **THREE** questions only. No credit will be given for attempting a further question.

Each question carries 20 marks. The mark *provisionally allocated* to each section is indicated in the margin.

TURN OVER WHEN INSTRUCTED

GENERAL PHYSICAL CONSTANTS

Permeability of vacuum	m_0	=	$4\pi \times 10^{-7}$	$\mathrm{H\ m^{-1}}$
Permittivity of vacuum	e_0	=	8.85×10^{-12}	$\mathrm{F\ m^{-1}}$
	$1/4\pi e_0$	=	9.0×10^{9}	$\mathrm{m\ F^{-1}}$
Speed of light in vacuum	c	=	3.00×10^{8}	$\mathrm{m\ s^{-1}}$
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}	$\mathrm{C\ kg^{-1}}$
Planck constant	h	=	6.63×10^{-34}	J s
	h = $h/2\pi$	=	1.05×10^{-34}	J s
Boltzmann constant	k	=	1.38×10^{-23}	$\mathrm{J\ K^{-1}}$
Stefan-Boltzmann constant	s	=	5.67×10^{-8}	$\mathrm{W\ m^{-2}\ K^{-4}}$
Gas constant	R	=	8.31	$\mathrm{J\ mol^{-1}\ K^{-1}}$
Avogadro constant	N_A	=	6.02×10^{23}	$\mathrm{mol^{-1}}$
Gravitational constant	G	=	6.67×10^{-11}	$\mathrm{N\ m^{2}\ kg^{-2}}$
Acceleration due to gravity	g	=	9.81	$\mathrm{m\ s^{-2}}$
Volume of one mole of an ideal gas at STP		=	2.24×10^{-2}	$\mathrm{m^{3}}$
One standard atmosphere	P_0	=	1.01×10^{5}	$\mathrm{N\ m^{-2}}$

MATHEMATICAL CONSTANTS

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

PART MARKS

1. (a) By the use of probability arguments explain why the equilibrium state of an isolated system corresponds to that of maximum entropy. **[6]**

(b) 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 temperature, pressure and chemical potential of the two systems are equalised. **[8]**

(c) Since the equilibrium state has *maximum* entropy, discuss the *second derivative* of the entropy of the composite system. **[6]**

2. When the mean field theory of phase transitions is applied to the ferromagnetic transition in the absence of a magnetic field, the free energy is given approximately, in the vicinity of the transition, by

$$F = \frac{Nk}{2}\left(T - T_c\right)m^2 + \frac{Nk}{12}T_c m^4 .$$

(a) Explain the structure of this expression and indicate what the various quantities are. **[4]**

(b) By sketching the form of this expression, explain how the transition occurs as the temperature is lowered through T_c and discuss the magnitude of the fluctuations in the vicinity of T_c. **[4]**

(c) Using the above expression show that in the vicinity of the transition

$$m = \pm\sqrt{\frac{3\left(T_c - T\right)}{T_c}}$$

and sketch this behaviour. **[5]**

(d) What is the order of this transition? Explain your reasoning. **[3]**

(e) Show that below the transition there is a contribution to the entropy given by

$$\frac{3Nk}{2}\left(T - T_c\right)$$

and that this leads to a jump in the thermal capacity on cooling through the transition of

$$\Delta C = \frac{3NkT_c}{2}.$$ **[4]**

PART MARKS

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

(b) A measure of the size of the energy fluctuations is given by

$$s_E = \left\langle \left(E - \langle E \rangle \right)^2 \right\rangle^{1/2} .$$ **[3]**

What does this expression mean?

(c) Show that the mean square energy fluctuations are given by

$$s_E^2 = \left\langle E^2 \right\rangle - \left\langle E \right\rangle^2 .$$ **[2]**

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

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

[3]

In terms of probabilities, explain the meaning of this expression.

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

$$s_E = \sqrt{kT^2 C_V}$$ **[6]**

where C_V is the thermal capacity of the system.

(f) Discuss how the energy fluctuations depend on the size (number of particles) of the system. **[3]**

PART MARKS

4. (a) What is ferroelectricity and what is the order parameter below the ferroelectric transition? **[2]**

(b) By varying an external parameter, such as pressure, the ferroelectric transition can be either first or second order.

Sketch the variation of the free energy as a function of the order parameter which can account for the first order and the second order transitions. **[3]**

(c) Explain how the features of the ferroelectric transition may be treated by an expansion of the free energy in (even) powers of the order parameter up to the *sixth* power.

$$F = F_2 j^2 + F_4 j^4 + F_6 j^6$$

Give arguments for the absence of odd terms in the expansion. **[3]**

(d) Show how the order of the transition depends on the *sign* of the F_4 coefficient. **[2]**

(e) When the transition is *second order* explain why the F_6 term may be neglected and show that *at* the transition the F_2 term vanishes. **[3]**

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

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

Discuss the behaviour of the discontinuity as the transition becomes second order. **[5]**

(g) There is no latent heat involved in a second order transition. By considering the temperature variation of the F coefficients, discuss the relationship between the latent heat and the discontinuity in the order parameter. **[2]**

PART MARKS

5. (a) What is Brownian motion? **[2]**

(b) The force on a Brownian particle may be written as

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

where $f(t)$ is a randomly fluctuating force, v is the velocity and m the mobility of the particle. Discuss the separation of the force into these two parts. **[4]**

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

$$\frac{\mathrm{d}v(t)}{\mathrm{d}t} + \gamma v(t) = A(t)$$

and identify the terms. **[3]**

(d) The solution to the equation of motion may be written

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

Describe how this solution arises and explain its implications. **[3]**

(e) The autocorrelation function for the random force is defined by the average

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

Discuss the physical meaning of this expression and explain why it is independent of the time t. **[3]**

(f) Show how the motion of the Brownian particle depends on the autocorrelation function of the *velocity*. Explain, in general terms, how the velocity autocorrelation function follows from the solution to the Langevin equation and discuss how this relates to the *fluctuation-dissipation* theorem. **[5]**

END