UNIVERSITY OF LONDON

MSci EXAMINATION 2010

For Students of the
University of London

DO NOT TURN OVER UNTIL TOLD TO BEGIN

PH4211: STATISTICAL MECHANICS

Time Allowed: **TWO AND A HALF** hours

Answer **THREE** questions only

Please answer each question on a separate page.

Approximate part-marks for questions are given in the right-hand margin.

No credit will be given for attempting any further questions.

College Calculators are provided.

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

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

PART MARKS

1. The relationship between statistical mechanics and thermodynamics may be understood in different ways. According to Landau 'All the concepts and quantities of thermodynamics follow most naturally, simply and rigorously from the concepts of statistical physics', while Einstein's view was that thermodynamics was a fundamental discipline whose results were independent of the particular microscopic models used in statistical mechanics. **[20]**

   Write an essay discussing these contrary views; give examples supporting the Landau view, and examples supporting Einstein's view. Discuss the extent to which the work of both Landau and Einstein were actually more in line with the philosophy of the other. You should include mention of *emergence* as the key concept that resolves the Landau-Einstein conflict.

PART MARKS

2. In the Landau theory of phase transitions one expands an appropriate free energy in powers of the order parameter, to a finite number of terms.

   (i) What is meant by the term *order parameter*? **[3]**

   (ii) Why is the Landau expansion terminated, and what determines the highest power in the expansion? **[4]**

   (iii) In the case of the ferromagnetic transition and the ferroelectric transition there are no odd-power terms in the expansion. Why is this? **[2]**

   (iv) In the ferroelectric case the Landau expansion has terms up to sixth power. Show, with the aid of diagrams, why such an expansion can describe a first-order transition. **[3]**

   (v) This expansion will also allow a second-order transition. Discuss what requirements this puts on the sign of the terms in the Landau expansion and explain the occurrence of the second-order transition with the aid of diagrams. **[5]**

   (vi) Explain, in general terms, how the heat capacity in the vicinity of a phase transition can be understood from the perspective of the Landau theory. In particular, make the connection between the order of the transition and the existence or absence of latent heat. **[3]**

TURN OVER

PART MARKS

3. (a) The interaction between the molecules of a gas may be modelled by the hard core potential: **[4]**

$$U(r) = \infty \qquad r < \sigma$$
$$= 0 \qquad r > \sigma .$$

Make a labelled plot of this function and discuss the extent to which this potential gives a realistic description of such interactions.

(b) The second virial coefficient of a gas is related to the inter-atomic potential by **[4]**

$$B_2(T) = -2\pi \int_0^\infty r^2 \left[e^{-U(r)/kT} - 1 \right] \mathrm{d}r .$$

Show that for the *hard core* interaction the second virial coefficient is given by

$$B_2(T) = \frac{2}{3}\pi\sigma^3.$$

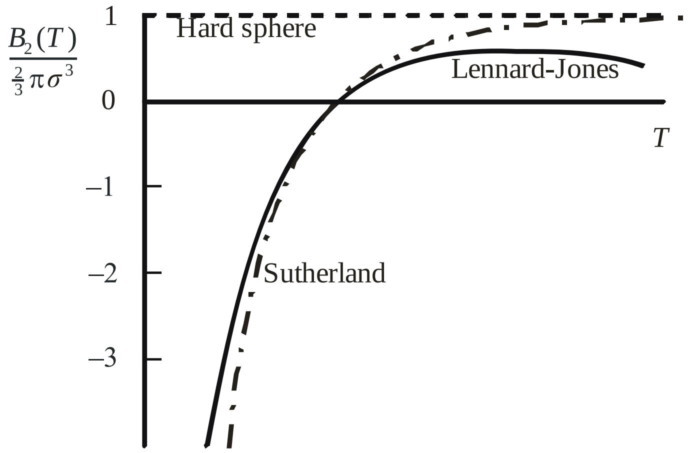
Demonstrate how this may be interpreted as an 'excluded volume' **[4]**

(c) The Sutherland potential is specified by: **[3]**

$$U(r) = \infty \qquad r < \sigma$$
$$= -\varepsilon \left(\frac{\sigma}{r} \right)^6 \qquad r > \sigma .$$

Sketch and label this potential. How realistic is this model as an approximation of a real inter-atomic interaction i) at short distances, and ii) at large distances?

(d) **[5]**



The figure shows the second virial coefficient corresponding to the hard sphere potential, the Sutherland potential and the Lennard-Jones 6-12 potential. Discuss and explain the differences and similarities.

TURN OVER

PART MARKS

4. The free energy of mixing of a binary alloy may be written as **[3]**

$$F_{\mathrm{m}} = Nsx(1-x)\varepsilon + NkT\left\{x\ln x + (1-x)\ln(1-x)\right\}.$$

Explain the meaning of the various terms and the structure of this equation.

What are the equilibrium (stable) states of this system i) at high temperatures, and ii) at low temperatures? **[5]**

How does one determine the equilibrium state of this system?

Explain why one may use the free energy of mixing rather than the full free energy.

Make a clearly labelled sketch of the transition between the homogeneous and the inhomogeneous phases in the $x - T$ plane. Indicate on this curve how the system evolves from a homogeneous high-temperature phase to an inhomogeneous low-temperature phase. **[2]**

Show that this system has a critical temperature given by **[4]**

$$T_{\mathrm{c}} = \frac{s\varepsilon}{2k}$$

and state the value of the critical concentration x_{c}.

Explain why the point (x_{c}, T_{c}) is called a critical point. **[2]**

Sketch the heat capacity for such a system as a function of temperature in the vicinity of the phase transition (i) for a mixture of critical concentration x_{c}, and (ii) for a mixture of concentration $x \ll x_{\mathrm{c}}$. **[4]**

These heat capacity signatures indicate there is *no* latent heat. What feature of the heat capacity indicates this?

It appears paradoxical that this first-order transition involves no latent heat. Why is this?

PART MARKS

5. (a) In an isolated system the probability $P(x)$ that a fluctuating quantity has the value x is given by the Einstein expression **[3]**

$$P(x) \propto e^{S(x)/k}$$

where S is the entropy and k is Boltzmann's constant. Give a justification for this formula.

Sketch and explain the functional form of $S(x)$ in the vicinity of the mean value $\langle x \rangle$. **[3]**

Hence discuss qualitatively why the fluctuations in x may follow a normal distribution. **[3]**

(b) The autocorrelation function of the fluctuating quantity x is given by **[4]**

$$G(t) = \langle x(t)\, x(0) \rangle$$

Where the angled bracket indicates an average. Explain how $G(t)$ describes the 'average' decay of the fluctuations. (Here the mean value $\langle x \rangle$ is taken to be zero).

The correlation time of the fluctuations is defined by **[4]**

$$\tau_{\mathrm{c}} = \frac{1}{G(0)} \int_0^\infty G(t)\,\mathrm{d}t\,.$$

What feature of the fluctuating quantity $x(t)$ does the correlation time describe? Give an explanation of this.

(c) Now consider the case where the fluctuations in x are normally distributed (and again the mean value $\langle x \rangle$ is taken to be zero). Then $P(x)$ is given by **[3]**

$$P(x) = \frac{1}{\sqrt{2\pi \langle x^2 \rangle}} e^{-x^2 / 2\langle x^2 \rangle}\,.$$

Show how the probability distribution function $P(x)$ is related to the autocorrelation function $G(t)$.

END