UNIVERSITY OF LONDON

MSci EXAMINATION 2005

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

PH4211A/29

2004-05

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

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

1. The Helmholtz free energy of mixing of a binary alloy, a regular mixture of two different atomic species, may be written as

$$F_{\mathrm{m}} = Nk\left[2T_{\mathrm{c}}x(1-x)+T\left\{x\ln x+(1-x)\ln(1-x)\right\}\right]$$

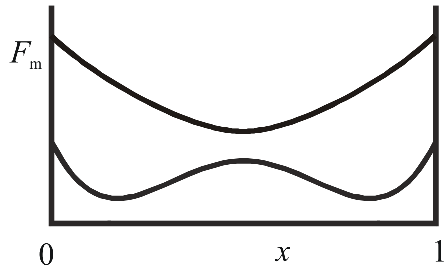
where x is the concentration of one of the species and

$$T_{\mathrm{c}} = \frac{s}{2k}\left\{\varepsilon_{\mathrm{ab}}-\frac{1}{2}\left(\varepsilon_{\mathrm{aa}}+\varepsilon_{\mathrm{bb}}\right)\right\}.$$

(a) Define the terms and explain the structure of these equations. Under what constraints is the equilibrium state of such a system determined by minimising the *Helmholtz* free energy $F = E - TS$? **[4]**

(b) Discuss how the zero-temperature state of this system depends upon the sign of the energy parameter $\varepsilon_{\mathrm{ab}} - \left(\varepsilon_{\mathrm{aa}}+\varepsilon_{\mathrm{bb}}\right)/2$. **[2]**

(c) When this energy parameter is positive, the form of F_{m} for temperatures below and above T_{c} is shown in the figure below.



Which curve corresponds to which case? **[2]**

(d) Explain why, in the low-temperature case, the system may lower its free energy by assuming an inhomogeneous state and discuss the nature of this state. **[4]**

(e) Show that the phase separation temperature as a function of x is given by $T_{\mathrm{ps}}/T_{\mathrm{c}} = 2(1-2x)/\ln\left((1-x)/x\right)$. Sketch and label this curve. **[4]**

(f) In a solid mixture of the isotopes ^{3}He and ^{4}He, T_{c} is 300mK. At what temperature will a homogeneous mixture of concentration $x_0 = 0.01$ phase separate? There is another initial concentration of mixture that is predicted to phase separate at the same temperature. What is this concentration? In reality, for these two initial concentrations the phase separation temperatures are observed to be somewhat different. What could be the explanation of this? **[4]**

PART MARKS

2. (a) The ferromagnetic transition and the ferroelectric transition have similarities and differences. For each case:

   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 can be the order of the transition? **[10]**

(b) Outline the arguments by which the Heisenberg Hamiltonian

$$H = -J \sum_{\substack{i,j \\ \text{neighbours}}} \mathbf{S}_i . \mathbf{S}_j$$

is approximated, in mean field theory, by a local magnetic field

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

where **M** is the magnetisation and λ is a constant. **[4]**

(c) The magnetisation of a non-interacting assembly of N 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 in the presence of a Heisenberg interaction between the spins, but no applied field, the spontaneous magnetisation in the mean field approximation, is given by

$$\frac{M}{M_0} = \tanh\left(\frac{M}{M_0}\frac{T_c}{T}\right)$$

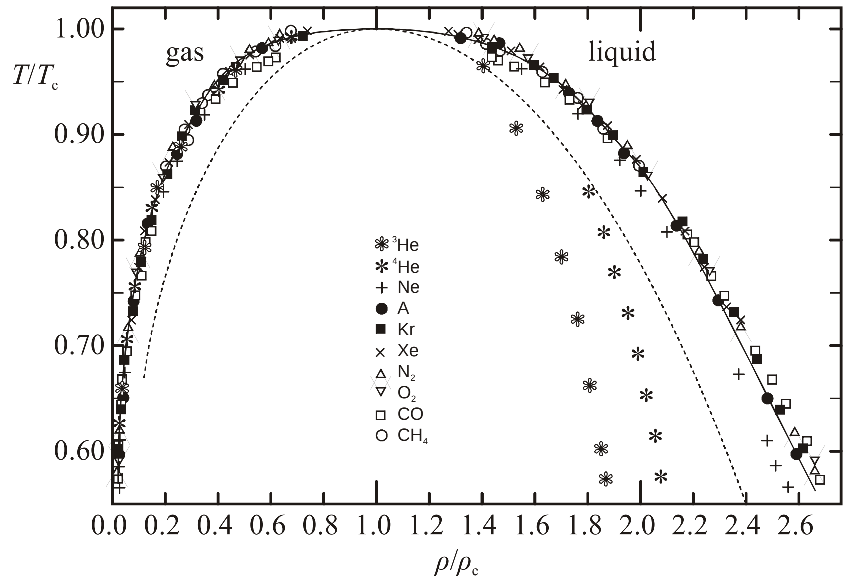
where $T_c = \lambda M_0^2 / Nk$. What is the interpretation of T_c? **[4]**

(d) Sketch the behaviour of the spontaneous magnetisation as a function of temperature and discuss the order of the transition. **[2]**

PART MARKS

3. (a) State the ‘law’ of corresponding states for a liquid-gas system. Discuss how this law arises from a consideration of the van der Waals equation of state and explain the microscopic basis for the law. **[5]**

(b) Liquid-gas coexistence data for a number of substances are plotted in the figure below, showing reduced temperature against reduced density. The dashed line is that calculated from the van der Waals equation of state. T_c and ρ_c are the critical temperature and critical density.



For the moment, ignore the helium data. Discuss the extent to which the other data support the law of corresponding states. Discuss why the van der Waals curve is not in agreement with the data, and why the critical exponent β is closer to $^1/_3$ than the mean field value of $^1/_2$. **[5]**

(c) There are no data very close to the critical point, because of experimental difficulties. However, the general behaviour of most of the materials is well-described by the continuous ‘universal’ curve. Discuss the behaviour of the helium isotopes very close to the critical point. In particular, to what extent do you expect them to give data falling on the universal curve and what do you expect the critical exponent β to be? Justify your speculations. **[5]**

(d) The thermal de Broglie wavelength is given by

$$\Lambda = \hbar\sqrt{\frac{2\pi}{mkT}}\,.$$

Explain the significance of this quantity. Discuss the importance of Λ in relation to the helium data in the figure that deviate from the universal curve. Why are the helium data on the right hand side of the curve falling away from the universal curve, but not on the left hand side? **[5]**

PART MARKS

4. The force on a Brownian particle in one dimension may be written as $F(t) = f(t) - v/\mu$ where $f(t)$ is a randomly fluctuating force, v is the velocity and μ the mobility of the particle.

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

(b) Show that the equation of motion for the Brownian particle of mass M (the Langevin equation) may be written as

$$M\frac{\mathrm{d}v(t)}{\mathrm{d}t} + \frac{1}{\mu}v(t) = f(t).$$ **[2]**

(c) The solution to the Langevin equation is given by

$$v(t) = v(0)e^{-t/M\mu} + \frac{1}{M}\int_0^t e^{(u-t)/M\mu} f(u)\,\mathrm{d}u .$$

Show, using appropriate approximations, that the equilibrium mean square velocity may be expressed as $\langle v^2 \rangle = (\mu/2M)\int_{-\infty}^{\infty}\langle f(0)f(t)\rangle \mathrm{d}t$ and invoking the equipartition theorem, it follows that

$$\frac{1}{\mu} = \frac{1}{2kT}\int_{-\infty}^{\infty}\langle f(0)f(t)\rangle \mathrm{d}t .$$ **[5]**

(d) Discuss how this may be regarded as an example of the fluctuation-dissipation theorem. **[2]**

(e) The voltage across an L-R circuit is given in terms of the current $I(t)$ by

$$L\frac{\mathrm{d}I(t)}{dt} + RI(t) = V(t)$$

where $V(t)$ may be regarded as a fluctuating voltage. By making the appropriate identifications, show that the resistance may be related to the voltage fluctuations through

$$R = \frac{1}{2kT}\int_{-\infty}^{\infty}\langle V(0)V(t)\rangle \mathrm{d}t .$$ **[4]**

(f) How may such voltage fluctuations be observed? **[2]**

PART MARKS

5. (a) In the context of statistical mechanics explain the meaning of the term *ensemble*. **[4]**

(b) Discuss and compare the Boltzmann and the Gibbs view of ensembles. **[4]**

(c) Explain the meaning of the term *phase space*, including a discussion of the difference between Boltzmann's view and that of Gibbs. **[4]**

(d) Liouville's theorem implies that the flow of points in phase space is incompressible. What assumptions go into the derivation of this theorem? **[2]**

(e) Paradoxically, Boltzmann's H theorem seems to contradict Liouville's theorem. Give a statement of Boltzmann's H theorem and explain the paradox. Show how the paradox may be resolved. **[6]**

END