UNIVERSITY OF LONDON

MSci EXAMINATION 2008

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

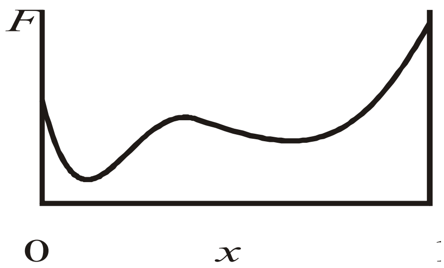
Permeability of vacuum	μ_0	=	$4\pi \times 10^{-7}$	$H\ m^{-1}$
Permittivity of vacuum	ε_0	=	8.85×10^{-12}	$F\ m^{-1}$
	$1/4\pi\varepsilon_0$	=	9.0×10^{9}	$m\ F^{-1}$
Speed of light in vacuum	c	=	3.00×10^{8}	$m\ s^{-1}$
Elementary charge	e	=	1.60×10^{-19}	C
Electron (rest) mass	m_e	=	9.11×10^{-31}	kg
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

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

PART MARKS

1. The Helmholtz free energy F for a binary alloy of two atomic species A and B with relative proportions x and $1-x$ is shown in the figure, at low temperatures.



(a) The equilibrium state in this case is found by the *double tangent construction*. In other systems the equilibrium state is found at the minimum of the free energy curve. Explain the distinction and the circumstances in which each procedure is used. **[4]**

(b) The free energy of mixing F_{m} for this system is given by

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

Identify the energy and the entropy terms and explain the structure of this equation. What is T_{c}?

Sketch the form of F_{m} as a function of x for high and low temperatures.

Why is F_{m} more convenient than F for the double tangent construction? **[4]**

(c) Show that the phase separation, or binodal, curve is given by

$$T_{\mathrm{ps}} = \frac{2(1-2x)}{\ln\left((1-x)/x\right)}T_{\mathrm{c}}.$$

Sketch and label this curve. **[4]**

(d) By reference to the phase separation curve, explain what happens as one cools through the phase separation transition. **[4]**

(e) How would one determine the order parameter critical exponent β from the phase separation curve? What value is predicted by the result in (c), and what value is found experimentally? Discuss the difference. **[4]**

PART MARKS

2. (a) Write down the *virial expansion* for the equation of state of a non-ideal gas. Under what circumstances would an expansion up to only the second virial coefficient be appropriate? **[3]**

(b) A gas of particles interacts with a square-well potential

$$\begin{aligned} U(r) &= \infty \qquad 0 < r < \sigma \\ &= -\varepsilon \qquad \sigma < r < \alpha\sigma \\ &= 0 \qquad \alpha\sigma < r < \infty. \end{aligned}$$

Sketch this and explain the significance of the parameter σ, ε and α. **[3]**

(c) The second virial coefficient for a gas interacting with a potential $U(r)$ is given by

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

Show that for a square-well gas B_2 is given by

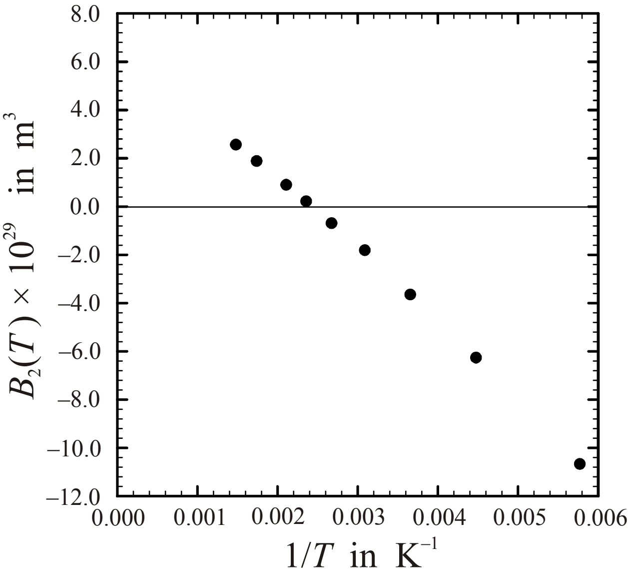
$$B_2(t) = \frac{2}{3}\pi\sigma^3 \left\{1 - \left(\alpha^3 - 1\right)\left(e^{\varepsilon/kT} - 1\right)\right\}.$$ **[6]**

In the limit that the range of the interaction becomes very large, while the depth of the attractive potential becomes very small, show that B_2 takes the form

$$B_2(T) = \frac{2}{3}\pi\sigma^3 \left(1 - \frac{\alpha^3\varepsilon}{kT}\right).$$ **[3]**

Continued over

Measurements of $B_2(T)$ for argon are plotted (as a function of *inverse* temperature) in the figure below.



What can you deduce, from this, about the inter-atomic interaction potential of argon? **[5]**

PART MARKS

3. (a) Give a statement of the *Third Law* of Thermodynamics. **[3]**

Discuss the microscopic origin of this law, paying particular attention to the question of the degeneracy of the ground state. **[4]**

(b) Show that the Third Law requires the heat capacity of bodies to go to zero as temperature $T \rightarrow 0$. The equipartition theorem implies a constant heat capacity. Explain the reason for this contradiction. **[3]**

(c) By writing the heat capacity (at constant volume) as $C_V = T\mathrm{d}S/\mathrm{d}T$, where S is the entropy, show that a constant heat capacity implies S varying as the *logarithm* of T. What would this imply about the $T \rightarrow 0$ entropy? **[3]**

Explain how this result may be understood in terms of the accessible regions of phase space. Then show how the incorporation of Quantum Mechanics recovers the Third Law of Thermodynamics. **[3]**

(d) It is sometimes stated that the Third Law of Thermodynamics implies the un-attainability of Absolute Zero. Show how a hypothetical system, violating the Third Law, can be used to reduce the temperature to $T = 0$ in a finite number of steps. Show how this is no longer possible if the system obeys the Third Law. **[4]**

PART MARKS

4. (a) The *Ising model* and the *Heisenberg model* are both models of ferromagnetism. In one case the transition corresponds to the breaking of a *discrete* symmetry, while in the other it corresponds to the breaking of a *continuous* symmetry. Explain this distinction, with particular reference to the nature of the order parameter of each model. **[4]**

(b) The essential qualitative features of these transitions are accounted for by the free energy

$$F = \text{const} \times \left\{ \left(\frac{T}{T_c} - 1 \right) \varphi^2 + \frac{1}{6} \varphi^4 \right\}.$$

(i) Sketch this free energy for different values of T/T_c, indicating how the system evolves as the transition proceeds.

(ii) What is the significance of T_c? **[4]**

(c) How is the free energy expression above modified in the presence of an applied magnetic field? **[2]**

(d) In the presence of an applied magnetic field one model exhibits hysteretic behaviour and the other does not. Explain this difference, particularly considering the fact that the free energy expression is formally the same for the two cases. **[6]**

(e) Explain, in principle, with the aid of diagrams, how one determines the limits of stability or the spinodal points in the hysteretic case. **[4]**

5. Write an essay on the Landau theory of phase transitions. You should include a discussion of: how this provides a common description of phase transition phenomena; the central assumptions of the theory; the application to both second order and first order transitions; and the limitations of the theory. **[20]**