UNIVERSITY OF LONDON

MSci EXAMINATION 2011

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

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

The total available marks add up to 60

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

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

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PART MARKS

1. (a) The partition function for a single particle of mass m at temperature T, in a box of volume V is given by

$$z = V\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2} = \frac{V}{\Lambda^3}.$$

Why is the quantity Λ referred to as the thermal de Broglie wavelength? **[3]**

(b) Explain why the partition function for a collection of N similar but distinguishable objects, each with partition function z, is given as

$$Z = z^N.$$ **[5]**

(c) On the assumption that (b) is correct for a gas of particles, show that the Helmholtz free energy for such a gas would be given by

$$F = -NkT\ln\left[V\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}\right].$$

[3]

(d) This expression gives a Helmholtz free energy that is *not extensive*. Explain what this means, and explain why this is a problem. **[4]**

(e) Discuss in detail how this problem may be resolved and give the resultant expression for F. **[5]**

2. (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) What is the order parameter for the *ferroelectric* transition? **[2]**

(c) When the Landau theory of phase transitions is applied to the ferroelectric transition the free energy is expressed by a polynomial of the form

$$F = F_0 + F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6,$$

where φ is the order parameter.

Explain why the power series is terminated and explain why there are no odd powers of φ in the expansion. **[4]**

(d) Show, by the use of sketches, how the above polynomial for the free energy can lead to a first-order transition. **[4]**

(e) Under what circumstances would the transition become second-order? **[3]**

(f) 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 what happens to this as the transition becomes second-order. **[4]**

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PART MARKS

3. (a) The virial expansion for a gas is given by

$$\frac{p}{kT} = \frac{N}{V} + \left(\frac{N}{V}\right)^2 B_2 + \left(\frac{N}{V}\right)^3 B_3 + \ldots;$$

here the B_n are the virial coefficients and the other symbols have their usual meaning. Under what conditions may the higher-order terms be ignored? **[2]**

(b) The van der Waals equation of state is written, in conventional form, as

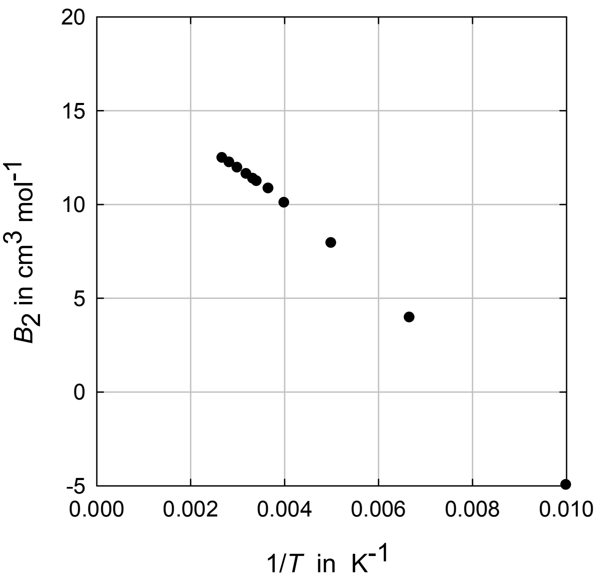
$$\left(p + a\frac{N^2}{V^2}\right)(v - Nb) = NkT\,.$$

Show that the second virial coefficient corresponding to this equation of state is

$$B_2 = b - \frac{a}{kT}\,.$$

[4]

(c) Measurements of the second virial coefficient of neon are shown in the figure below.



Estimate the values of the van der Waals parameters a and b. Be sure to state your units. Explain any approximations or assumptions. **[6]**

(d) The interaction between neon atoms is conventionally represented by the Lennard-Jones 6-12 potential

$$U(r) = \varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\};$$

what are ε and σ in this expression? **[2]**

(e) Outline briefly the arguments by which one makes the identification

$$a = \frac{4}{3}\pi\sigma^3\varepsilon \quad \text{and} \quad b = \frac{2}{3}\pi\sigma^3$$

and hence estimate ε and σ for argon. **[6]**

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PART MARKS

4. (a) Under what circumstances is the equilibrium state of a system determined by the minimum of the *Helmholtz* free energy, and under what circumstances is it determined by the minimum of the *Gibbs* free energy? **[2]**

(b) Discuss how a system may reduce its free energy by separating into regions of different density. What condition must the free energy satisfy for such a separation to occur? Is the system's order parameter *conserved* or *non-conserved*? **[3]**

(c) How does one determine the equilibrium state of such a system? **[3]**

(d) What is meant by the term *critical point*? **[2]**

(e) The free energy of mixing of a binary alloy may be written as

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

Explain the meaning of the various terms and the structure of this equation. **[2]**

(f) Show that this system has a critical temperature given by

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

[3]

(g) What is the value of x_c corresponding to this? **[2]**

(h) In what ways are the coexistence curves for the binary alloy and the liquid-gas system different; and in what ways are they similar? **[3]**

5. Write an essay on *The Second Law of Thermodynamics*, contrasting the ways that Einstein and Landau understood the Law. You should include a discussion of the relationship between the microscopic and the macroscopic approaches to the Law, and the importance of probability, mean values and fluctuations. **[20]**

END