UNIVERSITY OF LONDON

MSci EXAMINATION 2006

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/25

2005-06

GENERAL PHYSICAL CONSTANTS

Permeability of vacuum	μ_0	=	$4\pi \times 10^{-7}$	$\mathrm{H\,m^{-1}}$
Permittivity of vacuum	ε_0	=	8.85×10^{-12}	$\mathrm{F\,m^{-1}}$
	$1/4\pi\varepsilon_0$	=	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
	$\hbar = h/2\pi$	=	1.05×10^{-34}	J s
Boltzmann constant	k	=	1.38×10^{-23}	$\mathrm{J\,K^{-1}}$
Stefan-Boltzmann constant	σ	=	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

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

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

$$z = \frac{V}{\Lambda^3}$$

where the thermal de Broglie wavelength Λ is

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

(a) Why is Λ known as the thermal de Broglie wavelength? **[2]**

(b) Explain why the partition function Z of a gas of N identical particles may be written in terms of the partition function z of a single particle as

$$Z = \frac{1}{N!} z^N\,.$$

In particular, discuss the origin of the $N!$ term and the validity of this expression. **[5]**

(c) Write down the Helmholtz free energy in terms of the partition function and hence show that the free energy of the gas is given by

$$F = -NkT \ln\left(Ve/N\Lambda^3\right).$$

[5]

(d) What would the expression for the free energy be if the $N!$ term in the partition function were ignored? Why would such an expression be physically unacceptable? (Hint: Think how F would change if both N and V were doubled.) **[4]**

(e) Evaluate Λ for helium (^{4}He) gas at a pressure of 1 bar for temperatures of 3 K and 300 K and compare it with the mean distance between atoms. What physical meaning do you attach to these results? **[4]**

The mass of a ^{4}He atom is 6.64×10^{-27} kg.
Stirling's approximation: $\ln N! \simeq N\ln N - N$.

2. Write an essay on "The Arrow of Time". You should include a description of the problem in terms of *phase space* and you should include a discussion of *Liouville's theorem* and *Boltzmann's H theorem*. **[20]**

3. (a) The van der Waals equation of state for a fluid system is given by

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

Explain the form of this equation; in particular discuss the significance of the constants a and b, and how they account for the interactions between the particles. **[3]**

(b) Sketch a van der Waals p - V isotherm corresponding to liquid-gas coexistence. Indicate the *stable*, *metastable* and *unstable* regions of the curve. Sketch, also, an isotherm that indicates the *critical point*. **[3]**

(c) Show that the temperature and volume at the critical point are given by

$$kT_\mathrm{c} = \frac{8a}{27b}, \quad V_\mathrm{c} = 3Nb \, .$$

[4]

(d) Corrections to the ideal gas behaviour at low densities are conventionally written in terms of the virial expansion

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

Show that, for the van der Waals gas the second virial coefficient is given by $B_2\left(T\right) = b - a/kT$. **[3]**

(e) Experimental measurements of the second virial coefficient of Nitrogen yield

$$B_2\left(T\right) = -2.83\times10^{-29}\ \mathrm{m}^3 \quad \text{at} \quad T = 300\mathrm{K}$$
$$B_2\left(T\right) = -5.03\times10^{-30}\ \mathrm{m}^3 \quad \text{at} \quad T = 400\mathrm{K} \, .$$

Calculate the critical temperature that is predicted from these values. **[3]**

(f) The experimental value for the critical temperature of Nitrogen is found to be 126 K. Compare this with the value inferred from the second virial coefficient measurements and account for any discrepancy. **[2]**

(g) At 77K liquid Nitrogen normally boils at a pressure of one atmosphere. However it is possible, with care, to decrease the pressure below one atmosphere without boiling the liquid. With reference to the $p-V$ diagram describe this process and explain, in outline, how one may determine the minimum pressure at which this superheated liquid can exist (you are *not* required to calculate this). **[2]**

4. Write short notes on *two* of the following:

(a) Brownian motion; **[10]**

(b) universality and the classification of phase transitions; **[10]**

(c) the Ising model and its ubiquity. **[10]**

5. (a) What is meant by the term *order parameter* in the context of phase transitions? **[3]**

(b) Describe the behaviour of the order parameter in a first order transition and in a second order transition. **[3]**

(c) In the Landau treatment of phase transitions the appropriate free energy is expanded in powers of the order parameter. Discuss what considerations lead to the absence of terms from the expansion and what determines the order at which the expansion will be terminated. **[3]**

(d) Sketch the form of the free energy as a function of order parameter for a system exhibiting a second order transition, for temperatures above, equal to and below the critical temperature. **[3]**

(e) Show that, within the framework of the Landau model, the critical exponent, β, associated with the order parameter has the value $^1/_2$. **[6]**

(f) How does this compare with real systems? **[2]**

END