UNIVERSITY OF LONDON

MSci EXAMINATION 2013

For Students of the
University of London

<u>DO NOT TURN OVER UNTIL TOLD TO BEGIN</u>

PH4211: STATISTICAL MECHANICS

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

Answer **THREE** questions
No credit will be given for attempting any further questions

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

The total available marks add up to 120

All College-approved Calculators are permitted

GENERAL PHYSICAL CONSTANTS

Permeability of vacuum	μ_0	$=$	4π	$\times$	10^{-7}	H m^{-1}
Permittivity of vacuum	ε_0	$=$	8.85	$\times$	10^{-12}	F m^{-1}
	$1/4\pi\varepsilon_0$	$=$	9.0	$\times$	10^{9}	m F^{-1}
Speed of light in vacuum	c	$=$	3.00	$\times$	10^{8}	m s^{-1}
Elementary charge	e	$=$	1.60	$\times$	10^{-19}	C
Electron (rest) mass	m_{e}	$=$	9.11	$\times$	10^{-31}	kg
Unified atomic mass constant	m_{u}	$=$	1.66	$\times$	10^{-27}	kg
Proton rest mass	m_{p}	$=$	1.67	$\times$	10^{-27}	kg
Neutron rest mass	m_{n}	$=$	1.67	$\times$	10^{-27}	kg
Ratio of electronic charge to mass	e/m_{e}	$=$	1.76	$\times$	10^{11}	C kg^{-1}
Planck constant	h	$=$	6.63	$\times$	10^{-34}	J s
	$\hbar = h/2\pi$	$=$	1.05	$\times$	10^{-34}	J s
Boltzmann constant	k	$=$	1.38	$\times$	10^{-23}	J K^{-1}
Stefan-Boltzmann constant	σ	$=$	5.67	$\times$	10^{-8}	W m^{-2} K^{-4}
Gas constant	R	$=$	8.31			J mol^{-1} K^{-1}
Avogadro constant	N_{A}	$=$	6.02	$\times$	10^{23}	mol $^{-1}$
Gravitational constant	G	$=$	6.67	$\times$	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	$\times$	10^{-2}	m^{3}
One standard atmosphere	P_0	$=$	1.01	$\times$	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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1. The energy states of a *quantum* harmonic oscillator are given by

$$\varepsilon_n = \left(\frac{1}{2} + n\right)\hbar\omega$$

where the symbols have their usual meaning.

(a) Show that the partition function, Z, for this system may be written

$$Z = \frac{1}{2}\operatorname{cosech}\frac{\hbar\omega}{2kT}.$$

[5]

(b) By writing $\beta = 1/kT$, show that the internal energy may be obtained from Z as

$$E = -\frac{\partial \ln Z}{\partial \beta}.$$

[5]

(c) Hence obtain the following expression for E:

$$E = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}.$$

and comment on the structure of this expression. [5]

(d) The energy of the *classical* harmonic oscillator may be written

$$\varepsilon(p, x) = \frac{1}{2m}p^2 + \frac{k}{2}x^2.$$

By integrating $e^{-\varepsilon/kT}$ over p and x show that the partition function for the classical oscillator is

$$Z = kT/\hbar\omega$$

and explain what ω is. [5]

(e) Show that the internal energy for the classical oscillator is

$$E = kT.$$

[5]

(f) Show that at high temperatures the internal energy of the quantum oscillator may be expanded as

$$E = kT + \frac{\hbar^2\omega^2}{12kT} + \cdots .$$

[5]

(g) i. Sketch the classical and quantum internal energies as a function of temperature, indicating carefully where they agree and where they differ. [4]

ii. What would the figures look like if the quantum zero point motion were neglected. [3]

iii. It is sometimes stated that the zero point motion may be ignored as it has no measurable consequences. Comment on this in the light of the quantum-classical correspondence. [3]

You may find the following mathematical results helpful:

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}, \qquad \int_{-\infty}^{\infty} e^{-x^2}\mathrm{d}x = \sqrt{\pi},$$

$$\frac{\mathrm{d}}{\mathrm{d}z}\ln(\operatorname{cosech} z) = -\coth z, \quad \frac{1}{e^x - 1} \sim \frac{1}{x} - \frac{1}{2} + \frac{x}{12} + \cdots$$

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

$$F(\varphi) = F_0 + F_1\varphi + F_2\varphi^2 + F_3\varphi^3 + F_4\varphi^4 + \ldots.$$

(a) What is meant by the term *order parameter*? [4]

(b) What is the order parameter for i) the ferromagnetic transition, and ii) the ferroelectric transition? [4]

(c) In both the ferromagnetic transition and the ferroelectric transition the odd-order terms of the series are discarded. Why? [4]

(d) Why is the Landau expansion terminated, and what determines the highest power of the expansion? [4]

(e) In the ferromagnetic case show that there are three stationary points of $F(\varphi)$:

$$\varphi_+ = +\sqrt{-F_2/2F_4}, \quad \varphi_- = -\sqrt{-F_2/2F_4}, \quad \varphi_0 = 0.$$

[4]

(f) By choosing an appropriate temperature-dependence for F_2, show (i) that below the critical temperature T_c, $\mathrm{d}^2F/\mathrm{d}\varphi^2 > 0$ at the two roots φ_+ and φ_-, and (ii) that $\mathrm{d}^2F/\mathrm{d}\varphi^2 < 0$ at the root φ_0. Show (iii) that above T_c only the root φ_0 exists and (iv) that at this root $\mathrm{d}^2F/\mathrm{d}\varphi^2 > 0$.
Explain the physical significance of these points [20]

3. (a) Show that the partition function Z for a classical gas of N interacting particles may be written as

$$Z = Z_{\mathrm{id}} Q_N$$

where Z_{id} is the partition function for an ideal gas of non-interacting particles and the configuration integral Q_N is given by

$$Q_N = \frac{1}{V^N} \int e^{-\sum_{i<j} U(q_i,q_j)/kT} \mathrm{d}^{3N} q.$$

The symbols have their usual meanings. Be sure to explain the appearance of the V^N factor. [8]

(b) Show that the pressure of this gas may be expressed as

$$p = kT \left(\left. \frac{\partial \ln Z_{\mathrm{id}}}{\partial V} \right|_{T,N} + \left. \frac{\partial \ln Q_{\mathrm{N}}}{\partial V} \right|_{T,N} \right) = kT \left(\frac{N}{V} + \left. \frac{\partial \ln Q_{\mathrm{N}}}{\partial V} \right|_{T,N} \right)$$

[8]

(c) The interaction potential for a pair of *hard spheres* with centres a distance r apart is given by

$$\begin{aligned} U(r) &= \infty \qquad & r < \sigma \\ &= 0 \qquad & r > \sigma \end{aligned}$$

where σ is the hard core diameter.

Explain why the configuration integral Q_N for a hard-sphere gas is independent of temperature. Hence show that for such a gas p/kT is solely a function of the density N/V. What consequence does this have for the virial coefficients? [8]

(d) Argue that pV/NkT is a *universal function* of $\sigma^3 N/V$ and discuss ways that this universal equation of state may be determined. [8]

(e) Would you expect this gaseous system to exhibit a transition to an ordered phase? Explain your reasoning. [8]

4. Write an essay on 'The Arrow of Time'. You should include a discussion of the law of entropy increase, the nature of Liouville's theorem, the seeming incompatibility between these, and the resolution through coarse-graining. [40]

5. The partition function Z for an ideal classical gas of N identical particles of mass m at a temperature T is given by

$$Z = \frac{1}{N!} z^N \quad \text{where} \quad z = \frac{V}{\Lambda^3} \quad \text{and} \quad \Lambda = \sqrt{\frac{2\pi\hbar^2}{mkT}}.$$

Here z is the partition function for a single particle.

In the van der Waals approximation to the interacting classical gas the single-particle partition function is approximated by

$$z = \frac{V - V_{\mathrm{ex}}}{\Lambda^3} e^{-\varepsilon/kT}.$$

(a) By reference to a sketch of the inter-particle interaction, explain the rationale for the van der Waals approximation to z. [8]

(b) Show that the Helmholtz free energy for this system may be written

$$F = -NkT \ln \frac{z}{Ne}$$

and that, following from this the equation of state is

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

where

$$a = \frac{V^2}{N}\frac{\mathrm{d}\varepsilon}{\mathrm{d}V} \qquad \text{and} \qquad b = V_{\mathrm{ex}}/N.$$

[8]

(c) Sketch p as a function of V for a number of different temperatures indicating the liquid-gas coexistence region, the critical point and the gaseous region. [8]

(d) At the critical point the distinction between the gas and the liquid vanishes. The critical volume, pressure and temperature are given by

$$V_{\mathrm{c}} = 2Nb, \qquad p_{\mathrm{c}} = \frac{a}{4b^2}e^{-2}, \qquad kT_{\mathrm{c}} = \frac{a}{4b}$$

Explain how these expressions are obtained from the equation of state. [8]

(e) Thomas Andrew predicted the liquefaction temperature of carbon dioxide purely from measurements on the gas in the vicinity of room temperature. Discuss how he was able to do this. [8]

END