UNIVERSITY OF LONDON

MSci EXAMINATION 2015

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
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 van der Waals equation of state

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

where the symbols have their usual meanings, is found to provide a reasonable approximation to the behaviour of both the liquid and the gas phase of many substances.

(a) Make a labelled sketch of the interaction potential between two atoms. By reference to this sketch, outline briefly the arguments by which one may arrive at the van der Waals equation of state. [8]

(b) Sketch some isotherms of the van der Waals equation and identify gas and liquid regions. What is the *critical point*? Identify this point on your sketch. [5]

(c) Outline the arguments by which one identifies the critical temperature, pressure and volume as $kT_{\mathrm{c}} = 8a/27b$, $p_{\mathrm{c}} = a/27b^2$, $V_{\mathrm{c}} = 3Nb$. [5]

(d) The virial expansion for a gas is given by

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

where the B_n are the virial coefficients and the other symbols have their usual meanings. Under what conditions may the higher-order terms be ignored? [4]

(e) Show that the second virial coefficient for the van der Waals gas is

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

and sketch the variation of B_2 with temperature. [6]

(f) The *Boyle temperature* T_{B} is the temperature at which $B_2(T)$ goes through zero. Identify T_{B} on your sketch of $B_2(T)$. Show that, according to the van der Waals equation of state, $T_{\mathrm{c}} = \frac{8}{27}T_{\mathrm{B}}$. [5]

(g) The Boyle temperature of Argon is found to be 413 K. From this observation, what would the critical temperature be predicted to be? Argon's critical temperature is found to be 151 K. Compare your predicted value with this. Comment on the accuracy of the prediction and discuss possible reasons for any discrepancy. [7]

2. (a) What is *Brownian motion*? It has been stated that Brownian motion provides the definitive confirmation that atoms and molecules actually exist. Explain this statement. [7]

(b) In modelling the dynamics of a Brownian particle, Langevin wrote the force on the Brownian particle as

$$F(t) = f(t) - \frac{1}{\mu}v$$

where $f(t)$ is a randomly fluctuating force, v is the velocity and μ is the mobility of the particle. Discuss the separation of the force into these two parts. [6]

(c) Langevin's equation of motion for a Brownian particle of mass M may be written as

$$M\frac{\mathrm{d}v(t)}{\mathrm{d}t} + \frac{1}{\mu}v(t) = f(t)$$

and it has solution

$$v(t) = v(0)e^{-t/M\mu} + \frac{1}{M}\int\limits_0^\infty e^{-(t-\tau)/M\mu}f(\tau)\,\mathrm{d}\tau.$$

Describe how this solution arises and explain its implications. [7]

(d) The *mean square* velocity of the Brownian particle is given by

$$\langle v^2 \rangle = \frac{\mu}{M}\int\limits_0^\infty \langle f(0)f(t)\rangle\,\mathrm{d}t.$$

The expression $\langle f(0)f(t)\rangle$ is the *autocorrelation function* of the random force. What information about the random force is given by the autocorrelation function? Explain this. [7]

(e) The equipartition theorem gives $\langle v^2 \rangle = kT/M$, a *classical* result. This is true *even* if the Brownian particle is immersed in a quantum fluid. Why is this so? [6]

(f) Use of the equipartition expression allows one to write the mobility as a function of the force autocorrelation function and the temperature. Derive this expression. This is an example of the *Fluctuation-Dissipation theorem*. Explain what this means. [7]

3. In the Landau theory of phase transitions the free energy is expanded in powers of the order parameter to a finite number of terms.

   (a) In the context of phase transitions what is meant by the term *order parameter*? [4]

   (b) Why is the Landau expansion terminated, and what determines the highest power in the expansion? [6]

   (c) What is the distinction between a *conserved* order parameter and a *non-conserved* order parameter? Give an example of each. Describe how one determines the equilibrium state of the system in these two cases. [6]

   (d) Make a labelled sketch of the free energy for a binary alloy. Show curves for the temperature *above* and *below* the critical temperature. [6]

   (e) The free energy of mixing for the binary alloy may be written

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

   Explain the structure of this expression. [6]

   (f) The expansion of F_{m} may be written as

$$F_{\mathrm{m}} = F_0 + 2Nk\left\{(T-T_{\mathrm{c}})\left(x-\frac{1}{2}\right)^2 + \frac{2}{3}T_{\mathrm{c}}\left(x-\frac{1}{2}\right)^4 + \frac{16}{15}T_{\mathrm{c}}\left(x-\frac{1}{2}\right)^6 + \cdots\right..$$

   Discuss the Landau truncation of this expression; in particular explain at which term the series should be terminated. Why is the expansion written in powers of $x-\frac{1}{2}$? [6]

   (g) Within this model the order parameter critical exponent β has the value $1/2$. Show how this follows from the Landau free energy. The value $\beta = 1/2$ does *not* agree with experiment. Why is this? [6]

4. Write an essay on *negative temperatures*. You should include a description of what negative temperatures are, and the constraints on a system necessary for occurrence of negative temperatures. You should also describe how negative temperatures may be achieved, and give an example of a practical use of negative temperatures. [40]

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5. (a) Boltzmann's expression for entropy, $S = k \ln \Omega$ relates the macroscopic and the microscopic descriptions of the state of a system. Explain the meaning of the terms in this expression and discuss how it relates to the law of entropy increase. [10]

(b) Two isolated systems are brought into contact so that they may exchange energy, but without exchanging particles or doing work on each other. Show that the law of entropy increase leads to the concept of *temperature*; specifically demonstrate that systems will reach a state of equilibrium where their temperatures are equal, and explain what is meant by *equilibrium* in this context. [10]

(c) The demonstration in the previous part required that the entropy of the system be an *extremum* but there was no need for this extremum to be a *maximum*. Show that the requirement for the entropy to be a *maximum* has an important consequence for the *heat capacity*. [10]

(d) The *Third Law* of thermodynamics may be regarded as saying that as the temperature of a body goes to zero, the entropy goes to zero. Discuss how this may be understood from the perspective of the Boltzmann entropy expression. It is said that the Third Law follows as a consequence of quantum mechanics. Explain this. [10]

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