UNIVERSITY OF LONDON

MSc/MSci EXAMINATION 2018

For Students of the
University of London

DO NOT TURN OVER UNTIL TOLD TO BEGIN

PH4211: STATISTICAL MECHANICS
PH5911: 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

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

NEXT PAGE

1. In the Landau theory of phase transitions one expands an appropriate free energy in powers of the order parameter, to a finite number of terms.

   (a) What is meant by the term *order parameter*? [6]

   (b) Why is the Landau expansion terminated, and what determines the highest power in the expansion? [8]

   (c) There are no odd-power terms in the expansion, for both the ferromagnetic transition and the ferroelectric transition. Why is this? [6]

   (d) In the ferromagnetic case the Landau expansion has terms up to fourth power. Show, with the aid of diagrams, why such an expansion describes a second-order transition. [6]

   (e) In the ferroelectric case the Landau expansion has terms up to sixth power. Show, with the aid of diagrams, why such an expansion can describe a first-order transition. [6]

   (f) The ferroelectric transition can also become second-order. Discuss what requirements this puts on the sign of the terms in the Landau expansion. [8]

2. (a) By considering an isolated system containing a constraint, such as a dividing partition, explain using probabilistic arguments why the equilibrium state, upon removal of the constraint, corresponds to that of maximum entropy. [12]

   (b) Two systems are brought into contact so that they may exchange thermal energy, mechanical energy and particles. By using the appropriate definitions, show that the equilibrium state corresponds to that in which the temperatures, pressures and chemical potentials of the two systems are equalised. [16]

   (c) Since the equilibrium state has *maximum* entropy, this has implications for the *second derivative* of the entropy with respect to energy. Discuss the consequence of this for the heat capacity of the composite system. [12]

3. The free energy of mixing of a binary alloy may be written as

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

   (a) Explain the meaning of the various terms and the structure of this equation. [6]

   (b) Sketch the typical variation of F_{m} as a function of x at low and high temperatures. [6]

   (c) How does one determine the equilibrium state of this system? Indicate this on the sketch from Part (b). [6]

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

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

   Sketch and label this curve. Identify the *critical point*. [6]

   (e) By reference to the phase separation curve explain what happens as the system is cooled through the phase separation transition. [6]

   (f) The point on the phase separation curve at $T = T_{\mathrm{c}}$ is known as the *critical point*. Why is it called this? [4]

   (g) How would one determine the order parameter critical exponent β from the phase separation curve? What value is predicted by the expression in (d), and what value is found experimentally? Discuss the difference. [6]

4. Write an essay on the *Brownian Motion*. You should include a discussion of the observations of Robert Brown, and his inferences. You should go on to discuss Einstein's understanding of Brownian motion and his conclusions about the microscopic nature of matter. [40]

5. The partition function Z for a gas of N interacting atoms is given by

$$Z = \frac{1}{N!h^{3N}} \int e^{-\left(\sum_i \frac{p_i^2}{2m} + \sum_{i<j} U(q_i,q_j)\right)\Big/ kT} \,\mathrm{d}^{3N}p\,\mathrm{d}^{3N}q$$

where the symbols have their usual meaning.

(a) Show that Z may be expressed as

$$Z = Z_{\mathrm{id}} \frac{1}{V^N} \int e^{-\sum_{i<j} U(q_i,q_j)\big/ kT} \,\mathrm{d}^{3N}q \qquad \text{(Eq. 5.1)}$$

where Z_{id} is the partition function for an ideal (non-interacting) gas.

Be sure to explain the appearance of the V^N factor. [8]

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

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

where σ is the hard core diameter.

Sketch and label this interaction potential and relate σ to the radius of an atom in the gas. [4]

(c) The partition function for a gas of hard spheres might be approximated by

$$Z = Z_{\mathrm{id}} \left(\frac{V - Nb}{V}\right)^N .$$

Give a justification for this from the structure of Eq. 5.1. [6]

(d) The above approximation for the partition function leads to the equation of state

$$p(V - Nb) = NkT.$$

Express this equation in terms of the *virial expansion*

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

Hence find expressions for B_2 and B_3 and write down the general B_n. [8]

Question continued on next page

NEXT PAGE

(e) The virial coefficients for the hard sphere gas are independent of temperature. Why is this? [6]

(f) Exact calculations of the first few virial coefficients for the hard sphere gas give:

$$B_2 = b, \quad B_3 = \tfrac{5}{8}b^2, \quad B_4 = 0.29b^3$$

where $b = 2\pi\sigma^3/3$.

What do you conclude, by comparing these values with those you obtained in part (d) above? [8]

You may find this expansion useful in part (d)

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \ldots .$$

END