UNIVERSITY OF LONDON

MSc/MSci EXAMINATION 2014

For Students of the
University of London

DO NOT TURN OVER UNTIL TOLD TO BEGIN

PH4211: STATISTICAL MECHANICS
PH5211: STATISTICAL MECHANICS
PH5911: STATISTICAL MECHANICS
PH5211R and PH5911R: STATISTICAL MECHANICS - PAPER FOR RESIT CANDIDATES

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. (a) The ferromagnetic transition and the ferroelectric transition have similarities and differences. For each case:

    i. What is the order parameter? [4]

    ii. Is the order parameter conserved or non-conserved? [4]

    iii. What symmetry is broken at the transition? [4]

    iv. Is the broken symmetry continuous or discrete? [4]

    v. What is the order of the transition? [4]

   (b) Outline the arguments by which the Heisenberg Hamiltonian

$$\mathcal{H} = -J \sum_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

   is approximated, in mean field theory, by a local magnetic field

$$\mathbf{b} = \lambda \mathbf{M}$$

   where $\mathbf{M}$ is the magnetization and λ is a constant. [8]

   (c) The magnetization of a non-interacting assembly of N spin $1/2$ magnetic moments μ is given by

$$\frac{M}{M_0} = \tanh\left(\frac{M_0 B}{NkT}\right)$$

   where the saturation magnetisation is $M_0 = N\mu$ and the directions of $\mathbf{M}$ and the applied magnetic field $\mathbf{B}$ are parallel.

   Show that, in the presence of a Heisenberg interaction between the spins, in the mean field approximation the spontaneous magnetization is given by

$$\frac{M}{M_0} = \tanh\left(\frac{M}{M_0}\frac{T_\mathrm{c}}{T}\right)$$

   where $T_\mathrm{c} = \lambda M_0^2/Nk$. What is the interpretation of T_c? [8]

   (d) Sketch the behaviour of the spontaneous magnetization as a function of temperature and discuss the order of the transition. [4]

2. (a) The Boltzmann expression for entropy

$$S = k \ln \Omega$$

makes a connection between the macroscopic and the microscopic descriptions of matter. Explain the meaning of the terms in this expression and discuss how it is related to the law of entropy increase. [8]

(b) Show that when two isolated systems are brought into thermal contact they end up in the thermodynamic state for which

$$\frac{\partial \ln \Omega_1}{\partial E_1} = \frac{\partial \ln \Omega_2}{\partial E_2},$$

defining the terms Ω_1, Ω_2, E_1 and E_2 in this expression. How does this relate to temperature? [8]

(c) Now consider a small sub-system of a large isolated system. The total energy of the isolated system is E_t. The sub-system can exchange thermal energy with the large system. Show that when the sub-system is in a microstate of energy E the entropy of the combined system may be expressed as

$$S = S(E_\mathrm{t}) - E\frac{\partial S}{\partial E} + \frac{E^2}{2}\frac{\partial^2 S}{\partial E^2} + \cdots$$

[8]

(d) Show how the above result leads to the Boltzmann distribution function

$$P \propto e^{-E/kT},$$

explaining the meanings of the terms in this expression. You should include a clear justification for the truncation of the series at the first-order term. [8]

(e) Instead of expanding S in powers of E one might expand Ω. Discuss why, in this case, the series *cannot* be truncated. [8]

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

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

(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. [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. (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? [6]

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

$$Z = z^N.$$

[10]

(c) On the assumption that $Z = z^N$ is correct for a gas of particles, show that the Helmholtz free energy for such a gas would be given by

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

[6]

(d) This expression gives a Helmholtz free energy that is *not extensive*. Explain what this means, and explain why this is a problem. [8]

(e) Discuss in detail how this problem may be resolved and give the resultant expression for F. [10]

5. Write an essay on the Third Law of Thermodynamics. You should include a discussion of how the Law was discovered, the microscopic origins of the Law and its macroscopic consequences. You should also discuss whether negative temperatures are compatible with the Third Law. [40]

END