UNIVERSITY OF LONDON

MSc/MSci EXAMINATION 2017

For Students of the
University of London

DO NOT TURN OVER UNTIL TOLD TO BEGIN

PH4211: STATISTICAL MECHANICS
PH5211: 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

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

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1. (a) By the use of probability arguments explain why the equilibrium state of an isolated system corresponds to that of maximum entropy. [12]

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

   (c) Application of the above arguments to two systems exchanging *only* mechanical energy leads to the equality of p/T for the systems, whereas considerations of simple mechanical equilibrium would require just the equality of pressure. This is paradoxical.

      i. What is the paradox? [3]

      ii. Discuss the resolution of this paradox. [9]

2. The partition function Z for an ideal classical gas of N identical particles of mass m at a temperature T, in volume V 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

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

   (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

$$F = -NkT \ln \frac{ze}{N}.$$

   where $e = 2.718\ldots$. [8]

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(c) Show that, following from this expression for the free energy, the equation of state is

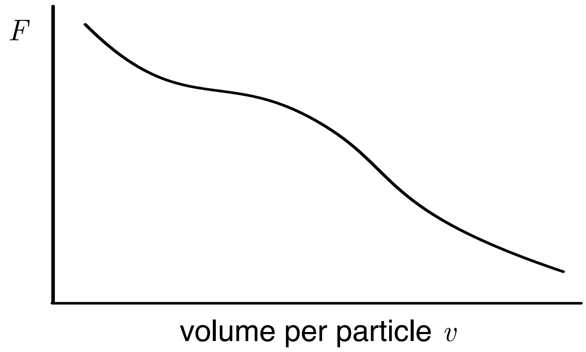
$$\left(p + a\frac{N^2}{V^2}\right)\left(V - Nb\right) = NkT$$

where

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

[8]

(d) Over a certain range of temperatures F has the following form.



You should draw a sketch of this and explain, using this sketch, how/why the system undergoes a phase transition to a coexisting state of fluid and gas. [8]

(e) In terms of the free energy curve, what determines the *critical point*? [8]

3. (a) Explain why a system in thermal equilibrium with a reservoir at temperature T has fluctuations in its energy E. [6]

(b) A measure of the size of the energy fluctuations is given by

$$\sigma_E = \left\langle (E - \langle E\rangle)^2 \right\rangle^{1/2}.$$

What does this expression mean? [6]

(c) Show that the mean square energy fluctuations are given by

$$\sigma_E^2 = \left\langle E^2 \right\rangle - \langle E\rangle^2.$$

[4]

(d) The mean energy of a system in thermal equilibrium at a temperature T may be written as

$$\langle E\rangle = \frac{1}{Z}\sum_j E_j\, e^{-E_j/kT}.$$

In terms of probabilities, explain where this expression comes from. [6]

(e) By considering the expression for the mean square energy $\langle E^2\rangle$ show that the size of the energy fluctuations may be written as

$$\sigma_E = \sqrt{kT^2 C_V}$$

where C_V is the thermal capacity of the system. [12]

(f) Discuss how the fluctuations depend on the size (number of particles) of the system. Thus show why, usually, fluctuations may be ignored, and give an example with explanation, where they are significant. [6]

4. When the mean field theory of phase transitions is applied to the ferromagnetic transition in the absence of a magnetic field, the free energy is given approximately, in the vicinity of the transition, by

$$F = \frac{Nk}{2}(T - T_{\mathrm{c}})m^2 + \frac{Nk}{12}T_{\mathrm{c}}m^4.$$

(a) Explain the structure of this expression and indicate what the various quantities are. [8]

(b) By sketching the form of this expression, explain how the transition occurs as the temperature is lowered through T_{c} and discuss the magnitude of the fluctuations in the vicinity of T_{c}. [8]

(c) Using the above expression show that in the vicinity of the transition

$$m = \sqrt{\frac{3(T_{\mathrm{c}} - T)}{T_{\mathrm{c}}}}$$

and sketch this behaviour. [10]

(d) What is the order of this transition? Explain your reasoning. [6]

(e) Show that below the transition there is a contribution to the entropy given by

$$\frac{3}{2}Nk\frac{T - T_{\mathrm{c}}}{T_{\mathrm{c}}}$$

and that this leads to a jump in the thermal capacity on cooling through the transition of

$$\Delta C = \frac{3}{2}Nk.$$

[8]

5. The microscopic laws of physics are *reversible*; this is exemplified by Liouville's theorem. But the macroscopic laws of physics are *irreversible*; this is exemplified by the Second Law of thermodynamics.

Write an essay discussing this apparent contradiction. You should discuss the reversibility of microscopic physics and the irreversibility of macroscopic physics. You should explain how the contradiction may be resolved by a consideration of the nature of the flow in phase space and you might also mention the possible role of quantum mechanics.

[40]

END