UNIVERSITY OF LONDON

MSc/MSci EXAMINATION 2020

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) The Boltzmann expression for entropy is written $S = k \ln \Omega$. Identify the terms in the equation, taking care to explain the meaning of Ω. [6]

   (b) By considering an isolated system containing a constraint, such as a dividing partition, explain clearly why the equilibrium state, upon removal of the constraint, corresponds to that of maximum entropy. [10]

   (c) 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 resultant equilibrium state corresponds to that in which the temperatures, pressures and chemical potentials of the two systems are equalized. [14]

   (d) Using the fact that the equilibrium state has maximum entropy, state what you can about the *second derivative* of the entropy with respect to energy of the composite system. Derive the implications for the heat capacity. [10]

2. (a) Write down the *virial expansion* for the equation of state of a non-ideal gas. Under what circumstances would an expansion up to only the second virial coefficient be appropriate? [6]

(b) The van der Waals equation of state for a non-ideal gas is given by

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

Show that the second virial coefficient for this gas is given by

$$B_2(T) = b - \frac{a}{kT}$$

and sketch this. [4]

(c) A gas of particles interacts with a square-well potential

$$\begin{aligned} U(r) &= \infty \qquad & 0 < r < \sigma \\ &= -\varepsilon \qquad & \sigma < r < \alpha\sigma \\ &= 0 \qquad & \alpha\sigma < r < \infty\,. \end{aligned}$$

Sketch this and explain the significance of the parameter σ, ε and α. [6]

(d) The second virial coefficient for a gas interacting with a potential $U(r)$ is given by

$$B_2(T) = -2\pi \int_0^\infty r^2 \left(e^{-U(r)/kT} - 1\right) \mathrm{d}r\,.$$

Show that for a square-well gas B_2 is given by

$$B_2(T) = \frac{2}{3}\pi\sigma^3\Big\{1 - \left(\alpha^3 - 1\right)\left(e^{\varepsilon/kT} - 1\right)\Big\}.$$

[12]

(e) In the limit that the range of the interaction becomes very large, while the depth of the attractive potential becomes very small, show that B_2 takes the form

$$B_2(T) = \frac{2}{3}\pi\sigma^3\left(1 - \frac{\alpha^3\varepsilon}{kT}\right)\,.$$

[6]

(f) By comparing this result with the van der Waals $B_2(T)$, discuss the interpretation of the van der Waals model in terms of the square well interaction. [6]

3. (a) Explain what is meant by the *order parameter* in the context of phase transitions and describe the difference in the behaviour of the order parameter for *first-order* and *second-order* transitions. [6]

   (b) What is the order parameter for the *ferroelectric* transition? [4]

   (c) When the Landau theory of phase transitions is applied to the ferroelectric transition the free energy is expressed as a polynomial of the form

$$F = F_0 + F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6$$

   where φ is the order parameter.

   Explain why the power series is terminated and explain why there are no odd powers of φ in the expansion. [8]

   (d) Show, by the use of sketches, how the above polynomial for the free energy can lead to a first-order transition. [8]

   (e) Under what circumstances would the transition become second-order? [6]

   (f) When the transition is first-order, show that the discontinuity in the order parameter at the transition is given by

$$\Delta\varphi = \sqrt{\frac{-F_4}{2F_6}}$$

   and discuss what happens to this as the transition becomes second-order. [8]

4. Albert Einstein wrote:

> A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability.
>
> Therefore the deep impression which classical thermodynamics made upon me; *it is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, will never be overthrown*.

And Lev Landau wrote:

> Statistical physics and thermodynamics together form a unit.
>
> All the concepts and quantities of thermodynamics follow most naturally, simply and rigorously from the concepts of statistical physics.
>
> Although the general statements of thermodynamics *can* be formulated non-statistically, their application to specific cases always requires the use of statistical physics.

Write an essay discussing these contrary views. You should:

- give examples supporting the Landau view, and examples supporting Einstein's view; [15]
- discuss the extent to which the work of both Landau and Einstein were actually more in line with the philosophy of the other; [15]
- include mention of *emergence* as a key concept that resolves the Landau-Einstein conflict. [10]

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5. (a) The partition function Z for a system of N indistinguishable non-interacting particles may be approximated by

$$Z = \frac{1}{N!} z^N$$

where z is the partition function for a single particle.
Explain the arguments that lead to this approximation. [6]

(b) The Helmholtz free energy $F = E - TS$ is given by

$$F = -kT \ln Z$$

where the symbols have their usual meanings. Show that the pressure p is given by

$$p = kT \left. \frac{\partial \ln Z}{\partial V} \right|_{T,N} .$$

[6]

(c) The partition function for a single particle moving freely in a volume V is given by

$$z = V \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} .$$

By evaluating the pressure for an assembly of N such indistinguishable particles, show that this results in the equation of state for an ideal gas. [6]

(d) The quantity $\Lambda = \sqrt{2\pi\hbar^2/mkT}$ is known as the *thermal de Broglie wavelength*. Explain the physical interpretation of this. [6]

(e) In the van der Waals description of an interacting gas the single particle partition function is approximated by

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

Discuss how the various features of the interparticle interaction are accounted for through the quantities V_{ex} and $\langle E \rangle$. [6]

(f) Why is this approach referred to as a *mean field* approximation? [4]

(g) Sketch a number of van der Waals $p - V$ isotherms and identify the stable, metastable, and unstable regions. [6]

END