

UNIVERSITY OF LONDON

MSc/MSci EXAMINATION 2022

For Students of the University of London

DO NOT TURN OVER UNTIL TOLD TO BEGIN

**PH4211: STATISTICAL MECHANICS
PH5211: STATISTICAL MECHANICS
PH5911: STATISTICAL MECHANICS
PAPER FOR FIRST SIT/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

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2021-22

GENERAL PHYSICAL CONSTANTS

Permeability of vacuum	μ_0	=	$4\pi \times 10^{-7}$	H m^{-1}
Permittivity of vacuum	ϵ_0	=	8.85×10^{-12}	F m^{-1}
	$1/4\pi\epsilon_0$	=	9.0×10^9	m F^{-1}
Speed of light in vacuum	c	=	3.00×10^8	m s^{-1}
Elementary charge	e	=	1.60×10^{-19}	C
Electron (rest) mass	m_e	=	9.11×10^{-31}	kg
Unified atomic mass constant	m_u	=	1.66×10^{-27}	kg
Proton rest mass	m_p	=	1.67×10^{-27}	kg
Neutron rest mass	m_n	=	1.67×10^{-27}	kg
Ratio of electronic charge to mass	e/m_e	=	1.76×10^{11}	C kg^{-1}
Planck constant	h	=	6.63×10^{-34}	J s
	$\hbar = h/2\pi$	=	1.05×10^{-34}	J s
Boltzmann constant	k_B	=	1.38×10^{-23}	J K^{-1}
Stefan-Boltzmann constant	σ	=	5.67×10^{-8}	$\text{W m}^{-2} \text{K}^{-4}$
Gas constant	R	=	8.31	$\text{J mol}^{-1} \text{K}^{-1}$
Avogadro constant	N_A	=	6.02×10^{23}	mol^{-1}
Gravitational constant	G	=	6.67×10^{-11}	$\text{N m}^2 \text{kg}^{-2}$
Acceleration due to gravity	g	=	9.81	m s^{-2}
Volume of one mole of an ideal gas at STP		=	2.24×10^{-2}	m^3
One standard atmosphere	P_0	=	1.01×10^5	N m^{-2}

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1. (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 a *ferromagnet*? [4]
- (c) When the Landau theory of phase transitions is applied to the ferromagnetic transition the free energy is expressed as a polynomial of the form

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

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 that in the ordered phase the order parameter is given by

$$\varphi = \sqrt{\frac{-F_2}{2F_4}}.$$

Discuss the sign and temperature dependence of the quantities in this equation, and show that this leads to a *second order* transition. [8]

- (e) How will the application of an external magnetic field modify the Landau free energy polynomial? [2]
- (f) In the Ising model the order parameter is a scalar. By sketching F as a function of φ show how the application of a magnetic field leads to *hysteresis* in this case. [6]
- (g) By contrast, explain why the Heisenberg magnet may not exhibit hysteresis. [6]

2. Write an essay on the concept of *temperature* in thermal physics.

- You should contrast the *microscopic* and the *macroscopic* views, including some historical context.
- You should discuss the consistency of the microscopic and the macroscopic approaches.
- You should include a discussion of the relevance of *equilibrium states*, the way such states emerge, and how they are characterised.

[40]

3. (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. [8]

- (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

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

Discuss how the various features of the inter-particle 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? [3]

- (g) Sketch a van der Waals isotherm indicating the *spinodal point(s)*. What are the special features of the spinodal point? [5]

4. (a) Explain what is meant by *phase space* in the context of classical Statistical Mechanics and contrast the Boltzmann and the Gibbs conception of phase space. [6]
- (b) Sketch and contrast the trajectories of an undamped harmonic oscillator and a damped harmonic oscillator in phase space. [6]
- (c) Give an expression for the entropy of a classical system in terms of ρ , the density of points in phase space. [5]
- (d) Liouville's theorem states that as a system evolves in time the density of points in phase space remains constant. This is incompatible with the Second Law of thermodynamics. Explain clearly this contradiction. [7]
- (e) Outline the resolution of this paradox by the use of coarse graining and discuss how quantum mechanics might be invoked to justify the procedure. [8]
- (f) State the *Third Law* of thermodynamics. Explain how this is understood from quantum mechanics. Contrast this with the prediction of classical mechanics. [8]

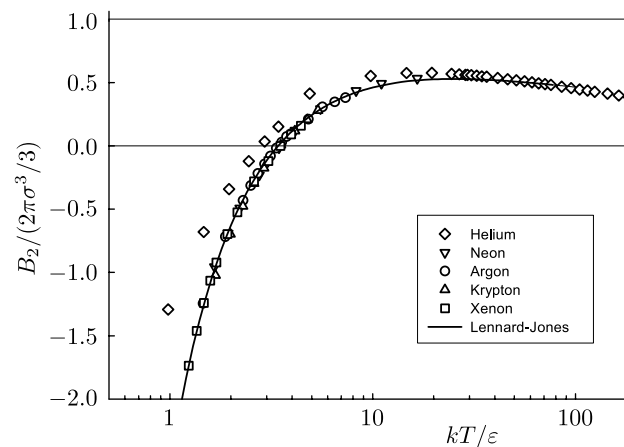
5. The second virial coefficient for an interacting (classical) gas is given by

$$B_2(T) = -2\pi \int_0^\infty r^2 (e^{-U(r)/kT} - 1) dr$$

where $U(r)$ is the interaction potential. The Lennard-Jones 6–12 interaction potential is

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right].$$

The figure shows the second virial coefficient for the inert gases.



- (a) Make a labelled sketch of $U(r)$, indicating ϵ and σ . [4]
- (b) i. What special feature of the interaction potential results in the collapse of the $B_2(T)$ points of the different gases onto the common curve? (Ignore helium.) [6]
 ii. Using a suitable change of integration variable in the integral for $B_2(T)$, show that the Lennard-Jones $U(r)$ does indeed lead to such a collapse. [10]
- (c) i. Sketch the form of $B_2(T)$ for a square well potential (with a hard core), showing how this differs from the Lennard-Jones $B_2(T)$, particularly at high temperatures. [6]
 ii. Explain the difference and discuss what information this might give about the short-distance form of the interaction potential. [8]
- (d) The $B_2(T)$ low temperature points for helium fall away from the universal curve. Explain this. [6]

END