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

- Handwrite your answers on paper, and write your candidate number and the module number at the top of each page. Photograph/scan the pages and keep the original paper versions, as they may be required by the examiners.
- For each question you attempt, please clearly state the question number.
- Please DO NOT include your name or Student ID Number anywhere on your work.
- **Academic Misconduct** We will check all assignments for academic misconduct. Suspected offences will be dealt with under the College's formal Academic Misconduct procedures. Please remember:
  - The work submitted is expected to be your own work and only your work. You may not ask for help from any source, or copy anyone else's work.
  - You must not give help to anyone else, including sending them any parts of the questions or copies of your solutions.
- **Submitting your work:**
  - Your document must be submitted through Moodle using the submission link in the module Moodle page. If possible please convert your document into a PDF document to make the submission process quicker and easier.
  - Emailed submissions will not be accepted.
  - **You must complete your exam upload within 1 hour of the exam finish time.**

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

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

1. (a) The free energy of mixing for the binary alloy may be written

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

Define the symbols and explain the origin of the two terms on the right hand side of this equation. [8]

(b) Make a labelled sketch of $F_{\mathrm{m}}(x)$ for a temperatures (i) *above*, (ii) *equal to*, and (iii) *below* T_{c}. Describe the important features of the curves – particularly in the $T = T_{\mathrm{c}}$ case. [8]

(c) Qualitatively explain how the equilibrium state of the system, at temperatures below T_{c}, is determined. Describe the nature of this state. [6]

(d) In the vicinity of the critical point F_{m} may be expanded as

$$F_{\mathrm{m}} = F_0 + 2Nk\left\{(T-T_{\mathrm{c}})\left(x-\frac{1}{2}\right)^2 + \frac{2}{3}T_{\mathrm{c}}\left(x-\frac{1}{2}\right)^4 + \frac{16}{15}T_{\mathrm{c}}\left(x-\frac{1}{2}\right)^6 + \cdots\right.$$

i. Why is the expansion expressed in powers of $(x-\frac{1}{2})$? [4]

ii. Although the binary alloy exhibits a *first order* phase transition, the Landau expansion of F_{m} above is terminated at the *second* term. Why might this seem surprising, and what is the explanation? [4]

(e) Within this model the order parameter critical exponent β has the value $\frac{1}{2}$. Show how this follows from the Landau free energy. The value $\beta = \frac{1}{2}$ does *not* agree with experiment. Why is this? [10]

2. Statistical Mechanics is based upon rather limited postulates. But again and again, arguments are invoked whereby the postulates are extended beyond their initial domain of applicability.

Write an essay on this topic. You should discuss, in particular, how one moves from isolated systems to open systems, and how one moves from equilibrium systems to non-equilibrium systems. [40]

3. (a) The virial equation of state for a non-ideal gas is given by

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

where the symbols have their usual meaning. Under what circumstances would an expansion up to the second virial coefficient be appropriate? [3]

(b) The interaction potential between two particles may be modelled with a *square well potential*:

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

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

(c) 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 the square well potential, B_2 is given by

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

[9]

(d) What is the $T \to \infty$ limit of this $B_2(T)$. Explain the significance of this. [8]

(e) The *Boyle temperature* T_B is the temperature for which $B_2(T)$ is zero. Show that

$$T_\mathrm{B} = \frac{\varepsilon/k}{\ln\left(\frac{\alpha^3}{\alpha^3 - 1}\right)} \,.$$

[4]

(f) Some measurements of $B_2(T)$ for xenon are shown in the figure below (plotted against $1/T$):

Question continued on next page

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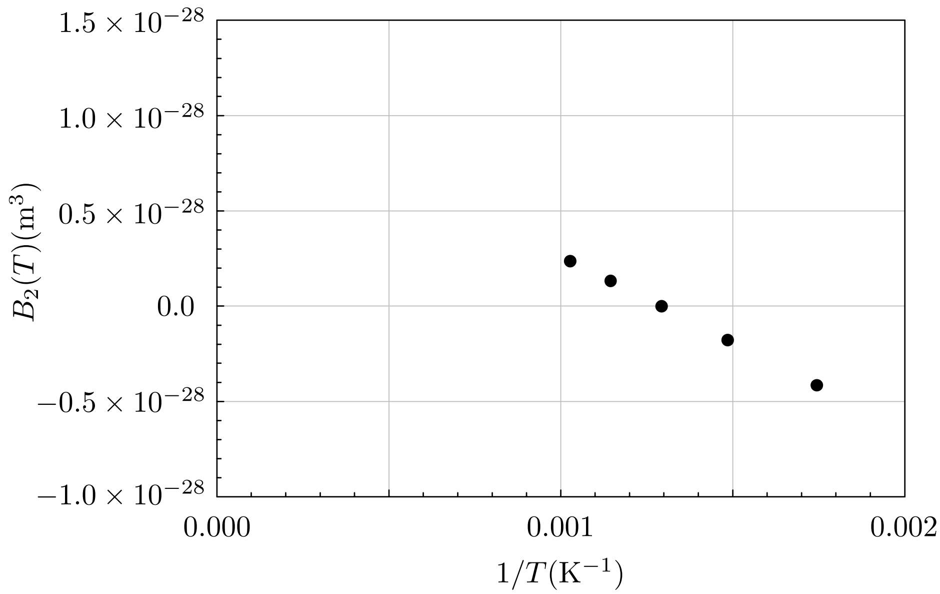


Using the results of (d) and (e) above, find estimates for the interaction parameters σ and ε. You should assume that α takes the typical value of 1.6.

[10]

4. (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

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

Explain the structure of this expression. [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

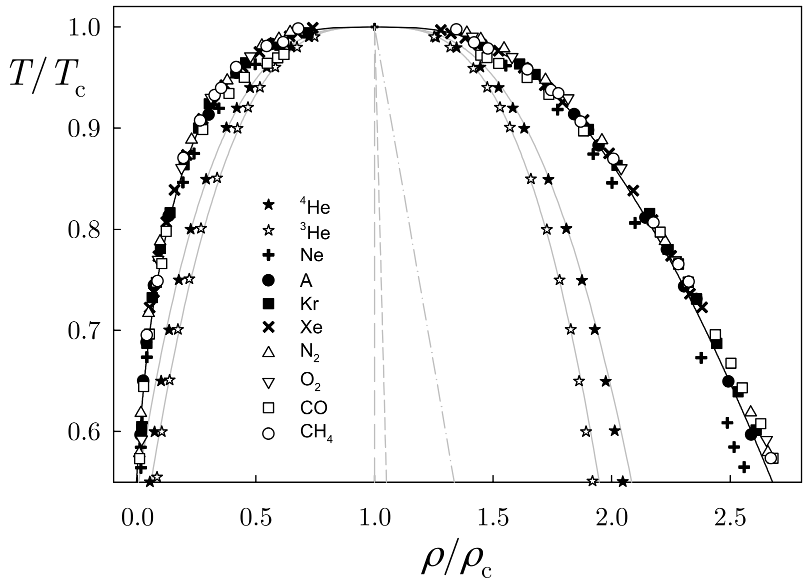
$$\sigma_E = \sqrt{kT^2 C_V}$$

where C_V is the thermal capacity of the system.
(Hint: remember the "beta trick".) [12]

(f) Discuss how the fluctuations depend on the size (number of particles) of the system. Thus show why, usually, fluctuations may be ignored. [4]

(g) Discuss the case of fluctuations at the critical point in the light of this result. [2]

5. The “Guggenheim plot” showing the liquid–gas coexistence curve of a selection of gases is shown in the figure.



(a) Explain clearly what the axes of the plot represent. [8]

(b) Most of the points (ignoring helium) fall on a single curve. Explain the microscopic origin of this feature. [9]

(c) In the *vicinity of the critical point* the data are well-approximated by

$$\frac{\rho - \rho_c}{\rho_c} = \frac{3}{4}\left(1 - \frac{T}{T_c}\right) \pm \frac{7}{4}\left(1 - \frac{T}{T_c}\right)^{1/3}.$$

i. The exponent $1/3$ is known as the *order parameter* critical exponent. Why is this? [5]

ii. The helium data fall away from this curve. Explain why. [5]

iii. Nevertheless, the order parameter critical exponent for the helium data is found to be $1/3$. Explain this. [5]

(d) The Guggenheim plot is often regarded to be the first demonstration of *universality* in phase transitions. Discuss the extent to which this is really true. [8]

END