

NATIONAL UNIVERSITY OF SINGAPORE

PC2230 Thermodynamics and Statistical Mechanics

(Semester II: AY 2016-17)

Time Allowed: 2 Hours

INSTRUCTIONS

1. Write down your student ID number. Do not write down your name.
2. This examination paper contains **FOUR** questions and comprises **THREE** pages.
3. Answer **ANY THREE** questions.
4. All questions carry equal marks.
5. Start each question on a fresh page.
6. This is a **CLOSED BOOK** examination.
7. Programmable calculators are **NOT** allowed.
8. A list of constants is provided.
9. One help sheet (A4 size, both sides, handwritten, lettering size no smaller than 12 points) is allowed.

Explain your working clearly. State all principles and assumptions used, and explain all symbols used. Express your answers in the simplest form.

1. (i) The density of allowed modes for standing waves in a three-dimensional enclosure is $D(k) = Vk^2/(2\pi^2)$, where k is the wavevector and V the volume of the enclosure. Use this information to show that, in the Debye model, the lattice heat capacity at constant volume of an insulating crystal of N atoms is given by

$$C_V = 3Nk \left[\frac{3}{x_D^3} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \right],$$

where $x = \hbar\omega/(kT)$, $x_D = \Theta_D/T$, ω , k , and Θ_D being the mode frequency, Boltzmann constant, and Debye temperature, respectively.

State all assumptions made.

- (ii) Determine C_V for temperatures (a) $T \gg \Theta_D$, and (b) $T \ll \Theta_D$. Discuss your answers with reference to the Dulong and Petit Law, and the third law of thermodynamics.
 (iii) State the physical significance of the Debye temperature.

$$\left[\text{Note: } \cosh x \approx 1 + \frac{x^2}{2!} + \frac{x^4}{4!} + \dots \quad (x \ll 1); \quad \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4\pi^4}{15} \right]$$

2. A paramagnetic crystal comprising N dipoles is placed in a magnetic field B . The crystal comprises a very large number N of dipoles, each with magnetic moment μ and a spin of $1/2$. There are n dipoles oriented parallel to the field and the rest are antiparallel to it.

- (a) Determine the energy of the crystal.
 (b) Determine the entropy of the crystal.
 (c) The crystal is next immersed in a heat reservoir at temperature T .

(i) Find the mean energy \bar{E} of the crystal in terms of $x [\equiv \mu B/(kT)]$, where k is the Boltzmann constant.

(ii) Hence, and using the answer to part (a), determine the temperature

dependence of n . $\left[\text{Note: } \tanh^{-1} y = \frac{1}{2} \ln \frac{1+y}{1-y} \right]$

(iii) Find the Helmholtz function of the crystal.

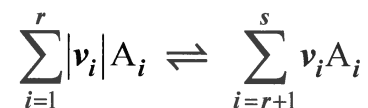
(iv) Hence, determine the net magnetic moment of the crystal.

3. A system, with a fixed number of three identical boson gas particles, is in equilibrium at temperature T . The system has four single-particle states labeled $i = 1, 2, 3$ and 4 , with respective energies $\varepsilon_i = \varepsilon, 2\varepsilon, 3\varepsilon$ and 4ε .
- Determine the partition function of the system.
 - Hence, determine (a) the mean energy and (b) the entropy of the system.
 - Calculate the mean occupation number \bar{n}_3 of the state $i = 3$.

Express all your answers in terms of ε .

4. (a) A certain monovalent metal has an atomic density of 4.5×10^{28} atoms/m³, and a Debye temperature of 350 K.
- Calculate its Fermi energy (in electron volts) and Fermi temperature (in kelvins).
 - Hence, determine its heat capacity at constant volume per unit volume at 5 K.
- Express your answer in SI units.

- (b) A chemical reaction of perfect gases is represented by



where A_i are the chemical formulas and ν_i the stoichiometric coefficients of the gases $i = 1, 2, 3, \dots, s$ ($\nu_1, \nu_2, \dots, \nu_r$ are negative for reactants, and $\nu_{r+1}, \nu_{r+2}, \dots, \nu_s$ are positive for products). If the temperature T and volume V of the system are kept constant, show that the heat of reaction at constant volume is

$$Q_V = kT^2 \frac{d}{dT} \ln K_C(T),$$

where k is the Boltzmann constant, the equilibrium constant is $K_C(T) \equiv \prod_i [f_i(T)]^{\nu_i}$ and f_i is the single-particle partition function per unit volume of gas i .

(KMH)

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