NATIONAL UNIVERSITY OF SINGAPORE

PC2230 THERMODYNAMICS AND STATISTICAL MECHANICS

(Semester II: AY 2018-19)

Time Allowed: 2 Hours

INSTRUCTIONS TO CANDIDATES

1. Please write your student number only. **Do not write your name.**
2. This examination paper contains **EIGHT (8)** questions and comprises **FIVE (5)** printed pages.
3. Students are required to answer **ALL** questions in Part I and **ALL** questions in Part II.
4. Students should write the answers for each question on a new page.
5. This is a **CLOSED** book examination. You are allowed however to bring in **ONE** A4-sized help sheet.
6. Specific permitted devices: non-programmable calculators.

PART I

Question 1 **[8=3+5]**

Using the various thermodynamic potentials for a system of gas with a fixed number of particles, prove the following identities:

(a) $\left(\frac{\partial E}{\partial S}\right)_T = -P^2 \left[\frac{\partial}{\partial P}\left(\frac{T}{P}\right)\right]_V,$

(b) $\left(\frac{\partial T}{\partial P}\right)_H = \frac{T^2}{C_P} \left[\frac{\partial}{\partial T}\left(\frac{V}{T}\right)\right]_P.$

Question 2 **[8=3+5]**

Unlike an ideal gas, which cools down during an adiabatic expansion, a one-dimensional rubber band (with spring constant α and equilibrium position $x_0 = 0$) is increasing its temperature during adiabatic elongation.

(a) Write down the fundamental equation in the internal energy representation in the differential form for the rubber band. Define clearly all variables in your equation.

(b) If the rubber band is elongated isothermally, is the entropy increased, decreased or has no change? Substantiate your answer with calculations. You may assume that the rubber band follows Hooke's law and ignore the variation of the spring constant throughout the process.

Question 3 **[8=4+4]**

A physical system, having energy E, is composed of N identical but distinguishable particles. Each particle can be found in the state with energy 0 or $\epsilon > 0$. The ground state is not degenerate while the excited state has degeneracy $g = 4$.

(a) Find the entropy $S(E, N)$ of this system using microcanonical ensemble.

(b) Hence, find the ratio of the occupation numbers, N_2/N_1, for the two energy levels as a function of T. What is the value of this ratio in the limit of high temperatures?

Question 4 **[8=5+3]**

A system of two-dimensional gas, confined in the xy-plane, consists of N non-interacting particles. The Hamiltonian of each particle is

$$H(x, y, p_x, p_y) = \frac{1}{2m}\left(p_x^2 + p_y^2\right) + \frac{1}{2}m\omega^2\left[a\left(x^2 + y^2\right) + 2bxy\right],$$

where m, ω, a and b are constants with $a > 0$ and $a^2 > b^2$.

(a) Find the canonical partition function for this system.

(b) Find the heat capacity for this system. Is your result consistent with the classical equipartition theorem? Explain.

Question 5 **[8=3+5]**

Consider the equilibrium of a single-phase system in which the chemical reaction

$$\sum_{j=1}^{s} \nu_j A_j = 0,$$

occurs under constant temperature and constant volume.

(a) Derive the chemical equilibrium condition for this system.

(b) Now, consider an ideal gas formed by atoms of type A and atoms of type B. These atoms can bound to each other and form the molecule A_2B according to the reaction

$$2A_2 + B_2 \rightleftharpoons 2A_2B,$$

taking place at temperature T in a volume V. If N_A, N_B, N_{A_2B} are the numbers ($\gg 1$) of particles for the species at chemical equilibrium, show that

$$\frac{N_{A_2B}^2}{N_A^2 N_B} = \frac{f_{A_2B}^2}{f_A^2 f_B},$$

where $f_X \equiv f_X(T, V)$, $X = A, B, A_2B$, is the single-particle canonical partition function.

END OF PART I

PART II

Question 6 **[20=4+8+8]**

The following data apply to the triple point of H_2O.

Temperature: $0.01°\mathrm{C}$;
Pressure: $4.6\,\mathrm{mm\,Hg}$
Specific volume of solid: $1.12\,\mathrm{cm}^3/\mathrm{g}$
Specific volume of liquid: $1.00\,\mathrm{cm}^3/\mathrm{g}$
Heat of melting: $334.72\,\mathrm{J/g}$
Heat of vaporization: $2510.4\,\mathrm{J/g}$

(a) Sketch a P-T diagram for H_2O which need not be to scale but which should be qualitatively correct. Label the various phases and triple point.

(b) The pressure inside a container enclosing H_2O, which is maintained at $T = -1.0°\mathrm{C}$, is slowly reduced from an initial value of $10^5\,\mathrm{mm\,Hg}$. Describe what happens and *estimate* the pressure at which the phase changes occur. Assume the vapor phase behaves like an ideal gas.

(c) Show that the change in specific latent heat with temperature $\mathrm{d}L/\mathrm{d}T$ at a point (P, T) along a phase equilibrium line is given by

$$\frac{\mathrm{d}L}{\mathrm{d}T} = \frac{L}{T} + (C_{P_1} - C_{P_2}) - (\alpha_1 V_1 - \alpha_2 V_2)\,\frac{L}{V_1 - V_2}\,.$$

Here, C_{P_i} is the constant-pressure heat capacity, V_i is the specific volume and α_i is the isobaric expansivity of respective phases.

Useful information: Molar mass of water $= 18.0\,\mathrm{g/mol}$, Boltzmann constant $k = 1.38 \times 10^{-23}\,\mathrm{J/K}$

Question 7 **[20=6+10+4]**

A one-dimensional array of N lattice sites is in thermal equilibrium at temperature T. These sites can be closed (with energy 0) or open (with energy ϵ). A signal is produced from open sites and can transmit from left to right. The signal can be transmitted from an open site, only if its nearest neighbour is open. The first site of the array always produces a signal that can transmit up to a given point of the lattice. From that point onwards, there cannot be any other production of signals.

(a) Find the canonical partition function of the system.

(b) Find the average number of open sites $\langle n \rangle$ and the fluctuation of the number of open sites $\langle (\Delta n)^2 \rangle$.

(c) Show that $\langle n \rangle$ and $\langle (\Delta n)^2 \rangle$ are independent of N at low temperatures. Explain.

Question 8 **[20=10+10]**

Both energy and particle number of a system described by the grand canonical ensemble fluctuate because the system can exchange energy and particles with the reservoir at constant temperature T and constant chemical potential μ.

(a) Applying purely thermodynamic considerations, establish the following relation

$$\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial V}{\partial P}\right)_{T,\langle N \rangle} \left[\left(\frac{\partial P}{\partial \mu}\right)_{T,V}\right]^2 .$$

Hence, show that

$$\frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle^2} = \frac{\kappa_T}{\beta V},$$

where κ_T is the isothermal compressibility.

(b) Evaluate the grand canonical partition function of the classical ideal gas. Hence, show that

$$\frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle^2} = \frac{1}{\langle N \rangle}, \qquad \frac{\langle (E - \langle E \rangle)^2 \rangle}{\langle E \rangle^2} = \frac{5}{3}\frac{1}{\langle N \rangle},$$

for the classical ideal gas.

END OF PART II

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END OF PAPER