

1. One-component thermodynamical system (20 marks)

For a system that can be characterized by entropy S , volume V , and mole number n , show that

$$v \left(\frac{\partial P}{\partial v} \right)_T = \left(\frac{\partial \mu}{\partial v} \right)_T,$$

where $v = V/n$ is the molar volume.

2. Ideal classical gas (20=12+8 marks)

An atom in a gas has the velocity vector $\mathbf{v} = \mathbf{p}/m$ and moves at the speed $|\mathbf{v}|$.

(a) Find the average speed $\langle |\mathbf{v}| \rangle$ and also the average reciprocal speed $\langle |\mathbf{v}|^{-1} \rangle$ for the atoms of an ideal classical gas at temperature T . Confirm that $\langle |\mathbf{v}| \rangle \langle |\mathbf{v}|^{-1} \rangle \geq 1$.

(b) Demonstrate that, quite generally, the inequality $\langle X \rangle \langle X^{-1} \rangle \geq 1$ holds for any positive quantity X .

Hint: Consider $\langle (\lambda X^{\frac{1}{2}} - X^{-\frac{1}{2}})^2 \rangle$ and adjust the value of the parameter λ .

3. An Ising-type model (40=15+5+15+5 marks)

Consider a one-dimensional chain (or ring) of particles with N next-neighbor links and no on-site energy. The energy of the k th microstate is

$$E_k = -J \sum_j s_j s_{j+1} \quad \text{with } s_j = 0 \text{ or } +1 \text{ or } -1.$$

Note that we have the additional option of $s_j = 0$ here, while there is only $s_j = \pm 1$ in the standard Ising model.

(a) Show that the canonical partition function is

$$Q(K, N) = \left(\cosh(K) + \frac{1}{2} + \sqrt{[\cosh(K) - \frac{1}{2}]^2 + 2} \right)^N$$

where $K = \beta J$.

(b) What is the free energy per site?

(c) Determine the heat capacity per site at low temperatures ($K \gg 1$) and high temperatures ($K \ll 1$). In both cases, state the leading term.

(d) Confirm that this system obeys the Third Law.

Hint: A 3×3 matrix of the form $\begin{pmatrix} a & 1 & b \\ 1 & 1 & 1 \\ b & 1 & a \end{pmatrix}$ has $\begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$ as an eigencolumn.

4. Berthelot gas (20 marks)

The equation of state of the Berthelot gas is

$$P(T, v) = \frac{RT}{v - b} - \frac{a}{v^2 RT},$$

where v is the molar volume and a and b are positive material constants. Determine all the virial coefficients $a_1(\beta)$, $a_2(\beta)$, $a_3(\beta)$, \dots .