Problem 1 (**40**=20+10+10 marks)
The thermodynamical equilibrium states of a single-substance gas are fully specified by T, V, and n — the temperature, the volume, and the number of moles, respectively. The isothermal equation of state of the gas under consideration is

$$P^2V = \text{constant when } T \text{ and } n \text{ are constant,}$$

and its adiabatic equation of state is

$$PV^2 = \text{constant when } S \text{ and } n \text{ are constant,}$$

where P is the pressure and S is the entropy. From these equations of state, we want to draw conclusions about C_V and C_P, the heat capacities for constant volume and constant pressure.

(a) Explain why there must be functions $a(S/n) > 0$ and $b(T) > 0$ such that

$$P = \frac{a(S/n)}{(V/n)^2} = \frac{b(T)}{\sqrt{V/n}}\,,$$

and conclude that $a(s) = \dfrac{s^3}{3w}$ and $b(T) = \dfrac{1}{3}\sqrt{wT^3}$ with a material constant w.

(b) What is the SI unit of w? What is the relation between PV and TS?

(c) Now use statements in Section 1.10 of the lecture notes to find the values of $\dfrac{C_P}{C_V}$ and $\dfrac{C_P - C_V}{PV/T}$.

Hint: In Part (a), recognize two differential equations, one for $U(S, V, n)$, the other for $F(T, V, n)$, and recall how T and S are related to one another; ensure that $a(S/n)$ is consistent with $b(T)$. — Parts (b) and (c) can be answered without first completing Part (a).

Problem 2 (**20**=10+5+5 marks)
The thermal equation of state for the van der Waals gas is

$$P = \begin{cases} \dfrac{nRT}{V-nb} - \dfrac{an^2}{V^2} & \text{outside the coexistence region,} \\ P(T) & \text{inside the coexistence region,} \end{cases}$$

where $P(T)$ is the coexistence pressure at temperature T.

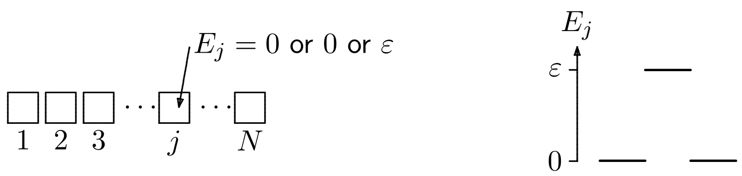
(a) What is $C_P - C_V$ outside the coexistence region?

(b) What do you get for $C_P - C_V$ at the critical point?

(c) There is no meaningful value of $C_P - C_V$ inside the coexistence region. Why?

Problem 3 (**15** marks)
In the microcanonical ensemble, we have the entropy $S(E, V, N)$ and can solve for the internal energy $E = U(S, V, N)$. In the canonical ensemble, we have the free energy $F(\beta, V, N) = -\beta^{-1}\log\big(Q(\beta, V, N)\big)$ and the expected energy $\langle E\rangle = -\left(\dfrac{\partial \log Q}{\partial \beta}\right)_{V,n}$. Show that $\langle E\rangle = F + \beta\left(\dfrac{\partial F}{\partial \beta}\right)_{V,n}$ and then infer that $U = \langle E\rangle$.

Problem 4 (**25**=5+5+5+5+5 marks)
We consider a model system in which we have N noninteracting constituents:



Each constituent has two degenerate ground states and one excited state. That is, we have the possible energy values 0, 0, and $\varepsilon > 0$ for each constituent.

(a) For the microcanonical ensemble, find the entropy $S(E, N)$. Then express E as a function of $N\varepsilon$ and $\beta\varepsilon$.

(b) For the canonical ensemble, find the free energy $F(\beta, N)$ and the expected energy $\langle E\rangle$.

(c) Confirm that the two ensembles are equivalent.

(d) How large are the energy fluctuations in the canonical ensemble?

(e) What is the partition function $Z(\beta, z)$ of the grand-canonical ensemble?