$\boxed{\mathbf{1}}$ We recall that the internal energy is a function of the form $U(S,V,n) = nU(S/n,V/n,1)$ and the free energy is of the form $F(T,V,n) = nF(T,V/n,1)$, and the pressure is the negative V derivative of both U and F.

(a) Accordingly, the isothermal equation tells us that

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,n} = \frac{b(T)}{\sqrt{V/n}}$$

with $b(T)$ to be determined, and the adiabatic (= isentropic) equation tells us that

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,n} = \frac{a(S/n)}{(V/n)^2}$$

with $a(s)$ to be determined. We conclude that

$$F(T,V,n) = -2\sqrt{Vn}\,b(T) + nf_0(T)$$

with some function $f_0(T)$, and that

$$U(S,V,n) = \frac{a(S/n)}{V/n^2} + nu_0(S/n)$$

with some function $u_0(S/n)$. It follows that temperature and entropy are related to one another by

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,n} = 2\sqrt{Vn}\,b'(T) - nf_0'(T)$$

and also by

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n} = \frac{a'(S/n)}{V/n} + u_0'(S/n)\,.$$

Consistency requires that

$$a(s) = (V/n)^{\frac{3}{2}} b\big((V/n)^{-1}a'(s) + u_0'(s)\big)$$

and also that

$$b(T) = (V/n)^{-\frac{3}{2}} a\Big(2(V/n)^{\frac{1}{2}} b'(T) - f_0'(T)\Big)\,.$$

We infer that $u_0'(s) = 0$ and $f_0'(T) = 0$, and that $a(s) = c_a s^3$ and $b(T) = c_b T^{\frac{3}{2}}$ with proportionality constant c_a and c_b. They are such that $27c_a c_b^2 = 1$, so that $c_a = \frac{1}{3w}$ and $c_b = \frac{1}{3}\sqrt{w}$ is a convenient parameterization.

(b) The SI unit of w is that of $S^3/(PV^2)$ or of P^2V/T^3, that is $\mathrm{J^2\,K^{-3}\,m^{-3}}$ or $\mathrm{J^2\,K^{-3}\,m^{-3}\,mol^{-1}}$, depending on whether we think of n as just a number or as a count of moles. Since

$$(PV)^3 = P^2V\,PV^2 = \frac{wn}{9}T^3\,\frac{1}{3wn}S^3 = \frac{1}{27}(TS)^3\,,$$

we have $TS = 3PV$.

(c) The ingredients of (1.10.11) are provided by the isothermal equation,

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_{P,n}\left(\frac{\partial P}{\partial T}\right)_{V,n} = T\,\frac{3V}{T}\,\frac{3P}{2T} = \frac{9}{2}\frac{PV}{T}\,.$$

Both the isothermal and the isentropic equation provide the ingredients of (1.10.22),

$$\frac{C_P}{C_V} = \left(\frac{\partial P}{\partial V}\right)_{S,n}\left(\frac{\partial V}{\partial P}\right)_{T,n} = \frac{-2P}{V}\,\frac{-2V}{P} = 4\,.$$

$\boxed{2}$

(a) Here, too, we exploit (1.10.11), but now with

$$0 = \frac{nR}{V-nb} - \left[\frac{nRT}{(v-nb)^2} - \frac{2an^2}{V^3}\right]\left(\frac{\partial V}{\partial T}\right)_{P,n} \quad\text{and}\quad \left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{nR}{V-nb}\,,$$

so that

$$C_P - C_V = nR\left[1 - \frac{2an}{RT}\frac{(V-nb)^2}{V^3}\right]^{-1}\,.$$

(b) At the critical point, we have $V = 3nb$ and $RT = \dfrac{8a}{27b}$, so that

$$\frac{2an}{RT}\frac{(V-nb)^2}{V^3} = 2an\frac{27b}{8a}\frac{(2b)^2}{(3b)^3} = 1$$

and $C_P - C_V = \infty$.

(c) Inside the coexistence region, there is no $\mathrm{d}T \neq 0$ when $\mathrm{d}P = 0$ and, therefore, there is no meaning to $C_P = T\left(\dfrac{\partial S}{\partial T}\right)_{P,n}$.

$\boxed{3}$ Since

$$\langle E\rangle = -\left(\frac{\partial \log Q}{\partial \beta}\right)_{V,n} = \left(\frac{\partial(\beta F)}{\partial \beta}\right)_{V,n}$$

$$= F + \beta \left(\frac{\partial F}{\partial \beta}\right)_{V,n} = F - T \left(\frac{\partial F}{\partial T}\right)_{V,n} = F + TS = U\,,$$

the inference is an immediate consequence of the Legendre transformation between U and F.

$\boxed{\mathbf{4}}$ With n_1 and n_2 constituents in the two ground states, and n_3 constituents in the excited state, the energy is $E = n_3\varepsilon$.

(a) For given energy E, there are $n_3 = E/\varepsilon$ constituent in the excited state and $n_1 + n_2 = N - n_3$ constituents in the two ground states. Accordingly, we have

$$\Omega(E, N) = \frac{N!}{n_3!\,(N - n_3)!}\,2^{N-n_3}\bigg|_{n_3\,=\,E/\varepsilon}$$

microstates, where the power of 2 is the count of the different ways of assigning the two ground states to $N - n_3$ constituents, and obtain

$$\begin{aligned} S(E,N) &= k_\mathrm{B}\log\Big(\Omega(E,N)\Big) \\ &= k_\mathrm{B}N\left[\left(1 - \frac{E}{N\varepsilon}\right)\log\left(\frac{2}{1 - \frac{E}{N\varepsilon}}\right) - \frac{E}{N\varepsilon}\log\frac{E}{N\varepsilon}\right]\,. \end{aligned}$$

after using Stirling's approximation for the log-factorials. Then,

$$k_\mathrm{B}\beta = \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N = \frac{k_\mathrm{B}}{\varepsilon}\log\frac{N\varepsilon - E}{2E}\,,$$

which gives

$$E = \frac{N\varepsilon}{2\mathrm{e}^{\beta\varepsilon} + 1}\,.$$

(b) For the canonical ensemble, we have $Q(\beta, N) = q(\beta)^N$ with

$$q(\beta) = \sum_{E=0,0,\varepsilon} \mathrm{e}^{-\beta E} = 2 + \mathrm{e}^{-\beta\varepsilon}$$

and get

$$F(\beta, N) = -\frac{1}{\beta}\log Q = -\frac{N}{\beta}\log\Big(2 + \mathrm{e}^{-\beta\varepsilon}\Big)$$

as well as

$$\langle E\rangle = -\left(\frac{\partial \log Q}{\partial \beta}\right)_N = \frac{N\varepsilon}{2\mathrm{e}^{\beta\varepsilon} + 1}\,.$$

(c) Consistent with the general argument of Problem 3, we observe that

$$\langle E \rangle \Big|_{\text{canonical}} = E \Big|_{\text{microcanonical}} .$$

(d) In accordance with (2.5.17), we have

$$\langle \delta E^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = -\left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_N = \frac{2N\varepsilon^2 \mathrm{e}^{\beta\varepsilon}}{(2\mathrm{e}^{\beta\varepsilon}+1)^2} = \frac{2\mathrm{e}^{\beta\varepsilon}}{N} \langle E \rangle^2$$

for the variance and

$$\frac{\sqrt{\langle \delta E^2 \rangle}}{\langle E \rangle} = \sqrt{2\mathrm{e}^{\beta\varepsilon}/N} \propto \frac{1}{\sqrt{N}}$$

for the relative size of the fluctuations.

(e) Following Exercise 25, we have

$$Z(\beta, z) = \sum_{N=0}^{\infty} z^N Q(\beta, N) = \frac{1}{1 - zq(\beta)} = \frac{1}{1 - 2z - z\mathrm{e}^{-\beta\varepsilon}} .$$
