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

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

and also that

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

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 $J^2 K^{-3} m^{-3}$ or $J^2 K^{-3} m^{-3} \text{mol}^{-1}$, depending on whether we think of $n$ as just a number or as a count of moles. Since

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

we have $TS = 3PV$.

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

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

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

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

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

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

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

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

and $C_P - C_V = \infty$.

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

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 \( F \).

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

\[ S(E, N) = k_B \log \left( \Omega(E, N) \right) \]

\[ = k_B N \left[ \left( 1 - \frac{E}{N \varepsilon} \right) \log \left( \frac{2}{1 - \frac{E}{N \varepsilon}} \right) - \frac{E}{N \varepsilon} \log \frac{E}{N \varepsilon} \right]. \]

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

\[ k_B \beta = \frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_N = \frac{k_B \varepsilon}{\log N \varepsilon - E} \]

which gives

\[ E = \frac{N \varepsilon}{2 e^{\beta \varepsilon} + 1}. \]

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

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

and get

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

as well as

\[ \langle E \rangle = -\left( \frac{\partial \log Q}{\partial \beta} \right)_N = \frac{N \varepsilon}{2 e^{\beta \varepsilon} + 1}. \]
(c) Consistent with the general argument of Problem 3, we observe that
\[ \langle E \rangle \bigg|_{\text{canonical}} = E \bigg|_{\text{microcanonical}}. \]

(d) In accordance with (2.5.17), we have
\[ \langle \delta E^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = -\left( \frac{\partial \langle E \rangle}{\partial \beta} \right)_N = \frac{2N\varepsilon^2 e^{\beta \varepsilon}}{(2e^{\beta \varepsilon} + 1)^2} = \frac{2e^{\beta \varepsilon}}{N} \langle E \rangle^2 \]
for the variance and
\[ \frac{\sqrt{\langle \delta E^2 \rangle}}{\langle E \rangle} = \sqrt{2e^{\beta \varepsilon}/N} \propto \frac{1}{\sqrt{N}} \]
for the relative size of the fluctuations.

(e) Following Exercise 25, we have
\[ Z(\beta, z) = \sum_{N=0}^{\infty} z^N Q(\beta, N) = \frac{1}{1 - z q(\beta)} = \frac{1}{1 - 2z - ze^{-\beta \varepsilon}}. \]