**1**

**(a)** Since $U, S, L, n$ are extensive variables, we have first

$$U(\lambda S, \lambda L, \lambda n) = \lambda U(S, L, n) \quad \text{for} \quad \lambda > 0$$

and then

$$\begin{aligned} U(S, L, n) &= \frac{\partial}{\partial\lambda} U(\lambda S, \lambda L, \lambda n)\bigg|_{\lambda=1} \\ &= S\left(\frac{\partial U}{\partial S}\right)_{L,n} + L\left(\frac{\partial U}{\partial L}\right)_{S,n} + n\left(\frac{\partial U}{\partial n}\right)_{S,L} \\ &= ST + L\tau + n\mu\,, \end{aligned}$$

where $T, \tau, \mu$ are functions of $S, L, n$.

**(b)** In terms of $U(S, L, n)$, the equation of state is the differential equation

$$\left(S\frac{\partial}{\partial S} - 3L\frac{\partial}{\partial L}\right)U(S, L, n) = 0\,,$$

which is solved by any function of $S^3L$. Proper scaling requires the form

$$U(S, L, n) = nf(S^3L/n^4)$$

with an undetermined function $f(\ )$. We also know that

$$\tau L^{1/2} = L^{1/2}\frac{\partial}{\partial L}U(S, L, n) = \frac{1}{2}\frac{\partial}{\partial\sqrt{L}}U(S, L, n)$$

does not depend on $L$, which tells us that

$$f(S^3L/n^4) = (\text{const})\sqrt{S^3L/n^4} + (\text{const'})\,.$$

We can put $(\text{const'}) = 0$ because this contribution to

$$U(S, L, n) = (\text{const})\sqrt{S^3L/n^2} + (\text{const'})n$$

is of no thermodynamic consequence — it is just a fixed energy per rubber particle.

**(c)** For $U \propto \sqrt{S^3 L/n^2}$, we have

$$TS = S\frac{\partial U}{\partial S} = \frac{3}{2}U\,, \qquad \tau L = L\frac{\partial U}{\partial L} = \frac{1}{2}U\,, \qquad \mu n = n\frac{\partial U}{\partial n} = -U\,,$$

and

$$TS + \tau L + \mu n = \left(\frac{3}{2} + \frac{1}{2} - 1\right)U = U\,.$$

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**2**

**(a)** For the critical values, the first and the second derivative of the right-hand side of the equation of state with respect to $v$ must equal $0$. Except for the replacement $a \to a/(RT_{\mathrm{cr}})$, the pair of equations is the same as for the van der Waals gas. Therefore, we have

$$v_{\mathrm{cr}} = 3b \quad \text{and} \quad RT_{\mathrm{cr}} = \frac{8}{27}\frac{a}{bRT_{\mathrm{cr}}}\,,$$

so that

$$RT_{\mathrm{cr}} = \sqrt{\frac{8a}{27b}} = \frac{2}{3}\sqrt{\frac{2a}{3b}} \quad \text{and} \quad p_{\mathrm{cr}} = \frac{1}{12b}\sqrt{\frac{2a}{3b}}\,.$$

It follows that

$$\frac{p_{\mathrm{cr}}v_{\mathrm{cr}}}{T_{\mathrm{cr}}} = \frac{3}{8}R\,.$$

**(b)** With $p(T,v)$ given by the equation of state, we have

$$\overline{p}(T) = p\Big(T, v^{(1)}(T)\Big) = p\Big(T, v^{(2)}(T)\Big)\,.$$

Accordingly,

$$\frac{xp_{\mathrm{cr}}}{T_{\mathrm{cr}}} = \left.\frac{\mathrm{d}\overline{p}(T)}{\mathrm{d}T}\right|_{T=T_{\mathrm{cr}}} = \left(\frac{\partial p}{\partial T}\right)_v (T_{\mathrm{cr}}, v_{\mathrm{cr}}) + \left(\frac{\partial p}{\partial v}\right)_T (T_{\mathrm{cr}}, v_{\mathrm{cr}})\frac{\mathrm{d}v^{(1\text{ or }2)}}{\mathrm{d}T}(T_{\mathrm{cr}})\,,$$

where the second term vanishes at the critical point, and the first term gives

$$\frac{xp_{\mathrm{cr}}}{T_{\mathrm{cr}}} = \frac{R}{v_{\mathrm{cr}} - b} + \frac{aR}{(v_{\mathrm{cr}}RT_{\mathrm{cr}})^2} = \frac{R}{2b} + \frac{3R}{8b} = \frac{7R}{8b}\,.$$

Since $p_{\mathrm{cr}}/T_{\mathrm{cr}} = R/(8b)$, we have $x = 7$ and

$$\overline{p}(T) = p_{\mathrm{cr}}\left(7\frac{T}{T_{\mathrm{cr}}} - 6\right) \quad \text{for} \quad T_{\mathrm{cr}} - T \ll T_{\mathrm{cr}}\,.$$

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**3** For simplicity, we keep the common $X$ dependence implicit, that is: $\Omega(E)$ stands for $\Omega(E, X)$, $Q(\beta)$ stands for $Q(\beta, X)$, etc.

**(a)** We have $\beta F(\beta) = -\log Q(\beta)$, $S = -\frac{\partial F}{\partial T}$, and $(U =)E = F + TS$. Therefore,

$$\frac{S}{k_\mathrm{B}} = \log \Omega(E) = \beta E - \beta F = \beta E + \log Q(\beta) \quad \text{or} \quad \Omega(E) = Q(\beta)\mathrm{e}^{\beta E}$$

with

$$E = F - T\frac{\partial F}{\partial T} = E + \beta\frac{\partial F}{\partial \beta} = \frac{\partial(\beta F)}{\partial \beta} = -\frac{\partial \log Q(\beta)}{\partial \beta} = -\frac{1}{Q(\beta)}\frac{\partial Q(\beta)}{\partial \beta}$$

or

$$EQ(\beta) = -\frac{\partial Q(\beta)}{\partial \beta}\,.$$

**(b)** Now we have $S = k_\mathrm{B}\log\Omega(E)$, $\beta = \frac{\partial(S/k_\mathrm{B})}{\partial E} = \frac{\partial \log \Omega(E)}{\partial E}$, and

$$\log Q(\beta) = -\beta F(\beta) = \beta(TS - E) = \log \Omega(E) - \beta E$$
$$\text{or} \quad Q(\beta) = \Omega(E)\mathrm{e}^{-\beta E}$$

with $E$ such that

$$\beta = \frac{1}{\Omega(E)}\frac{\partial \Omega(E)}{\partial E} \quad \text{or} \quad \beta\Omega(E) = \frac{\partial \Omega(E)}{\partial E}\,.$$

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**4**

**(a)** Since

$$\langle n_j\rangle = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_j}\log Z = -\frac{1}{\beta Z}\frac{\partial Z}{\partial \varepsilon_j}\,,$$

we have

$$\langle n_j n_{j'}\rangle = \frac{1}{\beta^2 Z}\frac{\partial}{\partial \varepsilon_j}\frac{\partial Z}{\partial \varepsilon_{j'}} = -\frac{1}{\beta Z}\frac{\partial}{\partial \varepsilon_j}\Big(\langle n_{j'}\rangle Z\Big) = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_j}\langle n_{j'}\rangle + \langle n_j\rangle\langle n_{j'}\rangle\,,$$

so that

$$\begin{aligned}\langle n_j n_{j'}\rangle - \langle n_j\rangle\langle n_{j'}\rangle &= -\frac{1}{\beta}\frac{\partial\langle n_{j'}\rangle}{\partial \varepsilon_j} = -\delta_{jj'}\frac{1}{\beta}\frac{\partial\langle n_j\rangle}{\partial \varepsilon_j} = \delta_{jj'}\frac{\langle n_j\rangle^2}{\beta}\frac{\partial\langle n_j\rangle^{-1}}{\partial \varepsilon_j} \\ &= \delta_{jj'}\frac{\langle n_j\rangle^2}{\beta}\beta\mathrm{e}^{\beta(\varepsilon_j-\mu)} = \delta_{jj'}\langle n_j\rangle^2\left(\frac{1}{\langle n_j\rangle}\mp 1\right) \\ &= \delta_{jj'}\langle n_j\rangle\Big(1\mp\langle n_j\rangle\Big)\,.\end{aligned}$$

**(b)** We have

$$\langle \delta N^2 \rangle = \sum_{j,j'} \Big( \langle n_j n_{j'} \rangle - \langle n_j \rangle \langle n_{j'} \rangle \Big) = \sum_j \langle n_j \rangle \Big( 1 \mp \langle n_j \rangle \Big) = \langle N \rangle \mp \sum_j \langle n_j \rangle^2 ,$$

and said consistency follows from

$$\begin{aligned} \frac{\partial \langle N \rangle}{\partial(\beta\mu)} &= \sum_j \frac{\partial \langle n_j \rangle}{\partial(\beta\mu)} = - \sum_j \langle n_j \rangle^2 \frac{\partial}{\partial(\beta\mu)} e^{\beta\varepsilon_j - \beta\mu} = \sum_j \langle n_j \rangle^2 e^{\beta\varepsilon_j - \beta\mu} \\ &= \sum_j \langle n_j \rangle^2 \Big( \langle n_j \rangle^{-1} \mp 1 \Big) = \sum_j \langle n_j \rangle \Big( 1 \mp \langle n_j \rangle \Big) . \end{aligned}$$

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