In the Gibbs–Duhem relation \(0 = SdT - VdP + Nd\mu\), we consider changes for constant \(T\) and \(N\), that is \(dT \rightarrow 0\), \(dP \rightarrow (dP)_{T,N}\), and \(d\mu \rightarrow (d\mu)_{T,N}\). Then

\[
0 = 0 - V \left( \frac{\partial P}{\partial V} \right)_{T,N} + N \left( \frac{\partial \mu}{\partial V} \right)_{T,N} \quad \text{or} \quad N \left( \frac{\partial \mu}{\partial V} \right)_{T,N} = V \left( \frac{\partial P}{\partial V} \right)_{T,N}.
\]

See also (2.9.14)–(2.9.16) in the lecture notes.

Below the critical temperature, there are molar volumes \(v\) for which

\[
\frac{\partial P(T, v)}{\partial v} = P(T, v) \left[ -\frac{1}{v - b} + \frac{a}{v^2 RT} \right] = 0
\]

or

\[
\left( v - \frac{a}{2RT} \right)^2 = \left( \frac{a}{2RT} \right)^2 - \frac{ab}{RT}.
\]

This requires \(RT < \frac{a}{4b}\), so that the critical temperature is \(T_{cr} = \frac{a}{4bR}\) and the critical molar volume is \(v_{cr} = \frac{a}{2RT_{cr}} = 2b\). For the critical pressure, we find

\[
P_{cr} = P(T_{cr}, v_{cr}) = \frac{a}{4b^2} e^{-2}.\]

Together, they give \(\frac{P_{cr}v_{cr}}{T_{cr}} = 2e^{-2}R\).

We know that

\[
\left. \frac{dP(T)}{dT} \right|_{T_{cr}} = \left. \frac{\partial P(T, v)}{\partial T} \right|_{T_{cr}, v_{cr}}.
\]

Here, this gives

\[
\left. \frac{dP(T)}{dT} \right|_{T_{cr}} = \left( \frac{1}{T} + \frac{a}{vRT^2} \right) P(T, v) \Bigg|_{T_{cr}, v_{cr}} = \left( 1 + \frac{a}{v_{cr}RT_{cr}} \right) \frac{P_{cr}}{T_{cr}} = 3 \frac{P_{cr}}{T_{cr}}.
\]

Therefore, we have

\[
P(T) = \left( 3 \frac{T}{T_{cr}} - 2 \right) P_{cr}
\]

for temperatures just below the critical temperature.

We have, quite simply,

\[
\sum_{N=0}^{\infty} z^N Q(\beta, V, N) = \sum_k e^{-\beta E_k} \sum_{N=0}^{\infty} z^N \delta_{N,N_k} = \sum_k e^{-\beta E_k} z^{N_k}
\]

\[
= \sum_k e^{-\beta E_k} e^{\beta \mu N_k} = \sum_k e^{-\beta (E_k - \mu N_k)} = Z(\beta, V, z).
\]
(b) Since
\[ Z(\beta, V, z) = e^{Vz/\lambda^3} = \sum_{N=0}^{\infty} \frac{1}{N!} \left( \frac{Vz}{\lambda^3} \right)^N = \sum_{N=0}^{\infty} \frac{z^N}{N!} \left( \frac{V}{\lambda^3} \right)^N, \]
we read off that \( Q(\beta, V, N) = \frac{1}{N!} \left( \frac{V}{\lambda^3} \right)^N. \)

4

(a) \( F \) is intensive because it has the same value independent of the number of particles.

(b) The canonical partition function is
\[ Q(\beta, F, N) = \frac{1}{N!} \left[ \int \frac{(d\mathbf{r})(d\mathbf{p})}{(2\pi \hbar)^3} e^{-\beta \left( \frac{1}{2m} \mathbf{p}^2 + F \mathbf{r} \right)} \right]^N, \]
where [see Problem 3(b)]
\[ \int \frac{(d\mathbf{p})}{(2\pi \hbar)^3} e^{-\beta \frac{1}{2m} \mathbf{p}^2} = \frac{1}{\lambda^3} \]
and
\[ \int (d\mathbf{r}) e^{-\beta F \mathbf{r}} = 4\pi \int_0^\infty dr \, r^2 e^{-\beta F r} = \frac{8\pi}{(\beta F)^3}. \]
Accordingly, we have
\[ Q(\beta, F, N) = \frac{1}{N!} \left( \frac{8\pi}{(\lambda \beta F)^3} \right)^N. \]

(c) We have, \( \frac{1}{N} \langle E \rangle = -\frac{1}{N} \frac{\partial}{\partial \beta} \log Q(\beta, F, N) = -\frac{9}{2\beta} = \frac{9}{2} k_B T \) since \( Q \propto \beta^{-9N/2}. \)

(d) We note that the kinetic energy is inversely proportional to the mass \( m \) and the potential energy is proportional to \( F \), and \( Q(\beta, F, N) \propto m^{3N/2} F^{-3N}. \) Therefore, we have
\[ \frac{1}{N} \langle E_{\text{kin}} \rangle = \frac{m}{N \beta \partial m} \log Q(\beta, F, N) = \frac{3}{2\beta} = \frac{3}{2} k_B T = \frac{1}{3} \left( \frac{\langle E \rangle}{N} \right), \]
and
\[ \frac{1}{N} \langle E_{\text{pot}} \rangle = -\frac{F}{N \beta \partial F} \log Q(\beta, F, N) = \frac{3}{\beta} = 3k_B T = \frac{2}{3} \left( \frac{\langle E \rangle}{N} \right). \]
Clearly, \( \langle E_{\text{kin}} \rangle + \langle E_{\text{pot}} \rangle = \langle E \rangle. \)