$\boxed{1}$ In the Gibbs–Duhem relation $0 = S\mathrm{d}T - V\mathrm{d}P + N\mathrm{d}\mu$, we consider changes for constant T and N, that is $\mathrm{d}T \to 0$, $\mathrm{d}P \to (\mathrm{d}P)_{T,N}$, and $\mathrm{d}\mu \to (\mathrm{d}\mu)_{T,N}$. 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.

$\boxed{2}$

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

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

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 $T_{\mathrm{cr}} = \frac{a}{4bR}$ and the critical molar volume is $v_{\mathrm{cr}} = \frac{a}{2RT_{\mathrm{cr}}} = 2b$. For the critical pressure, we find $P_{\mathrm{cr}} = P(T_{\mathrm{cr}}, v_{\mathrm{cr}}) = \frac{a}{4b^2}\mathrm{e}^{-2}$. Together, they give $\frac{P_{\mathrm{cr}}v_{\mathrm{cr}}}{T_{\mathrm{cr}}} = 2\mathrm{e}^{-2}R$.

(b) We know that $\left.\frac{\mathrm{d}P(T)}{\mathrm{d}T}\right|_{T_{\mathrm{cr}}} = \left.\frac{\partial P(T,v)}{\partial T}\right|_{T_{\mathrm{cr}},v_{\mathrm{cr}}}$. Here, this gives

$$\left.\frac{\mathrm{d}P(T)}{\mathrm{d}T}\right|_{T_{\mathrm{cr}}} = \left(\frac{1}{T} + \frac{a}{vRT^2}\right)P(T,v)\Big|_{T_{\mathrm{cr}},v_{\mathrm{cr}}} = \left(1 + \frac{a}{v_{\mathrm{cr}}RT_{\mathrm{cr}}}\right)\frac{P_{\mathrm{cr}}}{T_{\mathrm{cr}}} = 3\frac{P_{\mathrm{cr}}}{T_{\mathrm{cr}}}.$$

Therefore, we have

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

for temperatures just below the critical temperature.

$\boxed{3}$

(a) We have, quite simply,

$$\sum_{N=0}^{\infty} z^N Q(\beta,V,N) = \sum_k \mathrm{e}^{-\beta E_k}\sum_{N=0}^{\infty} z^N \delta_{N,N_k} = \sum_k \mathrm{e}^{-\beta E_k}z^{N_k}$$
$$= \sum_k \mathrm{e}^{-\beta E_k}\mathrm{e}^{\beta\mu N_k} = \sum_k \mathrm{e}^{-\beta(E_k - \mu N_k)} = Z(\beta,V,z).$$

(b) Since

$$Z(\beta, V, z) = \mathrm{e}^{Vz/\lambda^3} = \sum_{N=0}^{\infty} \frac{1}{N!}\left(\frac{Vz}{\lambda^3}\right)^N = \sum_{N=0}^{\infty} \frac{z^N}{N!}\left(\frac{V}{\lambda^3}\right)^N ,$$

we read off that $Q(\beta, V, N) = \dfrac{1}{N!}\left(\dfrac{V}{\lambda^3}\right)^N$.

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

(b) The canonical partition function is

$$Q(\beta, F, N) = \frac{1}{N!}\left[\int \frac{(\mathrm{d}\boldsymbol{r})\,(\mathrm{d}\boldsymbol{p})}{(2\pi\hbar)^3}\,\mathrm{e}^{-\beta(\frac{1}{2m}\boldsymbol{p}^2 + Fr)}\right]^N ,$$

where [see Problem 3(b)]

$$\int \frac{(\mathrm{d}\boldsymbol{p})}{(2\pi\hbar)^3}\,\mathrm{e}^{-\beta\frac{1}{2m}\boldsymbol{p}^2} = \frac{1}{\lambda^3}$$

and

$$\int (\mathrm{d}\boldsymbol{r})\,\mathrm{e}^{-\beta F r} = 4\pi \int_0^\infty \mathrm{d}r\, r^2\,\mathrm{e}^{-\beta F r} = \frac{8\pi}{(\beta F)^3} .$$

Accordingly, we have

$$Q(\beta, F, N) = \frac{1}{N!}\left(\frac{8\pi}{(\lambda\beta F)^3}\right)^N .$$

(c) We have, $\dfrac{1}{N}\langle E\rangle = -\dfrac{1}{N}\dfrac{\partial}{\partial\beta}\log Q(\beta, F, N) = -\dfrac{9}{2\beta} = \dfrac{9}{2}k_{\mathrm{B}}T$ 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

$$\frac{1}{N}\langle E_{\mathrm{kin}}\rangle = \frac{m}{N\beta}\frac{\partial}{\partial m}\log Q(\beta, F, N) = \frac{3}{2\beta} = \frac{3}{2}k_{\mathrm{B}}T = \frac{1}{3}\frac{\langle E\rangle}{N}$$

and

$$\frac{1}{N}\langle E_{\mathrm{pot}}\rangle = -\frac{F}{N\beta}\frac{\partial}{\partial F}\log Q(\beta, F, N) = \frac{3}{\beta} = 3k_{\mathrm{B}}T = \frac{2}{3}\frac{\langle E\rangle}{N} .$$

Clearly, $\langle E_{\mathrm{kin}}\rangle + \langle E_{\mathrm{pot}}\rangle = \langle E\rangle$.
