$\boxed{1}$ We have $S = -\left(\frac{\partial F}{\partial T}\right)_V = -\frac{4}{T}F$ and therefore the entropy value for (T_j, V_j) is

$$S_j = \frac{4\pi^2}{45}\frac{k_\mathrm{B}^4}{(\hbar c)^3}V_j T_j^3\,,$$

and we can express all quantities in terms of the temperature and the entropy. In particular, we have $F = -\frac{1}{4}ST$ and $U = F + ST = \frac{3}{4}ST$.

(a) For the isothermal transitions $1 \to 2$ and $3 \to 4$, the work extracted is $W_{1\to 2} = F_1 - F_2 = -\frac{1}{4}(S_1 - S_3)T_1$ and $W_{3\to 4} = F_3 - F_4 = -\frac{1}{4}(S_3 - S_1)T_3$. For the isentropic transitions $2 \to 3$ and $4 \to 1$, the work extracted is $W_{2\to 3} = U_2 - U_3 = \frac{3}{4}S_3(T_1 - T_3)$ and $W_{4\to 1} = U_4 - U_1 = \frac{3}{4}S_1(T_3 - T_1)$.
The heat absorbed in the isothermal transitions $1 \to 2$ and $3 \to 4$ is $Q_{1\to 2} = (S_3 - S_1)T_1 > 0$ and $Q_{3\to 4} = (S_1 - S_3)T_3 < 0$, and there is no heat absorbed in the isentropic transitions $2 \to 3$ and $4 \to 1$, $Q_{2\to 3} = Q_{4\to 1} = 0$.
As a check, one verifies immediately that the total work extracted is equal to the net heat absorbed:

$$\begin{aligned} W_{1\to 2} + W_{2\to 3} + W_{3\to 4} + W_{4\to 1} &= (S_3 - S_1)(T_1 - T_3)\,, \\ Q_{1\to 2} + Q_{2\to 3} + Q_{3\to 4} + Q_{4\to 1} &= (S_3 - S_1)(T_1 - T_3)\,. \end{aligned}$$

(b) We get $\frac{(S_3 - S_1)(T_1 - T_3)}{(S_3 - S_1)T_1} = \frac{T_1 - T_3}{T_1}$ for the efficiency, which is the expected efficiency of a Carnot cycle.

$\boxed{2}$

(a) At the critical point, we have $\left(\frac{\partial P}{\partial v}\right)_T = 0$ and also $\left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$. These require

$$\frac{RT}{(v-b)^2} = \frac{2a}{(v+c)^3 T} \quad \text{and} \quad \frac{RT}{(v-b)^3} = \frac{3a}{(v+c)^4 T} \quad \text{or} \quad 3(v-b) = 2(v+c)\,.$$

Accordingly, the critical molar volume is $v_\mathrm{cr} = 3b + 2c$; then, the critical temperature is $T_\mathrm{cr} = \left(\frac{8}{27R}\frac{a}{b+c}\right)^{1/2}$, and the critical pressure is $P_\mathrm{cr} = \frac{1}{12}\left(\frac{2R}{3}\frac{a}{(b+c)^3}\right)^{1/2}$. These give $\frac{P_\mathrm{cr}v_\mathrm{cr}}{RT_\mathrm{cr}} = \frac{3b+2c}{8(b+c)}$.

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

$$\left.\frac{\mathrm{d}P(T)}{\mathrm{d}T}\right|_{T_{\mathrm{cr}}} = \left.\left(\frac{R}{v-b} + \frac{a}{(v+c)^2T^2}\right)\right|_{T_{\mathrm{cr}},v_{\mathrm{cr}}} = \frac{7}{8}\frac{R}{b+c} = 7\frac{P_{\mathrm{cr}}}{T_{\mathrm{cr}}}\,.$$

Therefore, we have

$$P(T) = \left(7\frac{T}{T_{\mathrm{cr}}} - 6\right) P_{\mathrm{cr}}$$

for temperatures just below the critical temperature.

3

(a) The single-particle energies are $(j_1 + j_2)\hbar\omega$ with $j_1 = j_2 = 0$ for the ground state and $j_1, j_2 = 0, 1, 2, 3, \ldots$ for the excited states (but not $j_1 = 0$ and $j_2 = 0$). For $j = j_1 + j_2$, there are $j+1$ states with energy $\varepsilon_j = j\hbar\omega$. Accordingly, the expected number of bosons in the ground state and in the exited states are

$$\langle N_0\rangle = \frac{z}{1-z}\,, \quad \langle N_{\mathrm{ex}}\rangle = \sum_{j=1}^{\infty} \frac{(j+1)z}{\mathrm{e}^{\beta\varepsilon_j} - z} = \sum_{j=1}^{\infty} \frac{(j+1)z}{\mathrm{e}^{j\beta\hbar\omega} - z}\,.$$

(b) For low temperature, $\beta\hbar\omega \gg 1$, we have $\dfrac{(j+1)z}{\mathrm{e}^{j\beta\hbar\omega} - z} \cong (j+1)z\mathrm{e}^{-j\beta\hbar\omega}$ and only the $j = 1$ term matters in the sum, so that

$$\langle N_{\mathrm{ex}}\rangle \cong 2z\mathrm{e}^{-\beta\hbar\omega} = \frac{2\langle N_0\rangle}{\langle N_0\rangle + 1}\mathrm{e}^{-\beta\hbar\omega}\,.$$

(c) The sum over j for $\langle N_{\mathrm{ex}}\rangle$ in (a) converges to a finite value for all positive temperatures and all values of the fugacity $z \leq 1$, including $z = 1$. It follows that there is a maximum number of bosons than can be in the excited states for $T > 0$, and we get Bose–Einstein condensation if there are rather more particles than can fit into the excited states.

4

(a) m and w are intensive because they have the same values independent of the system size; N is extensive since it is proportional to the system size.

(b) The canonical partition function is

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

where

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

as usual, and

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

Accordingly, we have

$$Q(\beta, m, w, N) = \frac{1}{N!}\left(\frac{4\pi}{3\lambda^3\beta w}\right)^N \propto \beta^{-\frac{5}{2}N} m^{\frac{3}{2}N} w^{-N}\,.$$

(c) It follows that

$$\begin{aligned}
\frac{1}{N}\langle E\rangle &= -\frac{1}{N}\frac{\partial}{\partial\beta}\log\Big(Q(\beta, m, w, N)\Big) = \frac{5}{2\beta} = \frac{5}{2}k_{\mathrm{B}}T\,,\\
\frac{1}{N}\langle E_{\mathrm{kin}}\rangle &= \frac{m}{N\beta}\frac{\partial}{\partial m}\log\Big(Q(\beta, m, w, N)\Big) = \frac{3}{2\beta} = \frac{3}{2}k_{\mathrm{B}}T = \frac{3}{5}\frac{\langle E\rangle}{N}\,,\\
\frac{1}{N}\langle E_{\mathrm{pot}}\rangle &= -\frac{w}{N\beta}\frac{\partial}{\partial w}\log\Big(Q(\beta, m, w, N)\Big) = \frac{1}{\beta} = k_{\mathrm{B}}T = \frac{2}{5}\frac{\langle E\rangle}{N}\,.
\end{aligned}$$

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