1 We recall the Gibbs–Duhem relation, $S\,\mathrm{d}T - V\,\mathrm{d}P + n\,\mathrm{d}\mu = 0$, divide by n, and consider constant T to arrive at $-v(\mathrm{d}P)_T + (\mathrm{d}\mu)_T = 0$ or $v(\mathrm{d}P)_T = (\mathrm{d}\mu)_T$. The changes associated with $(\mathrm{d}v)_T$ are, therefore, related to each other by $v\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial \mu}{\partial v}\right)_T$, indeed.

2

(a) With the Maxwell–Boltzmann weight $\mathrm{e}^{-\beta E}$ and the single-particle energy $E = \frac{1}{2m}\boldsymbol{p}^2$, we have $\langle f(\boldsymbol{p})\rangle = \frac{\int(\mathrm{d}\boldsymbol{p})\,\mathrm{e}^{-\frac{\beta}{2m}\boldsymbol{p}^2} f(\boldsymbol{p})}{\int(\mathrm{d}\boldsymbol{p})\,\mathrm{e}^{-\frac{\beta}{2m}\boldsymbol{p}^2}}$ for the expected value of a function of momentum $\boldsymbol{p}$. For $f(\boldsymbol{p}) = |\boldsymbol{v}| = |\boldsymbol{p}/m|$ and $f(\boldsymbol{p}) = |\boldsymbol{v}|^{-1}$ this gives

$$\langle\,|\boldsymbol{v}|\,\rangle = \frac{\frac{1}{m}\int_0^\infty \mathrm{d}p\,p^3\,\mathrm{e}^{-\frac{\beta}{2m}p^2}}{\int_0^\infty \mathrm{d}p\,p^2\,\mathrm{e}^{-\frac{\beta}{2m}p^2}} = \frac{\frac{1}{2m}(2m/\beta)^2}{\frac{1}{4}\sqrt{\pi}(2m/\beta)^{3/2}} = \sqrt{\frac{8}{\pi m\beta}}$$

and

$$\langle\,|\boldsymbol{v}|^{-1}\,\rangle = \frac{m\int_0^\infty \mathrm{d}p\,p\,\mathrm{e}^{-\frac{\beta}{2m}p^2}}{\int_0^\infty \mathrm{d}p\,p^2\,\mathrm{e}^{-\frac{\beta}{2m}p^2}} = \frac{\frac{m}{2}(2m/\beta)}{\frac{1}{4}\sqrt{\pi}(2m/\beta)^{3/2}} = \sqrt{\frac{2m\beta}{\pi}}\,.$$

We confirm that $\langle\,|\boldsymbol{v}|\,\rangle\langle\,|\boldsymbol{v}|^{-1}\,\rangle = 4/\pi > 1\,.$

(b) We have

$$\begin{aligned} 0 \le \left\langle\left(\lambda X^{\frac{1}{2}} - X^{-\frac{1}{2}}\right)^2\right\rangle &= \lambda^2\langle X\rangle - 2\lambda + \langle X^{-1}\rangle \\ &= \left(\lambda\langle X\rangle^{\frac{1}{2}} - \langle X\rangle^{-\frac{1}{2}}\right)^2 + \langle X^{-1}\rangle - \langle X\rangle^{-1} \end{aligned}$$

where the inequality holds for all values of λ, including in particular $\lambda = \langle X\rangle^{-1}$ for which the final expression is smallest. It follows that $\langle X^{-1}\rangle - \langle X\rangle^{-1} \ge 0$ or $\langle X\rangle\langle X^{-1}\rangle \ge 1\,.$

3

(a) We have $Q(K,N) = \{M^N\}$ with $M = \begin{pmatrix} \mathrm{e}^K & 1 & \mathrm{e}^{-K} \\ 1 & 1 & 1 \\ \mathrm{e}^{-K} & 1 & \mathrm{e}^K \end{pmatrix}$. According to the hint, one eigenvalue of M is $\lambda_0 = 2\sinh(K)$, and we find the other two eigenvalues from $M\begin{pmatrix} x \\ y \\ x \end{pmatrix} = \begin{pmatrix} 2x\cosh(K) + y \\ 2x + y \\ 2x\cosh(K) + y \end{pmatrix}$ or $\begin{pmatrix} x \\ y \end{pmatrix} \to \begin{pmatrix} 2\cosh(K) & 1 \\ 2 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} = \lambda\begin{pmatrix} x \\ y \end{pmatrix}$.

This gives $\lambda_\pm = \cosh(K) + \frac{1}{2} \pm \sqrt{(\cosh(K) - \frac{1}{2})^2 + 2}$.

The largest one of the three eigenvalues is λ_+ and, therefore, it is the only one that matters in $Q = \lambda_+^N + \lambda_0^N + \lambda_-^N = \lambda_+^N\Big[1 + (\lambda_0/\lambda_+)^N + (\lambda_-/\lambda_+)^N\Big]$ since N is a very large integer. It follows that

$$Q(K, N) = \lambda_+^N = \left(\cosh(K) + \tfrac{1}{2} + \sqrt{[\cosh(K) - \tfrac{1}{2}]^2 + 2}\right)^N .$$

(b) We have $\dfrac{F}{N} = -\dfrac{1}{N\beta}\log Q = -\dfrac{1}{\beta}\log\lambda_+ \,.$

(c) We recall that $C = T\dfrac{\partial S}{\partial T} = -\beta\dfrac{\partial S}{\partial\beta} = -\beta\dfrac{\partial}{\partial\beta}\left(-\dfrac{\partial F}{\partial T}\right) = -\beta\dfrac{\partial}{\partial\beta}\left(k_{\mathrm{B}}\beta^2\dfrac{\partial F}{\partial\beta}\right)$, so that $\dfrac{C}{Nk_{\mathrm{B}}} = \beta\dfrac{\partial}{\partial\beta}\beta^2\dfrac{\partial}{\partial\beta}\dfrac{\log\lambda_+}{\beta} = \beta^2\dfrac{\partial^2}{\partial\beta^2}\log\lambda_+ = K^2\dfrac{\partial^2}{\partial K^2}\log\lambda_+ \,.$

For $K \ll 1$, we have $\lambda_+ = 3 + \frac{2}{3}K^2 + O(K^4) \cong 3\Big(1 + \frac{2}{9}K^2\Big)$ and $\log\lambda_+ \cong \log(3) + \frac{2}{9}K^2 \,.$

For $K \gg 1$, we have $\lambda_+ = 2\cosh(K) + \cosh(K)^{-1} + O(\cosh(K)^{-2}) = \mathrm{e}^K + 3\mathrm{e}^{-K} + O(\mathrm{e}^{-2K}) \cong \mathrm{e}^K\Big(1 + 3\mathrm{e}^{-2K}\Big)$ and $\log\lambda_+ \cong K + 3\mathrm{e}^{-2K} \,.$

Accordingly, we find

$$\frac{C}{Nk_{\mathrm{B}}} \cong \begin{cases} \dfrac{4}{9}K^2 & \text{for } K \ll 1\,, \\ 12K^2\mathrm{e}^{-2K} & \text{for } K \gg 1\,. \end{cases}$$

(d) Yes, in the limit $T \to 0$, that is $\beta \to \infty$ or $K \to \infty$, we have $C \to 0$.

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4 We need to remember that v is the <u>volume per particle</u> in the virial expansion $\beta P v = \sum_{l=1} a_l(\beta)(\lambda^3/v)^{l-1}$, whereas v stands for the <u>molar volume</u> in the equation of state of the Berthelot gas. The two symbols v differ by Avogadro's number $N_{\mathrm{A}} = R/k_{\mathrm{B}}$, so that we have

$$\beta P v = \frac{N_{\mathrm{A}}v}{N_{\mathrm{A}}v - b} - \frac{a\beta v}{(N_{\mathrm{A}}v)^2 N_{\mathrm{A}}/\beta} = \sum_{l=1}\left(\frac{b}{N_{\mathrm{A}}v}\right)^{l-1} - \frac{a\beta^2}{N_{\mathrm{A}}^3 v}$$

after consistently expressing all volumes in terms of $v =$ volume per particle. We read off that

$$a_l(\beta) = \left(\frac{b}{N_{\mathrm{A}}\lambda^3}\right)^{l-1} \quad \text{for } l = 1, 3, 4, 5\ldots, \text{ and } \quad a_2(\beta) = \frac{b}{N_{\mathrm{A}}\lambda^3} - \frac{a\beta^2}{N_{\mathrm{A}}^3\lambda^3} \,.$$
