SUPPLEMENTARY INFORMATION

Towards bulk thermodynamics via non-equilibrium methods: gaseous methane as case study

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APPENDIX

For sake of completeness here below we give some standard lines of algebra to link the virial expansions of the compressibility factor versus volume and pressure at fixed temperature. Let us consider the expansion in terms of volume-per-particle,

$$Z(v,T) = 1 + B(T)/v + C(T)/v^2 + \ldots \qquad \text{(A1)}$$

and in terms of pressure,

$$Z(p,T) = 1 + B'(T)\,p + C'(T)\,p^2 + \ldots \qquad \text{(A2)}$$

By considering that $Z = \beta\, p\, v$, the particle-density is obtained as function of the pressure as $1/v = \beta\, p / Z(p,T)$, where $1/Z(p,T)$ can be expanded by employing $(1+x)^{-1} = 1 - x + x^2 + \ldots$ with $x = B'(T)\,p + C'(T)\,p^2 + \ldots$. By grouping the terms with same powers one gets $1/v = \beta\, p - \beta\, B'\, p^2 + \ldots$, and hence

$$Z = 1 + \beta\, B\, p + \left(\beta^2 C - \beta B\, B'\right) p^2 + ... \qquad \text{(A3)}$$

The comparison of eq (A3) with eq (A2) gives

$$\begin{aligned} B' &= \beta\, B \\ C' &= \beta^2 C - \beta\, B\, B' = \beta^2 \left(C - B^2\right) \end{aligned} \qquad \text{(A4)}$$

Relations between higher order coefficients can be obtained, if needed, from handling the terms which bring higher powers of the pressure. Now consider that

$$Z(v,T) = 1 + v^{-1} \frac{da(v)}{d(1/v)} \qquad \text{(A5)}$$

where $a(v) = \lim_{N\to\infty} \beta\Delta A_{\text{morph}} / N$ at the given temperature, according to eq 27 of the main text. By using in eq (A5) the expansion adopted in section 4 of the main text, that is

$$a(v) = -c_\infty^{(1)}(T)/v - c_\infty^{(2)}(T)/v^2 + ... \qquad \text{(A6)}$$

it follows

$$Z(v,T) = 1 - c_\infty^{(1)}(T)/v - 2\, c_\infty^{(2)}(T)/v^2 + ... \qquad \text{(A7)}$$

By comparing eqs (A7) and (A1) we identify $B(T) \equiv -c_\infty^{(1)}(T)$ and $C(T) \equiv -2c_\infty^{(2)}(T)$, to be inserted in eq (A4). This yields the final expressions which link the virial expansion eq (A2) to the free energy expansion eq (A6):

$$\begin{aligned} B' &= -\beta\, c_\infty^{(1)} \\ C' &= -\beta^2 \left(c_\infty^{(2)} + c_\infty^{(1)\;2}\right) \end{aligned} \qquad \text{(A8)}$$