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Statistical Mechanics
Homework 6

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H6.1

Applying cluster expansion when computing the partition function of a system with an interaction potential $U(\vec{r}) = \frac{\alpha}{r^n}$ with $\alpha > 0$, $n > 3$ leads in first order approximation to:

$$Z = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)\left(1 - \frac{N^2}{V}B(T)\right) \tag{1}$$

with $\lambda = \sqrt{\frac{\beta(2\pi\hbar)^2}{2\pi m}}$ and via $p = -\left(\frac{\partial F}{\partial V}\right)_T$, $F = -kT\log Z$ to the equation of state:

$$p\,V = N\,k\,T\left(1 + \frac{N}{V}B(T)\right) \tag{2}$$

where $B(T) = \frac{1}{2}\int \mathrm{d}^3r\left(1 - e^{-\beta U(r)}\right)$ is the first *virial coefficient*.

(a) Computing $B(T)$:

$$B(T) = 2\pi\int\limits_0^\infty \mathrm{d}r\,r^2\left(1 - e^{-\beta U(r)}\right)$$

Approximate the potential for suitable r_0:

$$U(r) \approx \begin{cases}\infty, & r < r_0\\ \frac{\alpha}{r^n}, & r \geq r_0\end{cases} \tag{3}$$

and expand the integrand (where $\gamma \equiv \alpha\beta$):

$$1 - e^{-\frac{\gamma}{r^n}} = 1 - 1 + \frac{\gamma}{r^n} - \mathcal{O}\left(\frac{1}{r^{2n}}\right)$$

Then:

$$B(T) \approx 2\pi\int\limits_0^{r_0}\mathrm{d}r\,r^2 + 2\pi\gamma\int\limits_{r_0}^{\infty}\frac{\mathrm{d}r}{r^{n-2}} \tag{4}$$

From (3) and (4) it is clear, that $r_0^2 = \frac{\gamma}{r_0^{n-2}} \implies r_0 = \gamma^{1/n}$.
It is then straightforward to integrate (4), which yields:

$$\boxed{B(T) = \frac{2\pi}{3}\frac{n}{n-3}\left(\frac{\alpha}{kT}\right)^{3/n}} \tag{5}$$

And for the derivative of (5), one finds:

$$\frac{\partial B}{\partial T} = -\frac{3B}{nT}$$

(b) Computing the heat capacity for constant volume (with $S = -\left(\frac{\partial F}{\partial T}\right)_V$, $F = -kT\log Z$):

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = kT\frac{\partial^2(T\log Z)}{\partial T^2} = kT\left(2\frac{\partial \log Z}{\partial T} + T\frac{\partial^2 \log T}{\partial T^2}\right)$$

One finds with (1):

$$\begin{aligned}\frac{\partial \log Z}{\partial T} &= \frac{3}{nT}\frac{N^2}{V - N^2B}\\ \frac{\partial^2 \log Z}{\partial T^2} &= -\frac{3}{nT^2}\frac{N^2B}{V-N^2B}\left(1+\frac{3}{n}\frac{N^2B}{V-N^2B}\right)\end{aligned}$$

Which gives:

$$\boxed{C_V = \frac{3k}{n}\frac{N^2B}{V-N^2B}\left(1+\frac{3}{n}\frac{N^2B}{V-N^2B}\right)} \tag{6}$$

The heat capacity for constant pressure can be obtained from the relation:

$$C_P - C_V = -T\frac{\left(\frac{\partial P}{\partial T}\right)_V^2}{\left(\frac{\partial P}{\partial V}\right)_T}$$

Working out the derivatives of (2):

$$\begin{aligned}\left(\frac{\partial P}{\partial T}\right)_V &= \frac{Nk}{V}\left(1+\frac{n-3}{n}\frac{NB}{V}\right)\\ \left(\frac{\partial P}{\partial V}\right)_T &= -\frac{NkT}{V^3}\left(V+2NB\right)\end{aligned}$$

Leading to:

$$\boxed{C_P = \frac{3k}{n}\frac{N^2B}{V-N^2B}\left(1+\frac{3}{n}\frac{N^2B}{V-N^2B}\right) + N\frac{\left(V+\frac{n-3}{n}NB\right)^2}{V^2+2NVB}} \tag{7}$$

(c) In order to compute the isothermic compressibility

$$\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

one can (ab-)use the fact that in thermodynamics all variables are considered as functions of each other, which allows to use the chainrule in this way:

$$\frac{\partial V}{\partial V} = \frac{\partial V}{\partial P}\frac{\partial P}{\partial V} = 1 \implies \frac{\partial V}{\partial P} = \frac{1}{\frac{\partial P}{\partial V}}$$

Therefor one can use (2) directly and with $\left(\frac{\partial P}{\partial V}\right)_T = -\frac{NkT}{V^3}(V + 2NB)$ write:

$$\boxed{\beta_T = -\frac{1}{V\left(\frac{\partial P}{\partial V}\right)_T} = \frac{V^2}{NkT(V + 2NB)}} \tag{8}$$

For the adiabatic compressibility, one can utilize the relation:

$$\gamma = \frac{\beta_T}{\beta_S} = \frac{C_P}{C_V} \iff \beta_S = \frac{\beta_T\, C_V}{C_P}$$

And after inserting (6), (7) and (8), one receives:

$$\boxed{\beta_S = \frac{\frac{3k}{n}\frac{N^2B}{V-N^2B}\left(1 + \frac{3}{n}\frac{N^2B}{V-N^2B}\right)\frac{V^2}{NkT(V+2NB)}}{\frac{3k}{n}\frac{N^2B}{V-N^2B}\left(1 + \frac{3}{n}\frac{N^2B}{V-N^2B}\right) + Nk\frac{\left(V+\frac{n-3}{n}NB\right)^2}{V^2+2NVB}}} \tag{9}$$

Now one could try to further work out (9) in order to find a more concise expression, if one had the patience to do so.