8.333 : STATISTICAL MECHANICS I

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7 Attractive shell potential

a

$$V(r) = \begin{cases} +\infty & 0 < r < a \\ -\varepsilon & a < r < b \\ 0 & b < r < \infty \end{cases}$$

$$B_2 = -\frac{1}{2}\int d^3 r_{12} \left[\exp\left(-\beta V(r_{12})\right) - 1\right]$$

$$= -\frac{1}{2} 4\pi \int_0^\infty dr\, r^2 \left(\exp\left(-\beta V(r)\right) - 1\right)$$

$$= -\frac{1}{2}(4\pi) \int_0^a dr\, r^2 [-1]$$

$$- \frac{1}{2}(4\pi) \int_a^b dr\, r^2 \left[\exp(+\beta\varepsilon) - 1\right]$$

$$- \cancel{\frac{1}{2}(4\pi) \int_b^\infty dr\, r^2 [1 - 1]} \to 0$$

$$= \frac{2a^3\pi}{3} + \frac{2}{3}(a^3 - b^3)(-1 + e^{\beta\varepsilon})\pi$$

$$= \boxed{\frac{2\pi}{3}\left[b^3 + (a^3 - b^3)e^{\beta\varepsilon}\right]}$$

3 $$B_2(T) = \frac{2\pi}{3}\left(b^3 + (a^3 - b^3) e^{\beta \varepsilon} \right)$$

- In the high-temp limit, $\beta \to 0$, so

$$\lim_{T \to \infty} B_2(T) = \frac{2\pi}{3}\left(b^3 + (a^3 - b^3)(1 + \beta \varepsilon) \right)$$

$$= \boxed{\frac{2\pi}{3} a^3 + \frac{2\pi}{3}(a^3 - b^3)\beta \varepsilon}$$

- At low temperatures, attractive components takes over...

$$B_2(T) \sim \boxed{\frac{2\pi}{3}(a^3 - b^3) e^{\beta \varepsilon}}$$

$$a < b \Rightarrow B_2(T) < 0$$

@ high temps, the hard core part of the potential is dominant

$$\boxed{B_2(T \to \infty) \sim \frac{2\pi}{3} a^3}$$

(c) High T limit again...

$$(P + an^2)(V - Nb) = Nk_B T$$

Recall that

$$\frac{PV}{Nk_B T} = 1 + \frac{N}{V} B_2(T)$$

$$\Rightarrow \frac{PV}{Nk_B T} = 1 + \frac{N}{V}\left[\frac{2\pi}{3}\left(a^3 + (d^3 - b^3)\beta\varepsilon\right)\right]$$

$$P = Nk_B T\left[\frac{1}{V} + \frac{N}{V^2}\left(\frac{2\pi}{3}\left(a^3 + (a^3 - b^3)\beta\varepsilon\right)\right)\right]$$

$$P + \cancel{Nk_B T}\,\frac{N}{V^2}\,\frac{2\pi}{3}(b^3 - a^3)\cancel{\beta}\varepsilon = k_B T\,\frac{N}{V}\left(1 + \frac{N}{V}\,\frac{2\pi}{3}a^3\right)$$

$$P + \frac{N^2}{V^2}\varepsilon\,\frac{2\pi}{3}(b^3 - a^3) = k_B T\,\frac{N}{V}\left(1 + \frac{N}{V}\,\frac{2\pi}{3}a^3\right)$$

Now...
$$1 + \frac{N}{V}\,\frac{2\pi}{3}a^3 = 1 + \frac{1}{2}n\left(\frac{4\pi}{3}a^3\right)$$

$$\approx V\left(V - \frac{N}{2}\,\frac{4\pi}{3}a^3\right)^{-1}$$

So

$$\boxed{\left(P + \frac{n^2\varepsilon}{2}\,\frac{4\pi}{3}(b^3 - a^3)\right)\left(V - \frac{N}{2}\,\frac{4\pi}{3}a^3\right) = Nk_B T}$$

$\rightarrow$

Van der Waals params

$$
\begin{cases}
a = \dfrac{\varepsilon}{2} \dfrac{4\pi}{3} \left(b^3 - a^3 \right) = \dfrac{2\pi \varepsilon}{3} \left(b^3 - a^3 \right) \\[2em]
b = \dfrac{2\pi}{3} a^3
\end{cases}
$$

2 Interacting point particles

$$Z(T,N,V) = Z_{ideal}(T,N,V)\, \exp(\beta N u(v))$$

a $Z_{ideal\ gas}(T,N,V) \approx \dfrac{V^N}{N!\,\lambda^{3N}} \sim V^x T^y$

where V is the volume

$\lambda = \dfrac{h}{\sqrt{2\pi m k_B T}}$ $\rightsquigarrow$ thermal wavelength. $(\sim T^{-1/2})$

so,
$$\boxed{\begin{aligned} x &= N \\ y &= +3N/2 \end{aligned}}$$

b Energy is given by

$E = \langle \mathcal{H} \rangle = \cancel{-k_B T}\ \ -\dfrac{\partial \ln Z}{\partial \beta}$

$\ln\left(\dfrac{1}{k_B \beta}\right)$

$$= -\frac{\partial}{\partial \beta}\left[N \ln V + \left(\frac{+3N}{2}\right)\ln T + \beta N u(v)\right]$$

$$= \boxed{-N u(v) + \frac{3N}{2\beta}}$$

(c) Heat capacity @ constant volume...

$$C_V = \frac{\partial E}{\partial T}\bigg|_V = \frac{\partial \langle \mathcal{H} \rangle}{\partial T} = \frac{\partial}{\partial T}\left[-N u(v) + \frac{3N}{2} k_B T \right]$$

$\boxed{dV = 0}$

$$= + \boxed{\frac{3N k_B}{2}}$$

(d) To find pressure, need to go to free energy...

$$F = -k_B T \ln Z = \ldots \quad \text{(Mathematica)}$$

$$\boxed{P} = \cancel{\text{cdx}} \; -\frac{\partial F}{\partial V}\bigg|_{T,N} =$$

$$= \frac{-\partial}{\partial V}\left[-k_B T \ln Z \right]_{T,N}$$

$$= k_B T \frac{\partial}{\partial V} \ln Z \bigg|_{T,N} \qquad v = V/N$$

$$= \frac{k_B T}{V}\left(N + V\beta u'(V/N) \right)$$

$$= \frac{k_B T N}{V} + u'(V/N) \qquad n = \frac{N}{V}$$

$$= \boxed{k_B T n + u'\left(\frac{1}{n}\right)}$$

e Isothermal compressibility

$$K_T(n) = -\frac{1}{v}\frac{\partial v}{\partial P}\Big|_T$$

$$= -\frac{1}{v}\left(\frac{\partial P}{\partial v}\right)^{-1}\Big|_T$$

$$= -\frac{n}{N}\,\frac{N\,\partial(1/n)}{\partial P}$$

$$= +n\,n^{-2}\left(\frac{\partial P}{\partial n}\right)^{-1}\Big|_T$$

$$= \cancel{\frac{1}{N}\left[\frac{k_B T}{v} k_B T - \frac{1}{n^2}u''(1/n)\right]}$$

$$\cancel{K_T = \frac{k_B T}{n} - \frac{1}{n^3}u''(1/n)}$$

$$\boxed{k_T = \frac{n}{k_B T n^2 - u''(1/n)}}$$

(f) Necessary condition for $u(v)$ for stability of particles?

To get ~~stab~~ mechanically stable system of particles, we ~~must~~ must have that

$$K_T > 0 \iff n^2 k_B T - u''(1/n) > 0$$

$$\iff \boxed{n^2 k_B T > u''(1/n)}$$

$v = 1/n$

or $\boxed{u''(v) < \frac{k_B T}{v^2}}$