Problem set 2 – Liquids

(7) $Z_N = \int \dots \int e^{-\beta u(\dots)} \, d\bar{r}_1 \dots d\bar{r}_N$

a). $u = \sum_{i>j}^{N} \phi_{ij} \quad \left(= \frac{1}{2} \sum_{i,j}^{N} \phi_{ij}\right)$

approximate total u by the sum of pair-interactions of all N-particles.

b). $f_{ij} = e^{-\beta \phi_{ij}} - 1$

$Z_N = \int \dots \int e^{-\beta u(\dots)} \, d\bar{r}_1 \dots d\bar{r}_N$

$\Rightarrow Z_N = \int \dots \int e^{-\beta \sum_{i>j}^{N} \phi_{ij}} \, d\bar{r}_1 \dots d\bar{r}_N$

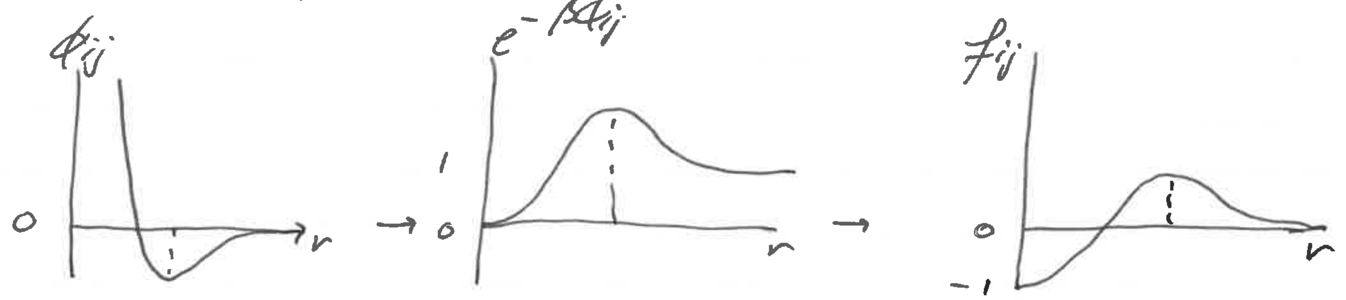
$\Rightarrow$ now $e^{\Sigma} \rightarrow \Pi e$

$Z_N = \int \dots \int \prod_{i>j}^{N} \left(e^{-\beta \phi_{ij}}\right) d\bar{r}_1 \dots d\bar{r}_N$

$e^{-\beta \phi_{ij}} = 1 + f_{ij}$

$= \int \dots \int \prod_{i>j}^{N} (1 + f_{ij}) \, d\bar{r}_1 \dots d\bar{r}_N$

c).



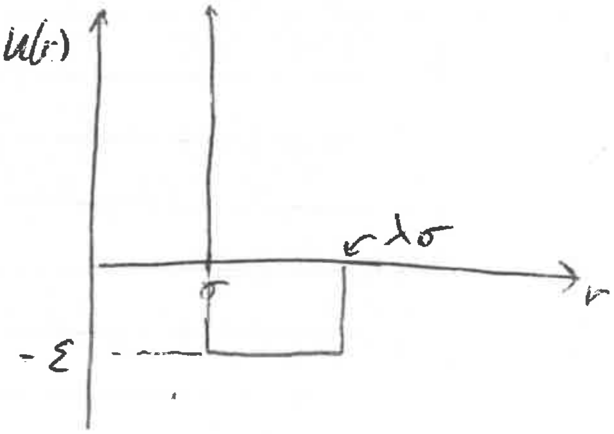
f_{ij} goes to 0 at large $r \rightarrow \int \dots \int f_{ij} \, d\bar{r} \dots$ converge

$e^{-\beta \phi_{ij}}$ goes to 1 as $r \rightarrow \infty$: problem.

8) $B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta u(r)} - 1\right) r^2 \, dr$

a).

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma < r < \lambda\sigma \\ 0 & r > \sigma \end{cases}$$



b). split integral in $B_2(T)$ in 3 parts:

$$B_2(T) = -2\pi \int_0^\sigma \left(e^{-\beta \underset{\substack{\uparrow \\ \infty}}{u(r)}} - 1\right) r^2 \, dr - 2\pi \int_\sigma^{\lambda\sigma} \left(e^{-\beta \underset{\substack{\uparrow \\ -\varepsilon}}{u(r)}} - 1\right) r^2 \, dr - 2\pi \int_{\lambda\sigma}^\infty \left(e^{-\beta \underset{\substack{\uparrow \\ 0}}{u}} - 1\right) r^2 \, dr$$

$$= 2\pi \int_0^\sigma r^2 \, dr - 2\pi \int_\sigma^{\lambda\sigma} \underbrace{\left(e^{\beta\varepsilon} - 1\right)}_{\text{cst!}} r^2 \, dr + 0 =$$

$$= \frac{2\pi\sigma^3}{3} - 2\pi\left(e^{\beta\varepsilon} - 1\right) \left[\frac{1}{3} r^3\right]_\sigma^{\lambda\sigma} =$$

$$= \frac{2\pi\sigma^3}{3} - 2\pi\left(e^{\beta\varepsilon} - 1\right)\left(\frac{1}{3}\lambda^3\sigma^3 - \frac{1}{3}\sigma^3\right) =$$

$$= \frac{2\pi\sigma^3}{3} - 2\pi\left(e^{\beta\varepsilon} - 1\right) \frac{1}{3}\sigma^3 \left(\lambda^3 - 1\right) =$$

$$= \frac{2\pi\sigma^3}{3} \left\{ 1 - \left(\lambda^3 - 1\right)\left(e^{\beta\varepsilon} - 1\right) \right\}$$

note that if $\lambda = 1 \rightarrow B_2(T) = \dfrac{2\pi\sigma^3}{3}$
$\varepsilon = 0 \rightarrow$ " "
$\Big\} = B_2(T)$ for hard spheres!

c). $\sigma = 3.067 \cdot 10^{-10}\,m$, $\lambda = 1.70$ $\frac{\varepsilon}{k_B} = 93.3\,K$

(a) Boyle temp $\rightarrow$ $B_2(T) = 0$

$$\therefore \frac{2\pi\sigma^3}{3}\left\{1 - (\lambda^3 - 1)(e^{\beta\varepsilon} - 1)\right\} = 0$$

$$\rightarrow (\lambda^3 - 1)(e^{\beta\varepsilon} - 1) = 1$$

$$e^{\beta\varepsilon} = \frac{1}{(\lambda^3 - 1)} + 1 = \frac{1}{(\lambda^3 - 1)} + \frac{(\lambda^3 - 1)}{(\lambda^3 - 1)} = \frac{\lambda^3}{(\lambda^3 - 1)}$$

$$\rightarrow \beta\varepsilon = \ln\left[\frac{\lambda^3}{\lambda^3 - 1}\right] = \frac{\varepsilon}{k_B T}$$

in other words: $\frac{1}{T} = \frac{k_B}{\varepsilon} \ln\left[\frac{\lambda^3}{\lambda^3 - 1}\right]$

putting in ~~the~~ numbers

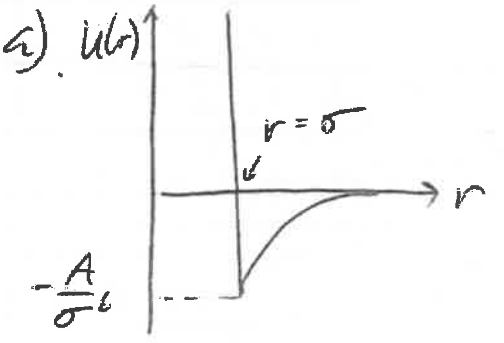
$$\frac{1}{T} = \frac{1}{93.3} \ln\left[\frac{1.7^3}{1.7^3 - 1}\right] = 0.002439$$

$$T_{Boyle} = 410\,K.$$

⑨ $u(r) = \begin{cases} \infty & r < \sigma \\ -\frac{A}{r^6} & r \geq \sigma \end{cases}$

$A = 1.11 \cdot 10^{-78}\ J m^6$
$\sigma = 0.356 \cdot 10^{-9}\ m$

a).



$$u(r=\sigma) = -\frac{A}{\sigma^6} = $$

$$= \frac{-1.11 \cdot 10^{-78}\ J m^6}{(0.356 \cdot 10^{-9})^6} =$$

$$= -5.45 \cdot 10^{-22}\ J \quad (= -0.13\ k_B T$$

b). so $u \ll kT \rightarrow$ so we can expand the exponential in:

$$B_2(T) = -2\pi \int_0^\infty (e^{-\beta u(r)} - 1)\, r^2\, dr =$$

1st split up: $B_2(T) = \underbrace{-2\pi \int_0^\sigma (e^{-\beta u(r)} - 1)\, r^2\, dr}_{\text{hard sphere } B_2(T)} + -2\pi \int_\sigma^\infty (e^{-\beta u(r)} - 1)\, r^2\, dr$

∞ $\quad -\frac{A}{r^6}$

$$B_2(T) = -2\pi \int_0^\sigma -1 \cdot r^2\, dr - 2\pi \int_\sigma^\infty (e^{-\beta u(r)} - 1)\, r^2\, dr$$

expand: $e^{-x} \simeq 1 - x \quad \therefore \quad e^{-\beta u(r)} \approx 1 - \beta u(r)$

$$\therefore B_2(T) = 2\pi \int_0^\sigma r^2\, dr - 2\pi \int_\sigma^\infty (1 - \beta u(r) - 1)\, r^2\, dr$$

$$= 2\pi \int_0^\sigma r^2\, dr + 2\pi \int_\sigma^\infty \frac{u(r)}{k_B T}\, r^2\, dr$$

c). $p = k_BT\left[\rho + \underbrace{\left(b - \frac{a}{k_BT}\right)}_{B_2(T)}\rho^2 + \dots\right]$

So: $2\pi\int_0^\sigma r^2 dr + 2\pi\int_\sigma^\infty \frac{u(r)}{k_BT} r^2 dr = b - \frac{a}{k_BT}$

$\therefore \quad a = -2\pi \int_\sigma^\infty u(r) r^2 dr$

$b = 2\pi \int_0^\sigma r^2 dr$

d). $a = -2\pi \int_\sigma^\infty -\frac{A}{r^6} r^2 dr = 2\pi A \int_\sigma^\infty \frac{1}{r^4} dr$

$= 2\pi A\left[-\frac{1}{r^3}\right]_\sigma^\infty = \frac{2\pi A}{\sigma^3} = \frac{2\pi \cdot 1.11\cdot 10^{-78}}{(0.356\cdot 10^{-9})^3} =$

$=$ ~~[illegible]~~

$= 1.55 \cdot 10^{-49}\ \mathrm{Jm^3}$ → accounts for interactions ~~[illegible]~~

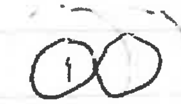
$b = 2\pi \int_0^\sigma r^2 dr = \frac{2\pi\sigma^3}{3} = 4\cdot V_0 = \frac{2\pi(0.356\cdot 10^{-9})^3}{3}$

$= 9.45\cdot 10^{-29}\ m^3$

Where $V_0 = \frac{4}{3}\pi\left(\frac{\sigma}{2}\right)^3 = \frac{\pi}{6}\sigma^3$

✓

excluded volume per sphere



$V_{ex} = \frac{8V_0}{2} = 4\cdot V_0$

b) a). $p = k_B T (\rho + B_2 \rho^2 + B_3 \rho^3 + \dots)$

$$\frac{p}{\rho kT} = 1 + B_2 \rho + B_3 \rho^2 + \dots$$

$$\frac{p\sigma^3}{\rho\sigma^3 kT} = 1 + B_2 \frac{\rho\sigma^3}{\sigma^3} + B_3 \frac{\rho^2\sigma^6}{\sigma^6} + \dots$$

now $\Rightarrow$ $\boxed{\begin{array}{l} \rho\sigma^3 = \rho^* \\ kT = T^* \varepsilon \\ \frac{p\sigma^3}{\varepsilon} = p^* \end{array}}$ $\quad \frac{p\sigma^3}{\rho\sigma^3 kT} = \frac{p\sigma^3}{\rho^* T^* \varepsilon} = \frac{p^*}{\rho^* T^*}$

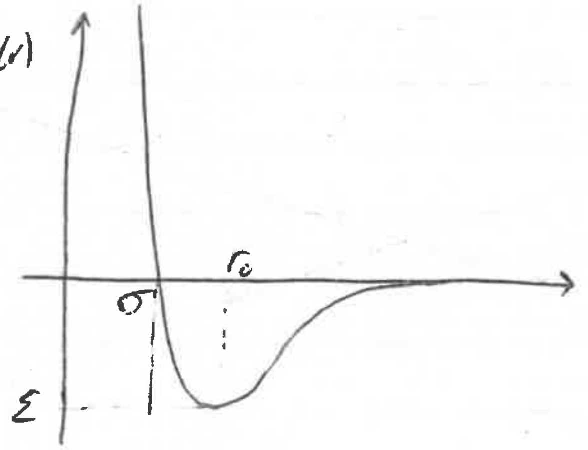
also. $B_n^*(T^*) = \frac{B_n(T)}{\sigma^{3(n-1)}}$

$\therefore$ $$\frac{p^*}{\rho^* T^*} = 1 + B_2^* \rho^* + B_3^* \rho^{*2} + \dots$$

10 - extra

$U(r) = 4\varepsilon\left[-\left(\frac{\sigma}{r}\right)^6 + \left(\frac{\sigma}{r}\right)^{12}\right]$

a).



I took this part out

a) ~~b)~~. $y = \frac{r}{\sigma}$ $\qquad B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta U(r)} - 1\right) r^2 dr$

$r = y\sigma$

$r^2 = y^2\sigma^2$

$\frac{dy}{dr} = \frac{1}{\sigma} \rightarrow dr = \sigma dy \therefore B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta U(y\sigma)} - 1\right) y^2\sigma^2\sigma\, dy$

$\therefore B_2(T) = -2\pi\sigma^3 \int_0^\infty \left(e^{-\beta U(y\sigma)} - 1\right) y^2 dy$

$U(y\sigma) = 4\varepsilon\left[-\left(\frac{\sigma}{y\sigma}\right)^6 + \left(\frac{\sigma}{y\sigma}\right)^{12}\right] =$

$= 4\varepsilon\left[-y^{-6} + y^{-12}\right]$

$\therefore \frac{B_2(T)}{\sigma^3} = -2\pi \int_0^\infty \left[\exp\left(-\frac{4\varepsilon}{k_B T}\left[-y^{-6} + y^{-12}\right]\right) - 1\right] y^2 dy$

$= -2\pi \int_0^\infty \left[\exp\left(-\frac{4}{T^*}\left[y^{-12} - y^{-6}\right]\right) - 1\right] y^2 dy$

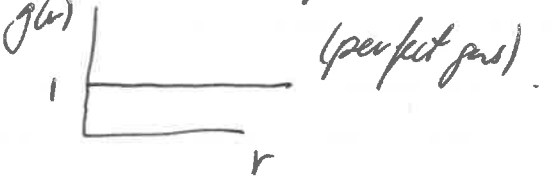
(11)

a) $\rho^2 g^{(2)}(\vec{r}_1, \vec{r}_2)\, d\tau_1 d\tau_2$

→ independent : prob particle 1 in $d\tau_1$: $\rho\, d\tau_1$
prob particle 2 in $d\tau_2$: $\rho\, d\tau_2$

total probability: $(\rho\, d\tau_1)\cdot(\rho\, d\tau_2) = \rho^2 d\tau_1 d\tau_2$

⇒ in this case $g^{(2)}(\vec{r}_1, \vec{r}_2) = 1$ $[\approx g^{(2)} = g(r)]$
as is the case for the perfect gas:



- totally indep. → no correlations (no interactions)
- interactions → induces correlations and the presence of particle 1* affects prob. of part 2 in $d\tau_2$, which is accounted for by $g(r)$. * and the others.

b). $p = \frac{N!}{(N-2)!} \times \frac{\int d\tau_3 .. \int d\tau_N\, e^{-\beta u(\ldots)} d\tau_1 d\tau_2}{Z_N}$

as : any mlc in $d\tau_1$: N
any mlc − 1 in $d\tau_2$: $N-1$
any mlc − 2 in $d\tau_3$: $N-2$
⋮

$N\cdot(N-1)\cdot(N-2)\ldots = N!$

- then you need to correct for the permutations of the $(N-2)$ particles, i.e. not particles 1 & 2:

$$(N-2)(N-3)(N-4)\ldots = (N-2)!$$

hence the factor $\frac{N!}{(N-2)!} \times \frac{\int d\tau_3 \ldots \int d\tau_N\, e^{-\beta u} d\tau_1 d\tau_2}{Z_N}$.

$$\rho = \frac{N}{V}$$

c). $$\frac{N!}{\rho^2 (N-2)!} = \frac{V^2}{N^2} \cdot \frac{N\cdot(N-1)\cdot\cancel{(N-2)\cdot\ldots}}{\cancel{(N-2)\cdot(N-3)\cdots}} =$$

$$= \frac{V^2(N^2-N)}{N^2} = V^2\left(1-\frac{1}{N}\right).$$

d). $$\rho^2 g^{(2)}(\vec{r}_1,\vec{r}_2)\,d\tau_1\,d\tau_2 = \rho^2 g(r)\,d\tau_1\,d\tau_2$$

b) & c): $$\frac{N!}{(N-2)!}\;\frac{\int d\tau_3 \ldots \int d\tau_N\, e^{-\beta u(\ldots)}\,d\tau_1\,d\tau_2}{Z_N}$$

$$\frac{N!}{\rho^2(N-2)!} = V^2\left(1-\frac{1}{N}\right) \underset{N\gg 1}{\simeq} V^2$$

$$\frac{N!}{(N-2)!}\;\frac{\int d\tau_3 \ldots \int d\tau_N\, e^{-\beta u(\ldots)}\,d\tau_1\,d\tau_2}{Z_N} = \rho^2 g(r)\,d\tau_1\,d\tau_2$$

$$\underbrace{\frac{N!}{\rho^2(N-2)!}}_{V^2}\;\frac{\int \text{-----}}{Z_N}\cancel{d\tau_1 d\tau_2} = g(r)\,\cancel{d\tau_1}\,\cancel{d\tau_2}$$

$$g(r) = \frac{V^2}{Z_N}\int d\tau_3 \ldots \int d\tau_N\, e^{-\beta u(\ldots)}$$

4

(12)

$$1 + 4\pi\rho\int_0^\infty h(r)\, r^2 dr = \rho k_B T \kappa_T$$

a). $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad \rho = \frac{N}{V} \rightarrow \quad \frac{\partial \rho}{\partial V} = -\frac{N}{V^2}$

so: $\partial \rho = -\frac{N}{V^2}\partial V \quad \longrightarrow \quad \partial V = -\frac{V^2}{N}\partial \rho$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial \rho}{\partial p}\right)_T \cdot \underbrace{-\frac{V^2}{N}}_{1/\rho} = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T$$

b). $B_2(T) = -2\pi\int_0^\infty \left(e^{-\beta\phi(r)} - 1\right) r^2 dr$

$g(r) = e^{-\beta\phi(r)} \qquad \kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T$

compr. eq: $1 + 4\pi\rho\int_0^\infty \underset{\substack{\downarrow \\ g(r)-1 = e^{-\beta\phi(r)}-1}}{h(r)}\, r^2 dr = \cancel{\rho} k_B T \cdot \frac{1}{\cancel{\rho}}\left(\frac{\partial \rho}{\partial p}\right)_T$

$$\Rightarrow 1 + 4\pi\rho\underbrace{\int_0^\infty \left(e^{-\beta\phi(r)} - 1\right) r^2 dr}_{-B_2/2\pi} = k_B T\left(\frac{\partial \rho}{\partial p}\right)_T$$

$$= 1 - 2\rho B_2 = k_B T\left(\partial\rho/\partial p\right)_T.$$

c). small $\rho \rightarrow$ Taylor expansion of $\frac{1}{1-2\rho B_2} \simeq 1 + 2\rho B_2 + \ldots$

$$\left(\frac{\partial p}{\partial \rho}\right)_T = k_B T\left(\frac{1}{1-2\rho B_2}\right) = k_B T\left(1 + 2\rho B_2 + \ldots\right)$$

$$\int dp = k_B T\int\left(1 + 2\rho B_2 + \ldots\right) d\rho \Rightarrow$$

$P = k_B T\left(\rho + B_2\rho^2 + \ldots\right) \quad \Rightarrow$ virial eq. of state!