Problem set 2 – Liquids

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

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

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

$\Bigg\} \; Z_N = \int \dots \int e^{-\beta \sum_{i>j}^{N} \phi_{ij}} d\vec{r}_1 \dots d\vec{r}_N$

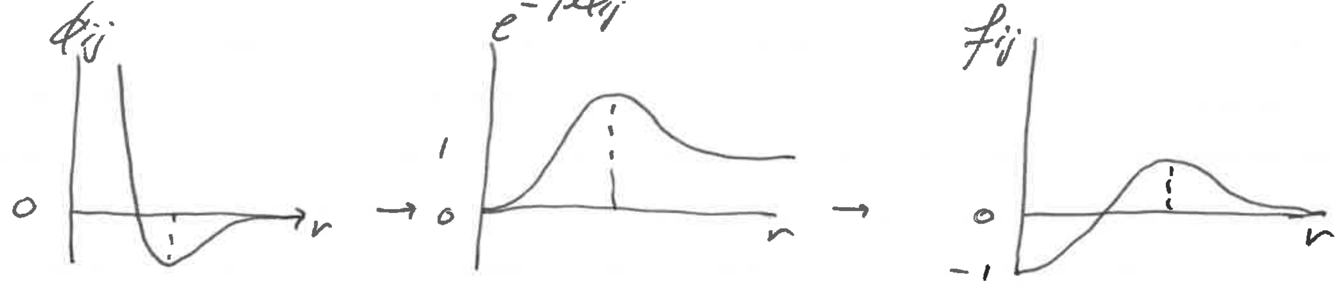
$\Rightarrow$ now $e^{\Sigma} \to \Pi e$

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

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

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

c).



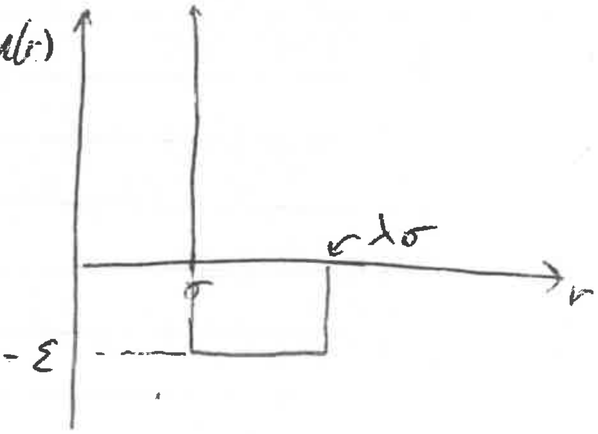
f_{ij} goes to 0 at large $r \to \int \dots \int f_{ij} \, d\vec{r} \dots$ converge

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

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

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

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

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

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

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

note that if $\lambda = 1 \rightarrow B_2(T) = \frac{2\pi\sigma^3}{3}$
$\varepsilon = 0 \rightarrow$ " "
$\Big\} = B_2(T)$ 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: $\frac{1}{T} = \frac{k_B}{\varepsilon}\ln\left[\frac{\lambda^3}{\lambda^3-1}\right]$

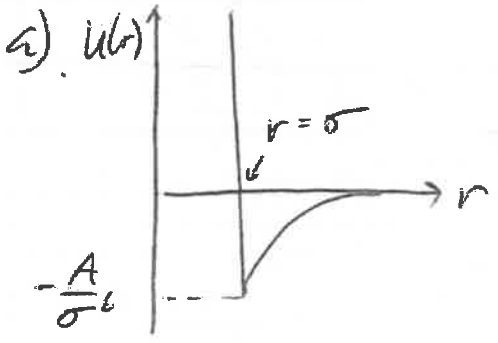
putting in ~~the~~ numbers

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

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

⑨ $U(r) = \begin{cases} \infty & r < \sigma \\ -\frac{A}{r^6} & r \geq \sigma \end{cases}$ $\quad A = 1.11 \cdot 10^{-78}\ \mathrm{J\,m^6}$, $\quad \sigma = 0.356 \cdot 10^{-9}\ \mathrm{m}$

a).



$$U(r=\sigma) = -\frac{A}{\sigma^6} = -\frac{1.11 \cdot 10^{-78}\ \mathrm{J\,m^6}}{(0.356 \cdot 10^{-9})^6} =$$

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

b). so $U \ll kT$ → so we can expand the exponential in:

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

1st split up: $B_2(T) = \underbrace{-2\pi \int_0^\sigma \left(e^{-\beta \overset{\uparrow}{U(r)}} - 1\right) r^2\, dr}_{\text{hard sphere } B_2(T)} + -2\pi \int_\sigma^\infty \left(e^{-\beta U(r)} - 1\right) r^2\, dr$ $\quad$ ($U(r) \to \infty$; $U(r) \to -\frac{A}{r^6}$)

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

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

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

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

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

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

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

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

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

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

$=$

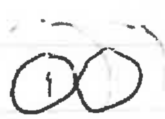
$= 0.52 \cdot 10^{-49}\ \mathrm{J\,m^3}$ → accounts for interactions

$$b = 2\pi \int_0^{\sigma} r^2 dr = \frac{2\pi \sigma^3}{3} = 4 \cdot V_0 = \frac{2\pi (0.356 \cdot 10^{-9})^3}{3}$$
$$= 9.45 \cdot 10^{-29}\ m^3$$

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

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

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

now $\Rightarrow$ $\boxed{\begin{aligned} \rho\sigma^3 &= \rho^* \\ kT &= T^*\varepsilon \\ \frac{p\sigma^3}{\varepsilon} &= p^* \end{aligned}}$ $\Bigg\}$ $\frac{p\sigma^3}{\rho\sigma^3 kT} = \frac{p\sigma^3}{\rho^* T^*\varepsilon} = \frac{p^*}{\rho^* T^*}$

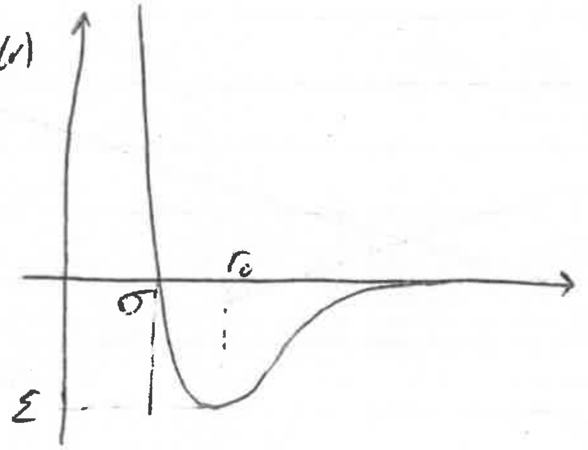
also. $B_n^*(T^*) = \frac{B_n(T)}{\sigma^{3(n-1)}}$

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

(10) - extra

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

a).



I took this part out

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

$r = y\sigma$

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

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

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

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

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

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

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

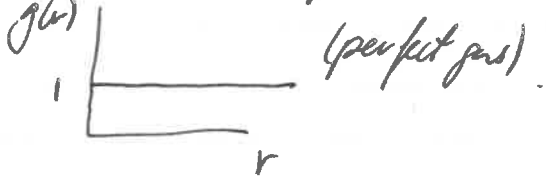
(11)

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

$\Rightarrow$ in this case $g^{(2)}(\vec{r}_1, \vec{r}_2) = 1$ $\quad [\,\hat{=}\; g^{(2)} = g(r)\,]$
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). $$p = \frac{N!}{(N-2)!} \times \frac{\int d\tau_3 \ldots \int d\tau_N\, e^{-\beta u(\ldots)}\, d\tau_1 d\tau_2}{Z_N}$$

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

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

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

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

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

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

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

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

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

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

$\mathcal{H}$

(12)

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

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

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

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

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: $1 + 4\pi\rho\int_0^\infty h(r)\, r^2 dr = \cancel{\rho} k_B T \cdot \frac{1}{\cancel{\rho}}\left(\frac{\partial \rho}{\partial p}\right)_T$

$$h(r) \downarrow\; g(r) - 1 = e^{-\beta\phi(r)} - 1$$

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

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

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

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

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

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

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