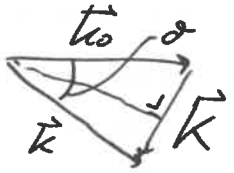
Problem set 3 – Liquids

13 a)



$$\sin\left(\frac{\vartheta}{2}\right) = \frac{\frac{1}{2}|\vec{K}|}{|\vec{k}|} = \frac{|\vec{K}|}{2k} = \frac{|\vec{K}|\lambda}{4\pi}$$

$k = \frac{2\pi}{\lambda}$

$$\Rightarrow |\vec{K}| = K = \frac{4\pi}{\lambda}\sin\left(\frac{\vartheta}{2}\right)$$

b). $K = 0.015\ \text{nm}^{-1}$
$\lambda = 532\ \text{nm}$

$$\rightarrow 0.015 = \frac{4\pi}{532}\sin\left(\frac{\vartheta}{2}\right) \rightarrow \sin\left(\frac{\vartheta}{2}\right) = \frac{0.015\times 532}{4\pi} = 0.635$$

$$\Rightarrow \vartheta = 1.37\ \text{rad} = 78.8^\circ\ \text{(large!!)}$$

$K = 0.015\ \text{nm}^{-1}$
$\lambda = 0.15\ \text{nm}$

$$\rightarrow \sin\left(\frac{\vartheta}{2}\right) = \frac{0.015\times 0.15}{4\pi} = 1.79\cdot 10^{-4}$$

$$\vartheta = 3.58\cdot 10^{-4}\ \text{rad} = 0.02^\circ\ \text{(small!!)}$$

→ this illustrates that the same 'K-info' is found at relatively large scattering angles in light scattering & at relatively small scattering angles in X-ray scattering.

c). $I(k) \sim P(k)S(k)$

1st: do experiment at very low concentrations, then $S(k) \Rightarrow 1$
for $\rho \to 0$: $S(k) = 1$, hence $I(k) \sim P(k)$.
(so you know $P(k)$).

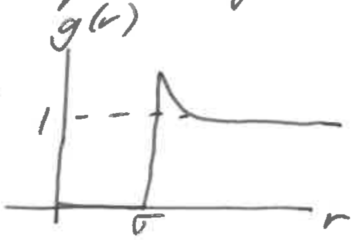
then: do experiment at higher ρ: $I(k) \sim P(k)S(k)$

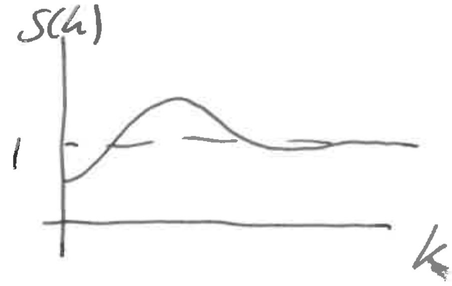
$S(k)$ is then obtained by "dividing out" $P(k)$:

$$S(k) \sim \frac{I(k)}{P(k)}.$$

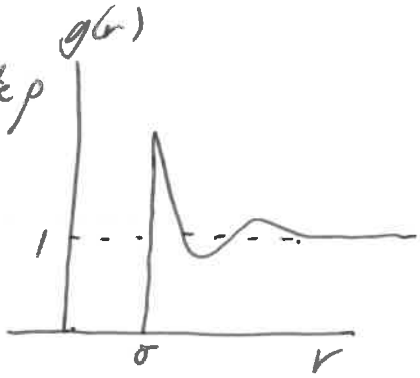
d). hard spheres $g(r)$ & $S(k)$ as ρ increases:

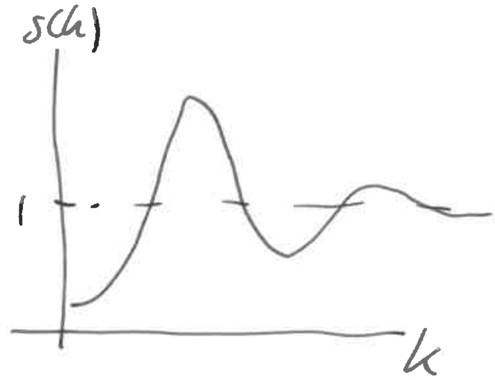
low ρ:



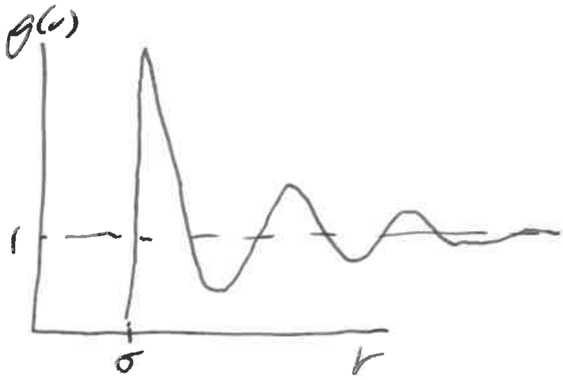


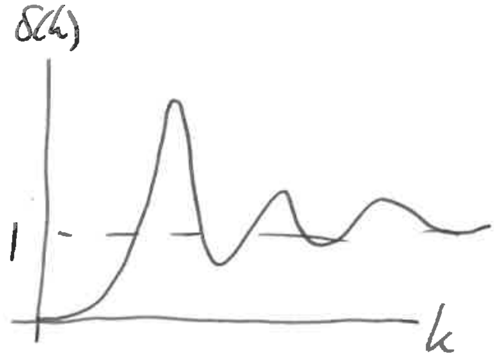
intermediate ρ





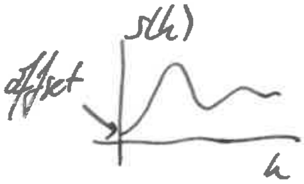
high(er) ρ





note $S(k \to 0) = \rho k_B T \kappa_T$

and compressibility κ_T decreases with increasing ρ



(14) $h_{12} = c_{12} + \rho \int d\vec{r}_3 \, c_{13} h_{32}$ (OZ)

a). $h_{12} = h(r_{12})$: total correlation function $\rightarrow h(r) = g(r) - 1$
$\hookrightarrow$ distance between particles 1 & 2

$h(r)$ [& $g(r)$]: characterises structure

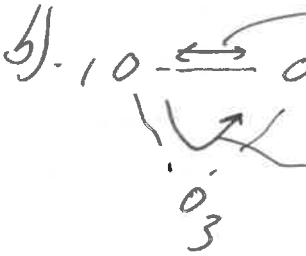
$c_{12} = c(r_{12})$: direct correlation function, accounting for structure due to direct interaction between particles 1 & 2.

closure relation: to solve OZ (integral equation) a closure relation is needed for $c(r)$ $\rightarrow$ relates this to $\phi(r)$ &/or $g(r)$.

e.g. Percus-Yevick: $c(r) = g(r)(1 - e^{\beta\phi(r)})$

Mean spherical approx: $c(r) = -\beta\phi(r)$

no need to learn these!

b). 

direct interaction

indirect interaction via particle 3

total interaction 1-2 = direct interaction 1-2 + indirect interactions through all other particles.

and/or

$$h_{12} = c_{12} + \rho \int c_{13} c_{32} \, d\vec{r}_3 + \rho^2 \iint d\vec{r}_3 d\vec{r}_4 \, c_{13} c_{34} c_{42} + \ldots$$

$$= c_{12} + \rho \int d\vec{r}_3 \, c_{13} \underbrace{\left(c_{32} + \rho \int d\vec{r}_4 \, c_{34} c_{42} + \ldots \right)}_{h_{32}.}$$

etc

c). $\hat{h}(k) = \hat{c}(k) + \rho \, \hat{c}(k) \hat{h}(k)$

$\downarrow$

$$1 + \rho \hat{h}(k) = \frac{1}{1 - \rho \hat{c}(k)}$$

(see other side)

$$\hat{h}(k) = \hat{c}(k) + \rho\hat{c}(k)\hat{h}(k)$$

$$\hat{h}(k) - \rho\cdot\hat{c}(k)\hat{h}(k) = \hat{c}(k)$$

$$\hat{h}(k)(1 - \rho\hat{c}(k)) = \hat{c}(k)$$

$\Big\downarrow \times\rho$

$$\rho\hat{h}(k)(1-\rho\hat{c}(k)) = \rho\hat{c}(k)$$

$\Big\downarrow \div(1-\rho\hat{c}(k))$

$$\rho\hat{h}(k) = \frac{\rho\hat{c}(k)}{(1-\rho\hat{c}(k))}$$

$\Big\downarrow$ + 1 both sides

$$1+\rho\hat{h}(k) = \frac{\rho\hat{c}(k)}{(1-\rho\hat{c}(k))} + \underbrace{\frac{(1-\rho\hat{c}(k))}{(1-\rho\hat{c}(k))}}_{=1}$$

$$\Rightarrow 1+\rho\hat{h}(k) = \frac{1}{1-\rho\hat{c}(k)}$$

importantly: $1+\rho\hat{h}(k) = S(k)$: structure factor

measurable in scattering experiments! (& from microscopy too using colloids).

$$S(k) = 1+\rho\hat{h}(k) = 1+\rho\int d\vec{r}\,[g(r)-1]\,e^{i\vec{k}\cdot\vec{r}}$$

$$S(k\to 0) = 1+\rho\hat{h}(k=0) = 1+\rho\int h(r)\,d\vec{r} = \rho k_B T \kappa_T$$

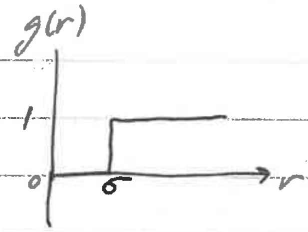
compressibility

no need to learn these!

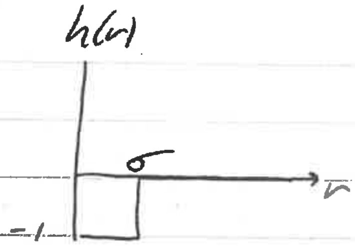
Liquids Answers

(15)

a).



$h(r) \equiv g(r) - 1$:



b).

OZ: $1 + 4\pi\rho \int_0^\infty h(r) r^2 dr = \rho k_B T \kappa_T = \rho k_B T \frac{1}{\rho}\left(\frac{\partial\rho}{\partial P}\right)_T$

P.T.O.

$$\Rightarrow 1 + 4\pi\rho \left\{ \int_0^\sigma -r^2 dr + \int_\sigma^\infty 0 \cdot r^2 dr \right\} = k_B T \left(\frac{\partial\rho}{\partial P}\right)_T$$

$$\Rightarrow 1 + 4\pi\rho \left[-\frac{r^3}{3} \right]_0^\sigma = 1 - \frac{4\pi\sigma^3}{3}\rho = k_B T \left(\frac{\partial\rho}{\partial P}\right)_T$$

use that: $v_0 = \frac{4\pi(\sigma/2)^3}{3} = \frac{1}{8}\frac{4\pi\sigma^3}{3}$ $\therefore$ $\frac{4\pi\sigma^3}{3} = 8v_0 = 2B_2$

$$\therefore \quad 1 - 2\rho B_2 = k_B T \left(\frac{\partial\rho}{\partial P}\right)_T$$

c). $S(k) = 1 + \frac{4\pi\rho}{k}\int_0^\infty h(r) \sin(kr) r\, dr = 1 + \frac{4\pi\rho}{k}\int_0^\sigma -\sin(kr) r\, dr$

$\Rightarrow$ integration by parts: $\int f g' = fg - \int f' g$ $\quad f = r \quad g' = \sin(kr)$

$$S(k) = 1 - \frac{4\pi\rho}{k}\left\{ \left[r \cdot \frac{-\cos(kr)}{k} \right]_0^\sigma - \int_0^\sigma \frac{-\cos(kr)}{k} dr \right\} =$$

$$= 1 - \frac{4\pi\rho}{k}\left\{ \left[\frac{-\sigma\cos(k\sigma)}{k} + 0 \right] + \frac{1}{k}\left[\frac{1}{k}\sin(kr) \right]_0^\sigma \right\} =$$

$$= 1 - \frac{4\pi\rho}{k}\left[-\frac{\sigma\cos(k\sigma)}{k} + \frac{1}{k^2}\sin(k\sigma) \right]$$

$$= 1 + \frac{4\pi\rho}{k^2}\left(\sigma\cos(k\sigma) - \frac{\sin(k\sigma)}{k} \right)$$

d) If $\sigma \to 0$ $\quad S(k) = 1 \rightarrow$ ideal gas. (p.T.o).

$$S(k\to 0) = \rho k_B T \kappa_T \underset{\uparrow}{=} k_B T \left(\frac{\partial \rho}{\partial P}\right)_T$$

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T$$

$\Rightarrow$ we've established that $S(k) = 1$ as $\sigma \to 0$, so $S(k=0) = 1$

$$\Rightarrow k_B T \left(\frac{\partial \rho}{\partial P}\right)_T = 1 \to \int dP = k_B T \int d\rho \to P = \rho k_B T$$

$\Rightarrow$ indeed perfect gas law.

b). $S(k) = 1 + \rho \int h(r) e^{i\vec{k}\cdot\vec{r}} d\vec{r}$

$$S(k\to 0) = 1 + \rho \int h(r) \underbrace{e^{i\cdot 0}}_{1} d\vec{r} = 1 + \rho \int h(r)\, d\tau$$ ($d\vec{r}$ = volume element $d\tau$)

$$= 1 + \rho \int h(r) 4\pi r^2 dr$$ (spherical coords).

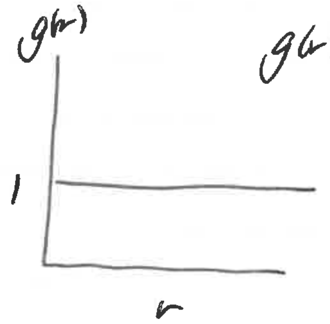
$$= 1 + 4\pi\rho \int_0^\infty h(r) r^2 dr = \rho k_B T \kappa_T$$

$$\Rightarrow S(k\to 0) = \rho k_B T \kappa_T$$

(16) as $\rho \to 0$ $\quad g(r) = e^{-\beta\phi(r)}$

a). perfect gas:

$\phi(r) = 0$

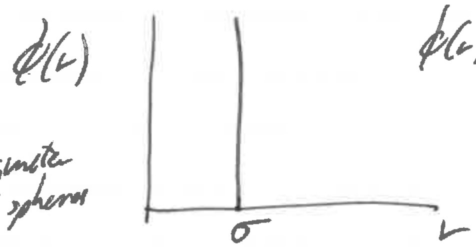


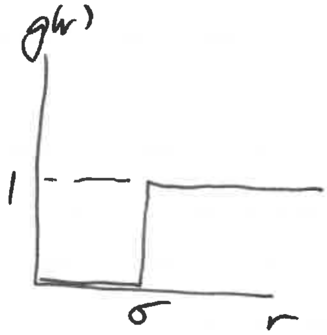
$g(r) = e^{-0} = 1$

b). hard sphere gas (dilute)

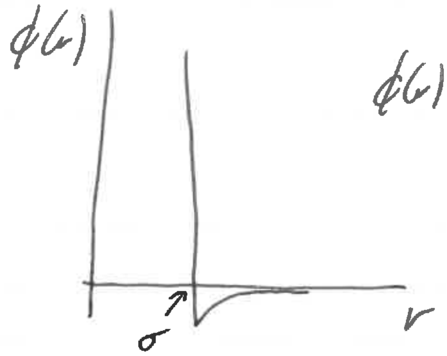
$\phi(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma \end{cases}$

σ = diameter hard spheres



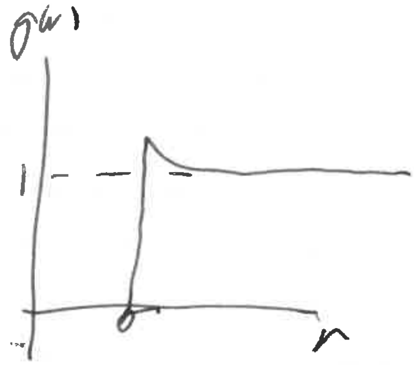


c). hard sphere gas + attraction



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

for example



(17) $E = kT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$ & $Q = \frac{1}{N!}\left(\frac{2\pi m kT}{h^2}\right)^{\frac{3N}{2}} Z_N$

a). $E = kT^2 \frac{\partial}{\partial T}\left\{ \ln\left(\frac{1}{N!}\right)^{\to 0} + \frac{3N}{2}\left(\frac{2\pi m kT}{h^2}\right) + \ln Z_N \right\}_{N,V} =$

$= kT^2 \left(\frac{3N}{2} \cdot \left(\cancel{\frac{h^2}{2\pi m kT}}\right) \cdot \left(\cancel{\frac{2\pi m k}{h^2}}\right) + \left(\frac{\partial \ln Z_N}{\partial T}\right)_{N,V} \right) =$

$= \frac{3N}{2} \cdot \frac{kT^{\cancel{2}}}{\cancel{T}} + kT^2 \left(\frac{\partial \ln Z_N}{\partial T}\right)_{N,V}$

$= \frac{3}{2} N k_B T + kT^2 \left(\frac{\partial \ln Z_N}{\partial T}\right)_{N,V}$ $\quad (= \underbrace{E_{kin}}_{\frac{3}{2}NkT} + \underbrace{\langle U \rangle}_{Z_N \text{ (interaction)}})$

b) $\langle U \rangle = kT^2 \left(\frac{\partial \ln Z_N}{\partial T}\right)_{N,V}$ & $Z_N = \int d\tau_1 \ldots \int d\tau_N \, e^{-\beta U(-)}$

$\langle U \rangle = kT^2 \frac{1}{Z_N} \left(\frac{\partial Z_N}{\partial T}\right)_{N,V}$ $\to$ convenient to change $\partial T \to \partial \beta$

$\beta = \frac{1}{kT} \to \frac{\partial \beta}{\partial T} = \frac{-1}{kT^2} \to \frac{1}{\partial T} = \frac{-1}{kT^2}\frac{1}{\partial \beta}$ $\quad (\text{or } d\beta = -\frac{1}{kT^2} dT)$

$\Rightarrow$ so: $\langle U \rangle = \cancel{kT^2} \frac{1}{Z_N} \cdot \frac{-1}{\cancel{kT^2}} \left(\frac{\partial Z_N}{\partial \beta}\right)_{N,V} = -\frac{1}{Z_N}\left(\frac{\partial Z_N}{\partial \beta}\right)_{N,V}$

$= -\frac{1}{Z_N} \int d\tau_1 \ldots \int d\tau_N \frac{\partial}{\partial \beta}\left(e^{-\beta U(..)}\right) =$

$= -\frac{1}{Z_N} \int d\tau_1 \ldots \int d\tau_N \, -U(..) \, e^{-\beta U(..)} =$

$$\langle U \rangle = \frac{\int d\tau_1 \ldots \int d\tau_N \, U \, e^{-\beta U(..)}}{Z_N}$$

(starting point in lecture 6)

also shown that this "definition" of mean U, just follows from stat. mech!

(of course: $\langle x \rangle = \frac{\int x f(x) dx}{Z_N}$).

c). see lectures : $\langle u \rangle = \dfrac{\int d\tau_1 .. \int d\tau_N \, u \, e^{-\beta u(..)}}{Z_N}$ $\qquad u = \sum_{i>j} \phi_{ij}$

$$\langle u \rangle = \frac{\int d\tau_1 .. \int d\tau_N \sum_{i>j} \phi_{ij} e^{-\beta u}}{Z_N} = \underset{\substack{\uparrow \\ \text{number of pairs \& no double counting.}}}{\frac{N(N-1)}{2}} \frac{\int d\tau_1 .. \int d\tau_N \, \phi_{12} e^{-\beta u}}{Z_N}$$

$$\langle u \rangle = \frac{N(N-1)}{2} \int d\tau_1 \int d\tau_2 \, \phi_{12} \underbrace{\left| \frac{\int d\tau_3 .. \int d\tau_N e^{-\beta u(..)}}{Z_N} \right|}_{} = \frac{g(r)}{V^2}$$

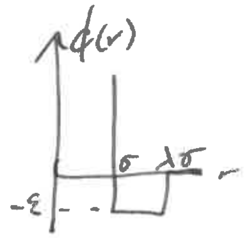
$$= \frac{N(N-1)}{2V^2} \int d\tau_1 \int d\tau_2 \, \phi_{12} \, g(r) \quad \rightarrow \text{particle 1 can be anywhere}$$

$r = |\vec{r}_1 - \vec{r}_2|$

$$= \frac{N \boxed{(N-1)}}{2 \underset{=\rho}{\boxed{V^{\cancel{2}}}}} \cdot \cancel{V} \int d\tau \, \phi(r) g(r)$$

$$= \frac{N\rho}{2} \int 4\pi r^2 \phi(r) g(r) \, dr = 2\pi \rho N \int_0^\infty r^2 \phi(r) g(r) \, dr.$$

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



& $g(r) = e^{-\beta\phi(r)}$

$$\langle u \rangle = 2\pi\rho N \left\{ \underbrace{\int_0^\sigma r^2 \cdot \infty \cdot \underset{=0,\ \text{explains}}{e^{-\beta \cdot \infty}} dr}_{=0} + \int_\sigma^{\lambda\sigma} r^2 \cdot -\varepsilon \cdot e^{+\varepsilon\beta} dr + \underbrace{\int_{\lambda\sigma}^\infty r^2 \cdot 0 \cdot e^{-\beta \cdot 0} dr}_{=0} \right\}$$

$$= -2\pi\rho N \varepsilon e^{\varepsilon\beta} \int_\sigma^{\lambda\sigma} r^2 dr = -2\pi\rho N \varepsilon e^{\varepsilon\beta} \left[\tfrac{1}{3} r^3\right]_\sigma^{\lambda\sigma} =$$

$$= -\frac{2\pi\rho N \varepsilon e^{\varepsilon\beta}}{3} \left((\lambda\sigma)^3 - \sigma^3 \right) \Rightarrow \langle u \rangle = -\frac{2\pi}{3} \rho N \varepsilon e^{\varepsilon\beta} \sigma^3 (\lambda^3 - 1)$$

$\Rightarrow$ if $\lambda = 1$: $\langle u \rangle = 0$, of course: hard sphere potential is recovered
no overlap $\rightarrow$ no potential energy!

π.