Physics 212 – Problem Set #4
Solutions

1.) a.) Since S is extensive, $S \sim N$ as $N \to \infty$

N, V, E are all extensive, so

(1) $$S = N f\left(\frac{V}{N}, \frac{E}{N}\right)$$

let $\frac{\partial}{\partial x_1} f(x_1, x_2) \equiv f_{,1}$ $\qquad$ $\frac{\partial}{\partial x_2} f(x_1, x_2) \equiv f_{,2}$

then

$$N \frac{\partial}{\partial N} S\Big|_{V,E} = N f + N \cdot N \cdot \left(-\frac{V}{N^2}\right) f_{,1} + N \cdot N \cdot \left(-\frac{E}{N^2}\right) f_{,2}$$

$$V \frac{\partial S}{\partial V}\Big|_{N,E} = N \cdot V \cdot \frac{1}{N} f_{,1}$$

$$E \frac{\partial S}{\partial E}\Big|_{V,N} = N \cdot E \cdot \frac{1}{N} f_{,2}$$

so $$N \frac{\partial S}{\partial N}\Big|_{V,E} + V \frac{\partial S}{\partial V}\Big)_{N,E} + E \frac{\partial S}{\partial E}\Big|_{V,N} = N f = S$$

(2) If $N \to \lambda N$ $\quad V \to \lambda V$ $\quad E \to \lambda E$ then $S \to \lambda S$

let $\lambda = 1 + \alpha$

$$\frac{\partial}{\partial \alpha} S(\alpha) = S = N \frac{\partial}{\partial N} S\Big|_{V,E} + V \frac{\partial S}{\partial V}\Big|_{N,E} + E \frac{\partial S}{\partial E}\Big|_{V,N}$$

Now $\quad \left.\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T} \qquad \left.\frac{\partial S}{\partial V}\right|_{N,E} = \frac{P}{T} \qquad \left.\frac{\partial S}{\partial E}\right|_{N,V} = \frac{1}{T}$

so

$$S = -\frac{\mu}{T}N + \frac{P}{T}V + \frac{E}{T}$$

or

$$S = \frac{E + PV - \mu N}{T} \qquad E = TS - PV + \mu N$$

Here is another proof of this relation:

We proved in class $\quad \Phi = -PV$

but $\quad \Phi = E - TS - \mu N$

b) For the ideal gas

$$S = \frac{5}{2}N + N \log\left[\frac{V}{N}\left(\frac{E}{N}\right)^{3/2} \cdot C\right]$$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{3}{2}N\frac{1}{E}$$

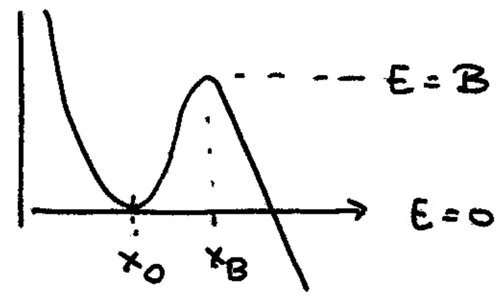
$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{N}{V}$$

$$-\frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_{V,E} = \frac{5}{2} + \log\left[\frac{V}{N}\left(\frac{E}{N}\right)^{3/2} C\right] - \frac{5}{2}\frac{N}{N}$$

$$\frac{1}{T}(E + PV - \mu N) = \frac{3}{2}N + N + N \cdot \log\left[\frac{V}{N}\left(\frac{E}{N}\right)^{3/2} C\right]$$

$$= \frac{5}{2}N + N \log \frac{V}{N}\left(\frac{E}{N}\right)^{3/2} \cdot C \quad = \quad S \quad ✓$$

2.) a) We have a potential $U(x)$



For particles in equilibrium in the well, the phase space distribution is

$$\int \frac{dx\,dp}{2\pi\hbar} \quad e^{-\beta U(x)} \quad e^{-\beta p^2/2m}$$

so $$\frac{\rho(x_B)}{\rho(x_0)} = e^{-\beta B}$$

b) At the bottom of the well $\quad U(x) = \frac{1}{2} M\omega^2 (x-x_0)^2$

so $$\rho(x) \sim e^{-\beta \cdot \frac{1}{2} M\omega^2 (x-x_0)^2}$$

and we can normalize this distribution:

$$\rho(x) = \frac{1}{\sqrt{2\pi/\beta M\omega^2}} \exp\left[-\frac{\beta M\omega^2}{2}(x-x_0)^2\right]$$

so $$\rho(x_0) = \left(\frac{M\omega^2}{2\pi T}\right)^{\frac{1}{2}}$$

This result is not exact, because the potential deviates from a quadratic function for $(x-x_0)$ large. However, these corrections are suppressed by an exponential factor

$$e^{-\frac{\beta}{2} M\omega^2 (\Delta x)^2}$$

c.) Given ~~that~~ a particle has reached the top of the barrier, it can cross the barrier if $v > 0$

$$\begin{pmatrix} \#\text{ of particles crossing} \\ \text{in } \Delta t \end{pmatrix} = \rho(x_B) \cdot \int \frac{dp}{\sqrt{2\pi M/\beta}} \, e^{-\beta p^2/2M}$$

$$\cdot \; \Theta(p) \cdot \frac{p}{m} \Delta t$$

so

$$\underset{\text{decays/time}}{\Gamma} = \rho(x_B) \cdot \frac{1}{\sqrt{2\pi M T}} \cdot \int_0^\infty dp \, \frac{p}{M} \, e^{-\beta \frac{p^2}{2m}}$$

$$= \rho(x_B) \cdot \frac{1}{\sqrt{2\pi M T}} \cdot \frac{1}{\beta}$$

$$= \left(\frac{M\omega^2}{2\pi T}\right)^{1/2} \frac{1}{[2\pi M T]^{1/2}} \cdot T \cdot e^{-B/T}$$

or

$$\Gamma = \frac{\omega}{2\pi} \, e^{-B/T}$$

Note that the units are correct: $\Gamma \sim \frac{1}{\text{sec.}}$

3.) a.) We consider the system

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (E:S) \xrightarrow{k_{cat}} E + P$$

the rate equations are:

$$\frac{d}{dt}[E:S] = k_1 [S][E] - k_{-1} [E:S]$$

$$\frac{d}{dt}[P] = k_{cat} [E:S]$$

Now assume:

① the first reaction runs to equilibrium:

$$[E:S] = \frac{k_1}{k_{-1}} [S][E]$$

② the amount of E is fixed: $[E] + [E:S] = E_{tot}$.

$$[E:S] = \frac{k_1}{k_{-1}} [S] (E_{tot} - [E:S])$$

$$\left(1 + \frac{k_1}{k_{-1}}[S]\right) [E:S] = \frac{k_1}{k_{-1}} [S] E_{tot}.$$

$$[E:S] = \frac{[S]\ E_{tot}}{\frac{k_{-1}}{k_1} + [S]}$$

then
$$\frac{d[P]}{dt} = \frac{k_{cat}\ E_{tot}\ [S]}{\frac{k_{-1}}{k_1} + [S]}$$

This has the Michaelis-Menten form with

$$V_{max} = k_{cat} E_{tot} \qquad K_M = \frac{k_{-1}}{k_1}$$

b.) Next consider

$$E + nS \underset{k_u}{\overset{k_b}{\rightleftharpoons}} E:nS \xrightarrow{k_{cat}} E + P$$

now $$\frac{d}{dt}[E:nS] = k_b[E][S]^n - k_u[E:nS]$$

in equilibrium

$$[E:nS] = \frac{k_b}{k_u}[E][S]^n$$

If we assume $[E] + [E:nS] = E_{tot}$. we can eliminate $[E:nS]$ just as in part (a). This gives

$$\frac{d}{dt}[P] = \frac{k_{cat}\, E_{tot}\, [S]^n}{\frac{k_u}{k_b} + [S]^n}$$

This has the form of the Hill equation with

$$V_{max} = k_{cat} E_{tot} \qquad K_H^n = \frac{k_u}{k_b}$$

4.) Work this problem using the grand canonical ensemble.
The partition function for an ideal gas is

$$\Xi = \sum_{N=0}^{\infty} \frac{1}{N!} \xi^N V^N = \exp[\xi V]$$

$$\xi = \left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} e^{\beta\mu} \quad \underset{\text{(in class)}}{\Rightarrow} \quad \xi = n = \frac{N}{V}$$

a.)

$$\rho(x_1, x_2) = \frac{\sum_{N=2}^{\infty} \frac{1}{N!} \xi^N \int d^{3N}x \sum_{i \neq j} \delta(\vec{x}_i - \vec{x}_1)\, \delta(\vec{x}_j - \vec{x}_2)}{\Xi}$$

$\bar{N} = N-2$

$$= \frac{1}{\Xi} \sum_{\bar{N}=0}^{\infty} \frac{1}{(\bar{N}+2)!} \xi^{\bar{N}+2} V^{\bar{N}} \cdot \underbrace{N(N-1)}$$

number of ways to choose x_i, x_j

$$= \frac{1}{\Xi} \sum_{\bar{N}=0}^{\infty} \frac{1}{\bar{N}!} \xi^{\bar{N}} V^{\bar{N}} \cdot \xi^2 = \xi^2 = n^2$$

so, for the ideal gas $\rho(\vec{x}_1, \vec{x}_2) = n^2$

b.) In a large volume where the typical atom is far from a wall, $\rho(\vec{x}_1, \vec{x}_2)$ satisfies:

$$\rho(\vec{x}_1 + \vec{a}, \vec{x}_2 + \vec{a}) = \rho(\vec{x}_1, \vec{x}_2) \qquad \text{indep of location}$$

so $\rho(\vec{x}_1, \vec{x}_2) = \rho(\vec{x}_1 - \vec{x}_2)$

If the atoms interact through central forces, ρ should also be invariant under rotations of the system of atoms. Then

$$\rho(\vec{x}_1, \vec{x}_2) = \rho(|\vec{x}_1 - \vec{x}_2|)$$

c.) Now add a contact potential between atoms. The numerator of the expression for ρ now becomes.

$$\sum_{N=2}^{\infty} \frac{1}{N!} \xi^N \int d^{3N}x \prod_{\substack{<k\ell> \\ \text{pairs}}} [1 + (e^{-\beta V(x_k - x_\ell)} - 1)]$$

$$\sum_{i \neq j} \delta(x_i - \vec{x}_1)\, \delta(x_j - \vec{x}_2)$$

the term w. all 1's gives

$$\sum_{N=2}^{\infty} \frac{1}{N!} \xi^N \; N(N-1) \; V^{N-2}$$

However, the term $(e^{-\beta V(x_k - x_\ell)} - 1)$ with $(x_k x_\ell) = (x_i\, x_j)$

gives a term of the same order in n:

$$\sum_{N=2}^{\infty} \frac{1}{N!} \xi^N \; N(N-1) \; V^{N-2} \cdot (e^{-\beta V(x_i - x_j)} - 1)$$

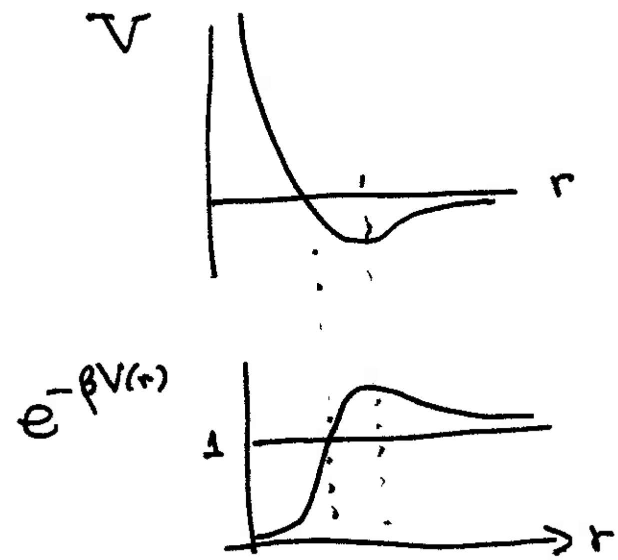
in all

$$\rho(x_1 x_2) = \frac{e^{\xi V} \cdot \xi^2 \cdot [1 + (e^{-\beta V(x_1 - x_2)} - 1)]}{\Xi}$$

$$= \xi^2 \; e^{-\beta V(x_1 - x_2)}$$

$$= n^2 \; e^{-\beta V(x_1 - x_2)} \qquad + O(n^3)$$

For a Lennard-Jones potential



so $\rho(r)$ is small when $r <$ radius of "hard core"
large in the attractive region of the potential
$\rightarrow n^2$ as $r \rightarrow \infty$

These are the expected properties.

d.) We can now expand the numerator of $\rho(x_1, x_2)$ to higher powers in $(e^{-\beta V}-1)$. A typical term is:

$$\sum_N^\infty \frac{1}{N!} z^N V^{N-6} \int dx_a\, dx_b\, dx_c\, dx_d\, dx_e\, dx_f$$

$$(e^{-\beta V(x_a - x_b)}-1)(e^{-\beta V(x_c-x_d)}-1)(e^{-\beta V(x_e-x_f)}-1)$$

$$\sum_{i \neq j} \delta(x_i - x_1)\, \delta(x_j - x_2) \quad \cdot \text{(counting factor)}$$

For the counting factor, the points identified with $\vec{x}_1$ and $\vec{x}_2$ are uniquely identified. There are $N(N-1)$ ways to choose these. The points $x_a - x_f$ might or might not be equal to those. In any case, if we identify p distinct points we get a counting factor

$$N(N-1)\cdots(N+1-p)\cdot\frac{1}{S}$$

where the symmetry factor S is the number of ways to interchange identifications of the unlabeled points. One identification associated with the term above is

$$x_a \to x_2 \qquad \text{all of } x_a - x_f \text{ distinct}$$

then we get:

$$\sum_{N=7}^{\infty} \frac{1}{N!}\, \xi^N\, V^{N-7} \int d^3x_b - d^3x_f$$

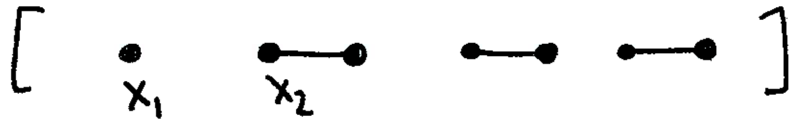
$$\left(e^{-\beta V(x_2-x_b)}-1\right)\left(e^{-\beta V(x_c-x_d)}-1\right)\left(e^{-\beta V(x_e-x_f)}-1\right)$$

$$\times\; N(N-1)\frac{(N-2)(N-3)(N-4)(N-5)(N-6)}{2\cdot 2\cdot 2}$$

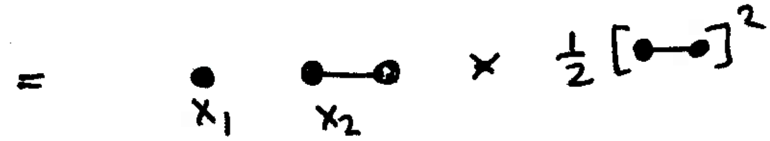
$$= e^{\xi V}\, \xi^7 \int d^3x_b \left[e^{-\beta V(x_2-x_b)}-1\right]$$

$$\cdot\frac{1}{2}\left(\frac{1}{2}\int d^3x_c\, d^3x_d \left[e^{-\beta V(x_c-x_d)}-1\right]\right)^2$$

We can associate with this term a diagram



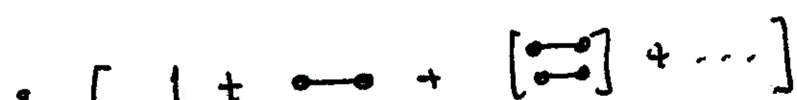
where points that are not labelled are to be integrated over. This is a disconnected diagram. It evaluates to a product of connected diagrams:



In general

(numerator of $\rho(x_1, x_2)$)

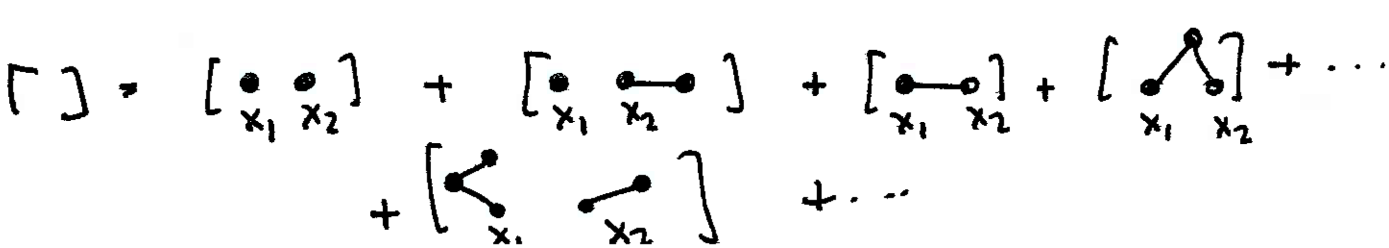
$$= e^{\xi V} \cdot \left[\text{ diagrams w. 2 labelled points } x_1, x_2 \right]$$



$$= e^{\xi V} \cdot \exp\left[\sum \text{ connected diagrams w. } \underline{\text{no}} \text{ labelled points} \right]$$

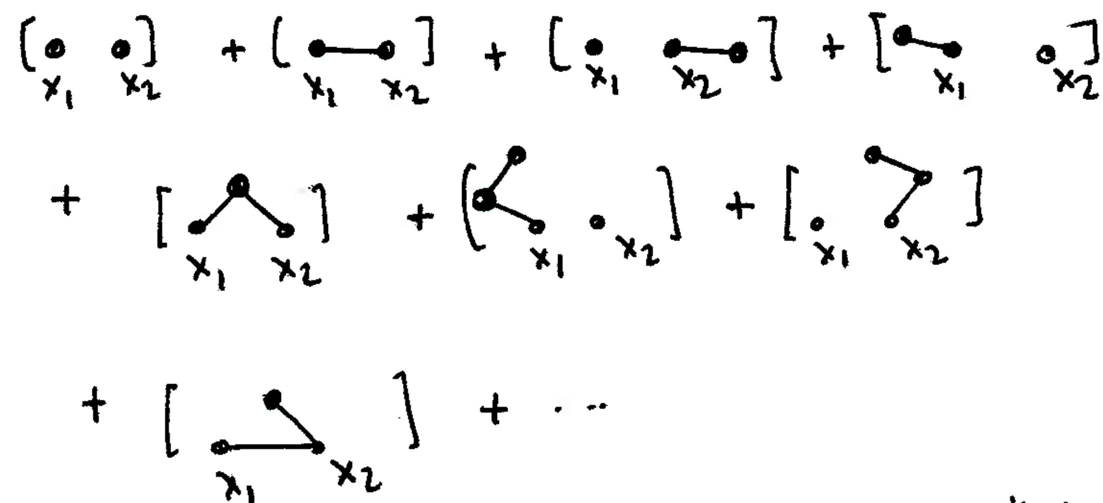
$$\cdot \left[\text{ diagrams w. 2 labelled points } x_1, x_2 \right]$$

the last factor is



so, dividing by the diagrammatic expression for Ξ

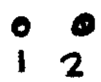
$\rho(x_1,x_2) =$

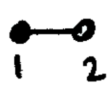


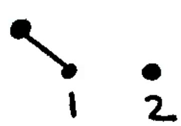
In each diagram, the integral over unlabelled points is controlled by the factor $(e^{-\beta V(r)}-1)$ which $\to 0$ as $r\to\infty$.

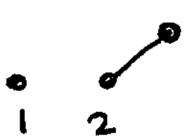
So each diagram is independent of the Volume.

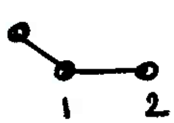
e.) Evaluate all diagrams of order up to ξ^3:

 $= 1\cdot\xi^2$

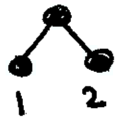
 $= \xi^2\left(e^{-\beta V(x_1-x_2)}-1\right)$

 $= \xi^3\int d^3x\left(e^{-\beta V(x_1-x)}-1\right)$

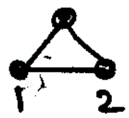
 $= \xi^3\int d^3x\left(e^{-\beta V(x_2-x)}-1\right)$

 $= \xi^3\int d^3x\left(e^{-\beta V(x_1-x)}-1\right)\left(e^{-\beta V(x_1-x_2)}-1\right)$

$$= \xi^3 \int d^3x \left(e^{-\beta V(x_2 - x)} - 1\right)\left(e^{-\beta V(x_1 - x_2)} - 1\right)$$



$$= \xi^3 \int d^3x \left(e^{-\beta V(x_1 - x)} - 1\right)\left(e^{-\beta V(x_2 - x)} - 1\right)$$



$$= \xi^3 \int d^3x \left(e^{-\beta V(x_1 - x)} - 1\right)\left(e^{-\beta V(x_2 - x)} - 1\right)\left(e^{-\beta V(x_1 - x_2)} - 1\right)$$

The first two diagrams give

$$\xi^2 e^{-\beta V(x_1 - x_2)}$$

The next four diagrams give

$$2 \xi^3 e^{-\beta V(x_1 - x_2)} \int d^3x \left(e^{-\beta V(x)} - 1\right)$$

The final two diagrams give

$$\xi^3 e^{-\beta V(x_1 - x_2)} \int d^3x \left(e^{-\beta V(x_1 - x)} - 1\right)\left(e^{-\beta V(x_2 - x)} - 1\right)$$

so

$$\begin{aligned} \rho(x_1, x_2) = {} & \xi^2 e^{-\beta V(x_1 - x_2)} \\ & + \xi^3 e^{-\beta V(x_1 - x_2)} \cdot \Big\{ 2 \int d^3x \left(e^{-\beta V(x)} - 1\right) \\ & \qquad + \int d^3x \left(e^{-\beta V(x_1 - x)} - 1\right)\left(e^{-\beta V(x_2 - x)} - 1\right) \Big\} \end{aligned}$$

where, as we derived in class

$$\xi = n - n^2 \int d^3x \, (e^{-\beta V(x)} - 1) + \mathcal{O}(n^3)$$

Make the substitution:

$$\rho(x_1, x_2) = n^2 e^{-\beta V(x_1 - x_2)} - 2n^3 e^{-\beta V(x_1 - x_2)} \int dx (e^{-\beta V(x)} - 1)$$

$$+ n^3 e^{-\beta V(x_1 - x_2)} \cdot 2 \int dx \, e^{-\beta V(x)} - 1$$

$$+ n^3 e^{-\beta V(x_1 - x_2)} \int dx \, (e^{-\beta V(x_1 - x)} - 1)(e^{-\beta V(x_2 - x)} - 1)$$

$$+ \mathcal{O}(n^4)$$

The second and third terms cancel and we find

$$\rho(x_1, x_2) = n^2 e^{-\beta V(x_1 - x_2)}$$

$$\cdot \left\{ 1 + n \int d^3x \, (e^{-\beta V(x_1 - x)} - 1)(e^{-\beta V(x_2 - x)} - 1) \right.$$

$$\left. + \mathcal{O}(n^2) \right\}$$

the second term in brackets goes to 0 when x is far from x_1 or x_2, so

$$\rho(x_1, x_2) \to n^2 \qquad \text{as } |x_1 - x_2| \to \infty$$

Evaluate this for hard spheres:

$$e^{-\beta V(r)} = \begin{cases} 0 & r<a \\ 1 & r>a \end{cases}$$

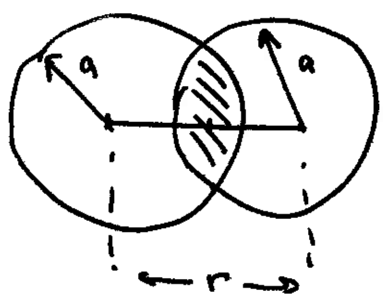
so in

$$\int d^3x \, (e^{-\beta V(x_1-x)}-1)(e^{-\beta V(x_2-x)}-1)$$

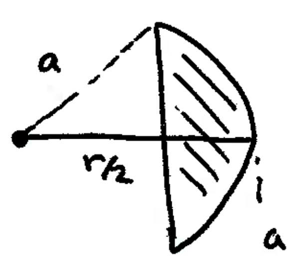
the integrand is $+1$ when both $|x_1-x|<a$ and $|x_2-x|<a$ and zero otherwise. Note that this is a positive contribution to $\rho(r)$

Because of the factor $e^{-\beta V(x_1-x_2)}$ in ρ, $|x_1-x_2|>a$

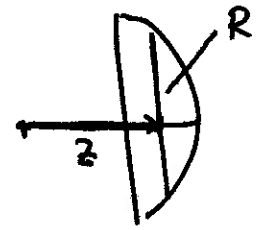
So, the region in which the integrand above is 1 has the form



and vanishes when $r>2a$. We can picture this volume as two lenses



Divide each lens into discs. The volume is



$$\int_{r/2}^{a} dz \;\; \pi R^2$$

$$= \int_{r/2}^{a} dz \;\; \pi (a^2 - z^2)$$

$$= \pi a^3 - \pi a^2 \frac{r}{2} - \frac{\pi}{3} a^3 + \frac{\pi}{3}\left(\frac{r}{2}\right)^3$$

$$= \frac{2\pi a^3}{3} - \frac{\pi a^2 r}{2} + \frac{\pi r^3}{24}$$

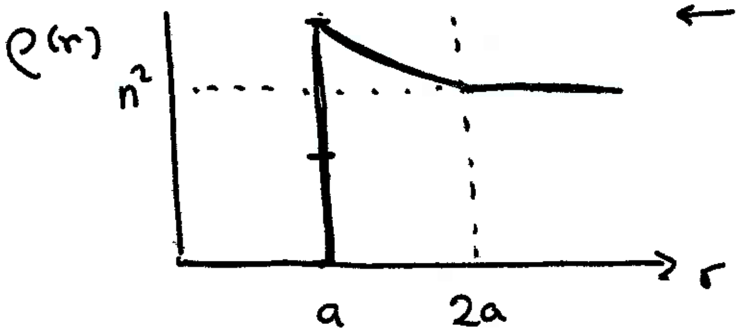
Check: if $r \to 0$ we get a half-sphere : $\frac{2\pi}{3} a^3$ ✓

if $r = 2a$ we get zero : $\frac{2}{3}\pi a^3 - \pi a^3 + \frac{\pi}{3} a^3 = 0$ ✓

then $$\int d^3x \, (e^{-\beta V(x_1 - x)} - 1)(e^{-\beta V(x_2 - x)} - 1)$$

$$= \frac{4\pi a^3}{3} - \pi a^2 r + \frac{\pi r^3}{12}$$

$$\rho(r) = \Theta(r-a) \Big\{ n^2 + n^3 \, \Theta(2a - r) \left[\frac{4\pi a^3}{3} - \pi a^2 r + \frac{\pi r^3}{12} \right] + \mathcal{O}(n^4) \Big\}$$



$$\leftarrow \quad n^2 + n^3 \cdot \frac{5\pi}{12} a^3 + \cdots$$

It is remarkable that the correction to ρ is positive.

This is an entropic attraction: The spheres at x_1, x_2 push other spheres away, so they can get closer.

In computer simulations, hard spheres liquify and even solidify at low enough temperature.