Lecture 3: The virial expansion.

Recap Generic classical Hamiltonian (no internal degrees of freedom)

$$H(\vec{r}^N, \vec{p}^N) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \underbrace{\Phi(\vec{r}^N)}_{\sum_{i=1}^{N} V_{ext}(\vec{r}_i) + \sum_{i<j} v(|\vec{r}_i - \vec{r}_j|) + \ldots}$$

The canonical partition function in the classical limit is

$$Z(N,V,T) = \frac{1}{h^{3N} N!} \int d\vec{p}^N \int d\vec{r}^N e^{-\beta H(\vec{r}^N, \vec{p}^N)}$$

$$= \frac{Q(N,V,T)}{N!\,\Lambda^{3N}} \qquad \text{with} \qquad Q(N,V,T) = \int d\vec{r}^N e^{-\beta \Phi(\vec{r}^N)}$$

momentum integrations are Gaussian

configurational integral

Here, $\Lambda = \dfrac{h}{\sqrt{2\pi m k_B T}}$

$\rightsquigarrow$ Problem boils down to computing $Q(N,V,T)$.

For now, let us consider the case where $V_{ext} = 0$ (homogeneous / bulk systems).

Furthermore, we neglect three-body interactions.

Then

$$Z(N,V,T) = \frac{1}{N!\,\Lambda^{3N}} \int d\vec{r}^N \underbrace{\exp\left[-\beta \sum_{i<j} v(r_{ij})\right]}_{\prod_{i<j} \left(\underbrace{e^{-\beta v(r_{ij})} - 1}_{:= f_M(r_{ij})} + 1 \right)}$$

$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$

$r_{ij} = |\vec{r}_{ij}|.$

Mayer function.

$$= \prod_{i<j} (1 + f_M(r_{ij})) = 1 + \sum_{i<j} f_M(r_{ij}) + \ldots$$

identical particles and there are $\frac{N(N-1)}{2}$ pairs.

2

$$\vec{R} = (\vec{r}_1 + \vec{r}_2)/2 \ ; \ \vec{r} = \vec{r}_1 - \vec{r}_2 .$$

$$= \frac{V^N}{N!\Lambda^{3N}} + \frac{V^{N-2}}{N!\Lambda^{3N}} \frac{N(N-1)}{2} \int d\vec{r}_1 \int d\vec{r}_2 \, f_M(r_{12}) = V \int d\vec{r} \, f_M(r)$$

$$= \frac{V^N}{N!\Lambda^{3N}} \left[1 - \frac{N(N-1)}{V} B_2 + \ldots \right]$$

where we have defined the second virial coefficient

$$B_2 = -\frac{1}{2} \int d\vec{r} \, f_M(r) \qquad \text{Note that } B_2 = B_2(T)$$

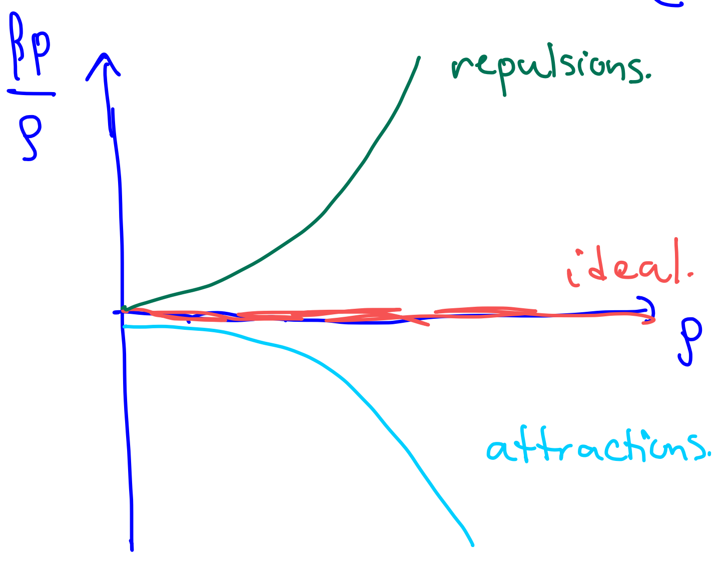
Define $F_{ex}(N,V,T) = F(N,V,T) - F_{id}(N,V,T)$

$$\Rightarrow f_{ex} = \frac{\beta F_{ex}(N,V,T)}{V} = \frac{N(N-1)}{V^2} B_2 \overset{N\gg 1}{=} \rho^2 B_2(T). \qquad f = \frac{F}{V}$$

We can obtain the pressure as $\beta p = -f + \rho \left(\frac{\partial f}{\partial \rho} \right)_T$ and find

$$\Rightarrow \beta p = \rho + B_2(T) \rho^2 + \ldots \quad \begin{cases} B_2 > 0 & \text{repulsions} \\ B_2 < 0 & \text{attractions} \end{cases}$$

corresponds to whether B_2 is dominated by attractions or repulsions!



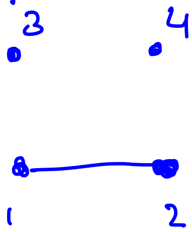
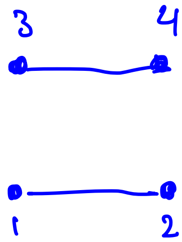
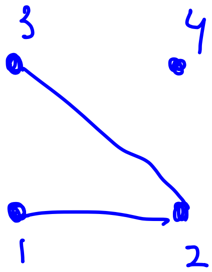
How to obtain higher order corrections?

$$Z(N,V,T) = \frac{1}{N!\Lambda^{3N}} \int d\vec{r}^N \left[1 + \sum_{i<j} + \sum_{i<j} \sum_{k<l} f_M(r_{ij}) f_M(r_{kl}) + \ldots \right]$$

This can be represented in a graphical way:

$$Z(N,V,T) = \frac{1}{N!\Lambda^{3N}} \sum_G W[G] \qquad \text{where } G \text{ are graphs.}$$

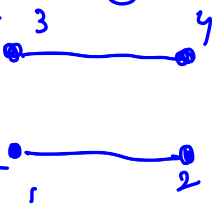
For example, $N=4$.

$f_{12} =$ 
$f_{12} f_{34} =$ 
$f_{12} f_{23} =$ 
etc.

where we introduced notation $f_{ij} = f_M(r_{ij})$.

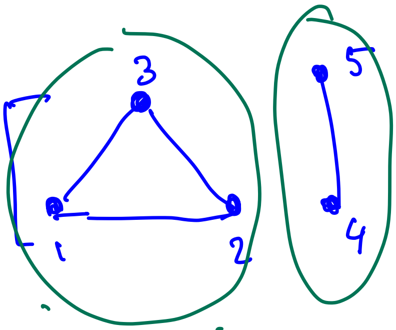
$W[G]$ integral over graph.

Note when graph is disconnected:

$W\Big[$  $\Big] = \left(\int d\vec{r}_1 \int d\vec{r}_2\, f_{12}\right)\left(\int d\vec{r}_3 \int d\vec{r}_4\, f_{34}\right)$ (i)

factorization of integrals.

or

$W\Big[$  $\Big]$ $\left(\int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_3\, f_{12} f_{23} f_{31}\right)\left(\int d\vec{r}_4 \int d\vec{r}_5\, f_{45}\right)$ (ii).

clusters

A cluster consisting of ℓ particles is called ℓ-cluster.

E.g., (i) has two 2-clusters and (ii) one 3-cluster and one 2-cluster.

For N-body system: $\sum_{\ell=1}^{N} m_\ell\, \ell = N$ (iii) with m_ℓ # ℓ-clusters.

It turns out that (we will not prove it here)

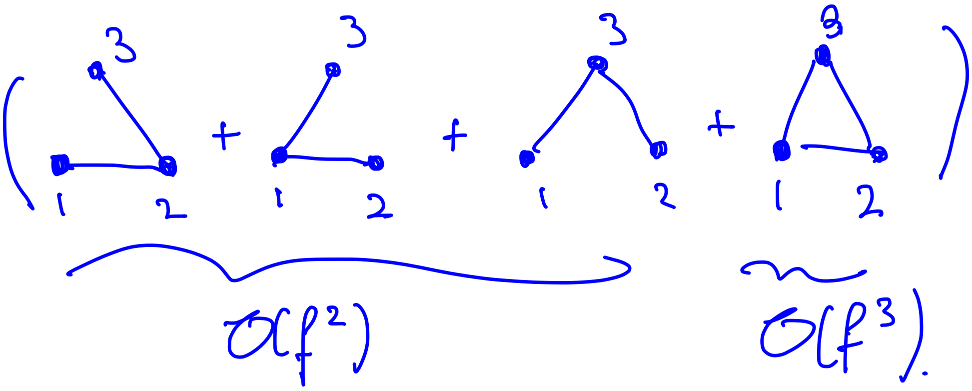
$$\sum_G W[G] = N! \sum_{\{m_\ell\}}{}' \prod_\ell \frac{\mathcal{U}_\ell^{m_\ell}}{(\ell!)^{m_\ell}\, m_\ell!}$$

which is a constraint sum under (iii)

with $\mathcal{U}_\ell := \int \prod_{i=1}^{\ell} d\vec{r}_i \sum_{G \in \ell\text{-cluster}} G$

For example,

$$\mathcal{U}_3 = \int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_3 \Big(\quad \Big)$$



So we find:

$$Z(N,V,T) = \frac{1}{\Lambda^{3N}} \sum_{\{m_\ell\}}{}' \prod_\ell \frac{\mathcal{U}_\ell^{m_\ell}}{(\ell!)^{m_\ell} m_\ell!}$$

Expansion not in f, but in number of atoms they connect!

How to handle constraint? $\Rightarrow$ Grand-canonical ensemble!

Define: $Q_N(V,T) := Q(N,V,T)$; $z = \frac{e^{\beta\mu}}{\Lambda^3}$ fugacity

Then $\Xi(\mu,V,T) = \sum_{N=0}^{\infty} \frac{z^N}{N!} Q_N(V,T)$

Furthermore, $\beta\Omega = -\ln \Xi$ and define $\beta\Omega = -V \sum_{n=1}^{\infty} b_n z^n$ $\Big\} \Rightarrow$

$$b_1 = \frac{Q_1}{V}, \quad b_2 = \frac{Q_2 - Q_1^2}{2!V}, \quad b_3 = \frac{Q_3 - 3Q_2Q_1 + 2Q_1^3}{3!V}, \ \ldots$$

where we used $\ln(1+x) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{x^n}{n}$.

We conclude that:

- $\Omega(\mu,V,T) = -p(\mu,T)V \Rightarrow \beta p(z,T) = \sum_{n=1}^{\infty} b_n z^n$.
- $\langle N \rangle = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{V,T} = -z\left(\frac{\partial \Omega}{\partial z}\right)_{V,T} \Rightarrow \rho(z,T) = \sum_{n=1}^{\infty} n b_n z^n$.

However, we want to express z in terms of ρ.

So we write $z = \sum_{n=1} a_n \rho^n$

$\Rightarrow a_1 = 1, \quad a_2 = -b_2, \quad a_3 = -3b_3 + 8b_2^2$

Compute pressure: $\beta p(\rho, T) = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \ldots\ldots$ $(*)$

where $B_2(T) = -\frac{1}{2V}\int d\vec{r}_1 \int d\vec{r}_2\, f_M(r_{12}) = -\frac{1}{2}\int d\vec{r}\, f_M(r)$

centre of mass coordinates.

$$B_3(T) = \frac{1}{3V}\int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_3\, f_M(r_{12})\, f_M(r_{13})\, f_M(r_{23}).$$

Remark: $B_2(T_B) = 0 \Leftrightarrow T_B$ Boyle temperature.

↳ signifies transition between repulsion/attraction dominated.

Furthermore, we can write:

$$f_{ex}(\rho, T) = \frac{F - F_{id}}{V k_B T} = \sum_{n=2}^{\infty} C_n(T)\rho^n$$

$$\beta p = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = -\beta f + \rho\left(\frac{\partial \beta f}{\partial \rho}\right)_T$$

$(*)$ $\Rightarrow C_n = \frac{B_n}{n-1}.$

We conclude that

$$f = \frac{\beta F}{V} = \rho\left[\log(\rho\Lambda^3) - 1\right] + B_2(T)\rho^2 + \frac{B_3(T)}{2}\rho^3 + \ldots$$

Recall that: $\Xi(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(N, V, T)$

$$= \sum_{N=0}^{\infty} e^{\beta\mu N}\frac{1}{\Lambda^{3N}}\sum_{m_\ell=0}^{\infty}\prod_{\ell=1}^{\infty}\frac{U_\ell^{m_\ell}}{(\ell!)^{m_\ell} m_\ell}\,\delta_{N, m_\ell \ell}$$

$$= \sum_{m_\ell=0}^{\infty}\prod_{\ell=1}^{\infty}\left(\frac{e^{\beta\mu}}{\Lambda^3}\right)^{m_\ell \ell}\frac{U_\ell^{m_\ell}}{(\ell!)^{m_\ell} m_\ell!} = \prod_{\ell=1}^{\infty}\exp\left(\frac{U_\ell z^\ell}{\ell!}\right)$$

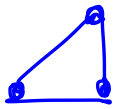
Hence: $\beta\Omega = -\log\Xi = -\sum_{\ell=1}^{\infty}\frac{U_\ell z^\ell}{\ell!}$ $\Rightarrow b_\ell = \frac{U_\ell}{\ell!\,V}$

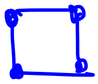
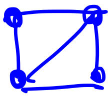
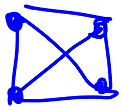
$\sum_{n=0}^{\infty}\frac{x^n}{n!}$

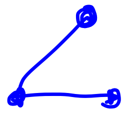
Compare with $\beta\Omega = -V\sum_{\ell=1}^{\infty} b_\ell z^\ell$ (sum over clusters)

However, one finds that

$B_2(T) = -\frac{1}{2V}\int d\vec{r}_1 \int d\vec{r}_2$ 

$B_3(T) = -\frac{1}{3V}\int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_3$ 

$B_4(T) = -\frac{1}{8V}\int d\vec{r}_1 \int d\vec{r}_2 \int d\vec{r}_3 \int d\vec{r}_4$ (3  + 6  + )

Note that diagrams like  drop out.

Only irreducible clusters: Still a connected graph when you cut one line.

Examples of virial expansion.

Very important model system is hard spheres.

We find: $B_2 = \frac{2}{3}\pi\sigma^3$

$$B_3 = \frac{5\pi^2}{18}\sigma^6$$

$$B_4 = \left[-\frac{89}{280} + \frac{219\sqrt{2}}{2240\pi} + \frac{4131}{2240\pi}\arccos\left(\frac{1}{\sqrt{3}}\right)\right]B_2^3.$$

Note that $B_n \neq f(T)$

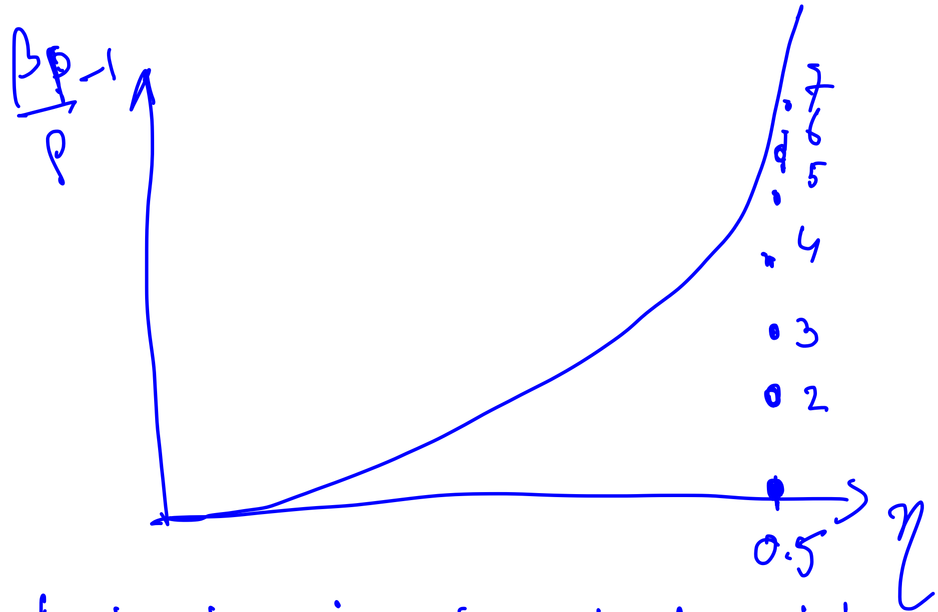
We can write: $\eta = \frac{\pi}{6}\sigma^3\rho.$

$$\frac{\beta p}{\rho} = 1 + 4\eta + 10\eta^2 + 18.365\eta^3 + 28.225\eta^4 + 39.74\eta^5 + 53.5\eta^6 + 70.8\eta^7 \ldots$$

$$\approx \sum_{n=1}^{\infty}(n^2+3n)\eta^n$$ Series can be summed.

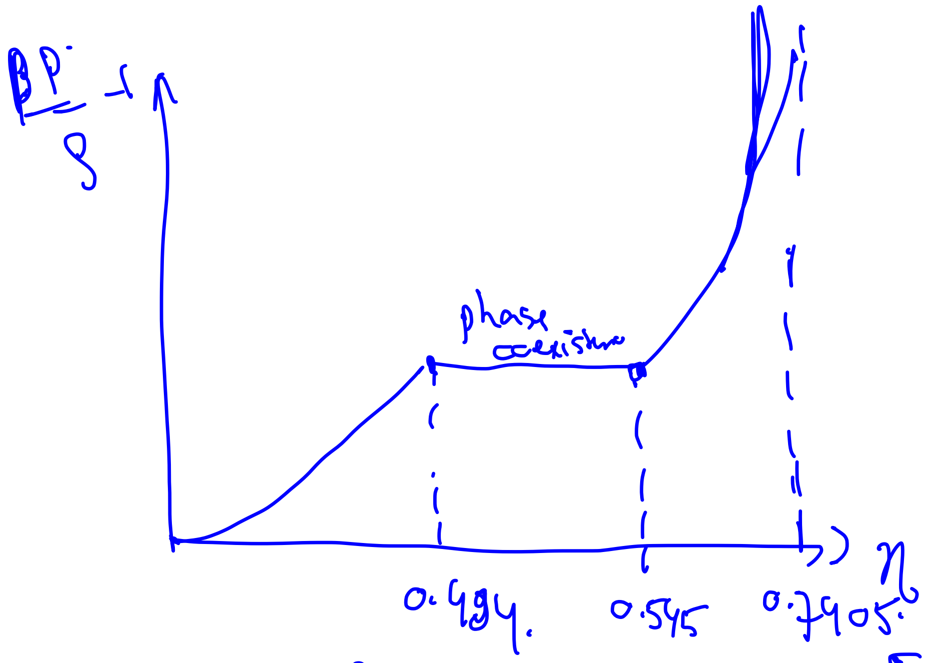
And we find: $\dfrac{\beta P}{\rho} = \dfrac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}$ Carnahan-Starling equation of state.

Check that: $\dfrac{\beta F}{N} = \log(\rho \Lambda^3) - 1 + \dfrac{4\eta - 3\eta^2}{(1-\eta)^2}$ | max 1% deviation in entire fluid range.



Virial expansions "converge slowly".

Hard spheres is an important model system.



Reason crystallisation: entropy
free volume at high η is higher when particles are ordered on a crystal lattice

- Virial coefficients become progressively harder to calculate for large n and more general model potentials.
- For some interaction potentials $B_n(T)$ is ill-defined.

  E.g.: Point Coulomb interactions, dipole-dipole int.
- Slowly converging series $\Rightarrow$ problem for dense fluids

Goal: Framework to describe dense fluids.

Today: Density-density correlation functions (interpretation)

↳ measurable quantity in experiments!

Routes to thermodynamics from the (local) structure of the fluid.

Definition $\hat{\rho}(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)$ Density operator (classical).

$\rho(\vec{r}) := \langle \hat{\rho}(\vec{r}) \rangle$ is the local density of a system. Why?

E.g. canonical ensemble:

$$\langle \hat{\rho}(\vec{r}) \rangle = \frac{1}{Q(N,V,T)} \int d\vec{r}^N \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)\, e^{-\beta \Phi(\vec{r}^N)}.$$

Take $\Phi(\vec{r}_1, \dots, \vec{r}_N)$ completely symmetric (identical particles)

$$= \frac{N}{Q(N,V,T)} \int d\vec{r}_2 \dots \int d\vec{r}_N\, e^{-\beta \Phi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)}$$

$$\int d\vec{r}\, \rho(\vec{r}) = \int d\vec{r} \langle \rho(\vec{r}) \rangle = \frac{N}{Q(N,V,T)} \underbrace{\int d\vec{r} \int d\vec{r}_2 \dots \int d\vec{r}_N\, e^{-\beta \Phi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)}}_{= Q(N,V,T).}$$

$$\Rightarrow \int d\vec{r}\, \rho(\vec{r}) = N.$$

$\Rightarrow$ $\rho(\vec{r})$ is the local density.

"Probability to find a particle at position $\vec{r}$, irrespective of other particles positions and momenta"

Homogeneous fluid ($V_{ext}(\vec{r}) = 0$) $\rho(\vec{r}) = \rho$ (Prove it!)

$= \text{constant}.$

Two-body density operator:

$$\hat{\rho}^{(2)}(\vec{r},\vec{r}\,') = \sum_{\substack{i\neq j\\ i}}^{N} \sum_{j=1} \delta(\vec{r}-\vec{r}_i)\,\delta(\vec{r}\,'-\vec{r}_j)$$

which defines the two-body correlation function $\rho^{(2)}(\vec{r},\vec{r}\,') = \langle \hat{\rho}^{(2)}(\vec{r},\vec{r}\,')\rangle$

Note normalisation: $\int d\vec{r} \int d\vec{r}\,' \, \rho^{(2)}(\vec{r},\vec{r}\,') = N(N-1)$.

Interpretation of $\rho^{(2)}(\vec{r},\vec{r}\,')$. The probability to find a particle at $\vec{r}$, and one at $\vec{r}\,'$, irrespective of the other particles positions (and momenta).

For suitable interaction potentials: $\rho^{(2)}(\vec{r},\vec{r}\,') \xrightarrow[|\vec{r}-\vec{r}\,'|\to\infty]{} \rho(\vec{r})\rho(\vec{r}\,')$

This motivates us to define a dimensionless correlation function:

$$g(\vec{r},\vec{r}\,') = \frac{\rho^{(2)}(\vec{r},\vec{r}\,')}{\rho(\vec{r})\rho(\vec{r}\,')}$$

with property:

$$g(\vec{r},\vec{r}\,') \longrightarrow 1 \qquad |\vec{r}-\vec{r}\,'| \longrightarrow \infty$$

<u>Note:</u> $V_{ext}(\vec{r}) = 0$

Translational invariance + isotropy: $g(\vec{r},\vec{r}\,') = g(|\vec{r}-\vec{r}\,'|)$.

$g(r)$: radial distribution function / pair correlation function.

How to interpret $g(r)$? Small reminder on probability theory

X, Y, continuous stochastic variables.

with joint probability density $p(x,y)$

"intergrate out" y

Marginal probability distribution: $p_X(x) = \int dy\, p(x,y)$

$$p_Y(y) = \int dx\, p(x,y).$$

Conditional probability: For example, conditional probability density of stochastic variable Y given that $X=x$

$$P(y|x) = \frac{P(x,y)}{P_X(x)}$$

Apply this to density-density correlation function:

$\dfrac{\rho^{(2)}(\vec{r},\vec{r}\,')}{N(N-1)}$: probability to find one particle at $\vec{r}$ and one at $\vec{r}\,'$

$\dfrac{\rho(\vec{r})}{N}$: probability to find one particle at $\vec{r}$.

$\Rightarrow$ $\dfrac{\rho(\vec{r})\,g(\vec{r},\vec{r}\,')}{N-1}$: probability to find particle at $\vec{r}$ knowing there is a particle at $\vec{r}\,'$.

$\Rightarrow$ $4\pi r^2 \rho\, g(r)\, dr$: given a particle in the origin, it says what is the number of particles between r and $r+dr$.

Schematically: