# Distribution functions in Configurational space

Phase space $\equiv$ Configurational space $\otimes$ Momentum space

$$\downarrow$$

$$(q_1 \ldots q_N; p_1 \ldots p_N) \equiv (q_1 \ldots q_N) \otimes (p_1 \ldots p_N)$$

Let us denote configurational space by $C$

$C(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N) \equiv$ Distribution of particles in C-space with particle 1 in $r_1$; 2 in $r_2$, ...., so on.

$c^{(2)}(\bar{r}_1, \bar{r}_2)$ = probability distribution of finding particle 1 at $\bar{r}_1$ and particle 2 at $\bar{r}_2$

$$= \underbrace{\int \cdots \int}_{N-2} d\bar{r}_3 \, d\vec{r}_4 \ldots d\vec{r}_N \; c(\bar{r}_1, \bar{r}_2, \ldots \bar{r}_N)$$

A <u>reduced</u> generic distribution is defined as:

$\rho^{(2)}(\vec{r}_1, \vec{r}_2)$ = probability distribution of finding <u>any</u> particle at $\vec{r}_1$ and another particle at $\vec{r}_2$

$$= N(N-1) \, c^{(2)}(\vec{r}_1, \vec{r}_2) \qquad (2)$$

In general, an n-body reduced distribution function is given by,

$$\rho^{(n)}(r_1, r_2 \ldots r_n) = \left[\frac{N!}{(N-n)!}\right] \times \frac{\int d\vec{r}_{n+1} \ldots d\vec{r}_N \, e^{-\beta V(\bar{r})}}{\int_N d\vec{r}_1 \ldots d\vec{r}_N \, e^{-\beta V(\bar{r})}}$$

For $n = 1$

$$\rho^{(1)}(\vec{r}_1) = \frac{N!}{(N-1)!} \cdot \frac{\int_{N-1} d\vec{r}_2 \ldots d\vec{r}_N \, e^{-\beta V(\vec{r})}}{\int_N d\vec{r}_1 \ldots d\vec{r}_N \, e^{-\beta V(\vec{r})}}$$

For isotropic fluid, we have

$$\cancel{\rho^{(1)}(\vec{r}_1, \vec{r}_2)}$$

$$\rho^{(1)}(\vec{r}_1) = \frac{N!}{(N-1)!} \cdot \frac{\int d\vec{r}_2 \ldots d\vec{r}_N \, e^{-\beta V(\vec{r})}}{\int_1 d\vec{r}_1 \cdot \int_{N-1} d\vec{r}_2 \ldots d r_N \, e^{-\beta V(r)}}$$

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

Similarly,

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{N!}{(N-2)!} \cdot \frac{1}{\int d\vec{r}_1 \, d\vec{r}_2} = \frac{N(N-1)}{V^2}$$

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

$$\simeq \rho^2$$

In general, we can write

$$g(\vec{r}_1, \vec{r}_2) = \frac{\rho^{(2)}(\vec{r}_1, \vec{r}_2)}{\rho^2} \qquad \left[\frac{\text{Non-ideal}}{\text{ideal}}\right]$$

to represent deviation

For systems which are isotropic,

$$g(\vec{r}_1, \vec{r}_2) = g(|\vec{r}_2 - \vec{r}_1|) = g(r)$$

$g(r)$ is a measure of the two-body correlation or distribution, and depends on the radial distances $|\vec{r}_2 - \vec{r}_1| = |r_{12}| = r$.

$g(r) \longrightarrow$ Radial distribution function.

Note that,

$$\frac{\rho^{(2)}(\vec{r}_1, \vec{r}_2)}{\rho^2} = g(\vec{r}_1, \vec{r}_2)$$

or,

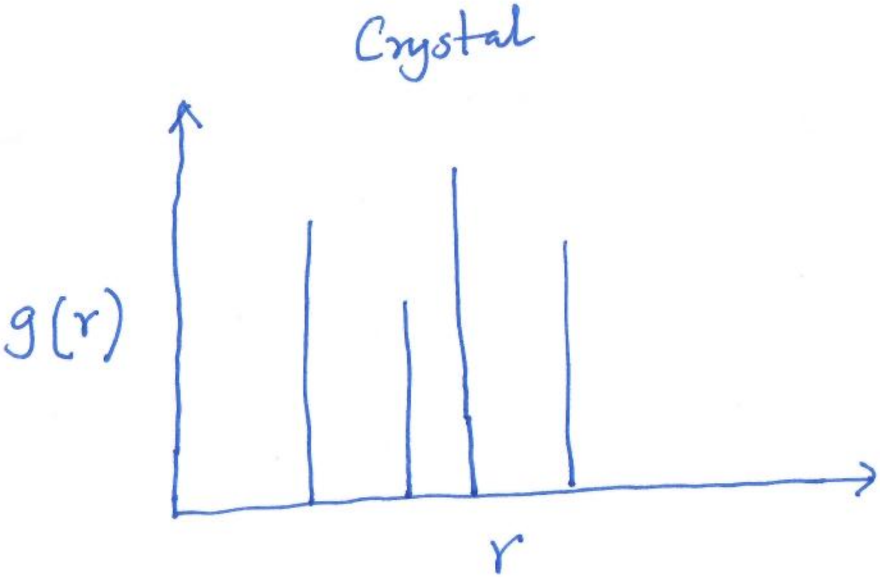
$$\frac{\rho^{(2)}(0, r)}{\rho} = \rho\, g(r) \qquad \left[ \text{Isotropic case} \quad r_1 = 0,\ r_2 = r \right]$$

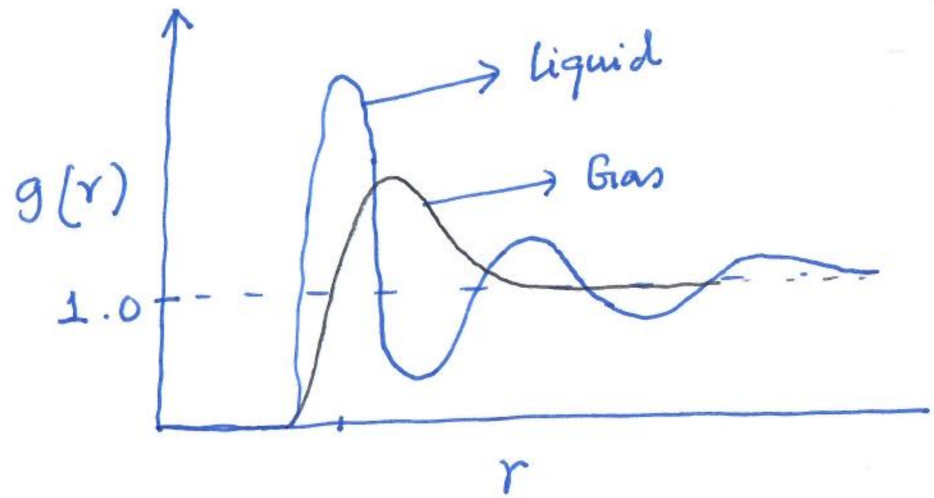
$\downarrow$

Represents the conditional probability that a particle is at $r$, given a particle is at $r=0$.

Thus, knowing $g(r)$ we can find the average density of particle at $r$, given a particle at the origin. This gives 'fluid' structure.

# g(r) for a crystal, a liquid and a gas



# Relation between g(r) and potential energy

* Average force between the particle $\vec{r}_1$ and $\vec{r}_2$ is related with $g(\vec{r}_1, \vec{r}_2)$

* $$\langle F_{12} \rangle = - \left\langle \frac{dW}{dr_1} \right\rangle_{\substack{\text{Avg. over all } r \\ \text{but } \vec{r}_1, \vec{r}_2}}$$

$$= K_B T \frac{d}{dr_1} \left[ \ln g(\vec{r}_1, \vec{r}_2) \right]$$

* $$g(r) = \exp\left[ - \frac{W}{K_B T} \right]$$

W = reversible work required to move $\vec{r}_1, \vec{r}_2$ from a large ~~and~~ distance to the current position $(\vec{r}_1, \vec{r}_2)$.

In liquid state physics it is often called

a potential of mean force

For details:

1. Evans
2. Hansen
3. Chandler

# Thermodynamic quantities from RDF

* Total energy (E) and pressure (P) of an interacting system can be expressed in terms of $g^{(2)}(\vec{r}_1, \vec{r}_2)$, $g^{(3)}(\bar{r}_1, \bar{r}_2, \bar{r}_3)$, etc.

* We study a special case of pair potentials

* $$V_{pair}(\{\bar{r}\}) = \sum_i \sum_{\substack{j \\ j>i}} \tilde{V}_p(|r_{ij}|) = \sum_i \sum_j{}' \tilde{V}_{ij}$$

* For pair potentials, only $g^{(2)}(\bar{r}_1, \bar{r}_2)$ is needed.
In general, for an n-body potential, we need all the $g^{(n)}(\bar{r}_1, \bar{r}_2, \ldots \bar{r}_n)$.

$$* \qquad E = \frac{3}{2} N k_B T + \boxed{2\pi N \rho \int_0^\infty dr\, v(r)\, g(r) . r^2}$$

$$\frac{P}{k_B T} = \rho - \boxed{\frac{2\pi \rho^2}{3 k_B T} \int_0^\infty dr\ r^3 \left(\frac{dv}{dr}\right) g(r)}$$

We derive the first relation only.

# Derivation

$$E = \sum_i \frac{p_i^2}{2m} + V_{pair}(\bar{r}_1, \ldots \bar{r}_N)$$

$$\langle E \rangle = \left\langle \sum_i \frac{p_i^2}{2m} \right\rangle + \left\langle V_{pair}(\bar{r}_1, \bar{r}_2 \ldots \bar{r}_N) \right\rangle$$

$$= \frac{3}{2} K_B T N + \left\langle V_{pair}(\{r\}) \right\rangle$$

By definition,

$$\langle V_{pair} \rangle = \frac{\int_N \int dr_1 \ldots dr_N \left\{ \sum_i \sum_j{}' \tilde{V}_p(\{r\}) \right\} e^{-\beta V_p(\bar{r})}}{Z}$$

$$= \frac{\sum_i \sum_j{}' \int_N \int dr_1 \ldots dr_N \; \tilde{V}_p(|r_i - r_j|) \, e^{-\beta V_p}}{Z}$$

Since there are $\frac{N(N-1)}{2}$ terms in the double sum, each time we calculate

$$\int_N dr_1 \ldots dr_N \, \tilde{v}_p(|r_i - r_j|)\, e^{-\beta V_p} = \int_N dr_1 \ldots dr_N \, \tilde{v}_p(|r_1 - r_2|)\, e^{-\beta V_p}.$$

for different i and j pair. The result will be the same.

So,

$$\langle V_p \rangle = \cancel{\left[\frac{N(N-1)}{2Z} \int dr_3 \ldots dr_N \, e^{-\beta V_p}\right] \times \left[\int dr_1\, dr_2 \, v_p(|r_1 - r_2|)\right]}$$

$$= \frac{N(N-1)}{2Z} \int d\bar{r}_1\, d\bar{r}_2 \, \tilde{v}_p(|r_1 - r_2|) \int dr_3 \ldots dr_N \, e^{-\beta V_p(\{r\})}$$

$$= \cancel{\frac{N(N-1)}{Z}} \frac{1}{2} \int dr_1\, dr_2 \, \tilde{v}_p(|r_1 - r_2|) \cdot \underbrace{\left[\frac{N(N-1)}{Z} \int dr_3 \ldots dr_N \, e^{-\beta V_p(\{r\})}\right]}_{\rho^{(2)}(\bar{r}_1, \bar{r}_2) \rightarrow \text{2-body correlation}}$$

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$$= \frac{1}{2} \int d\bar{r}_1 \, d\bar{r}_2 \, \tilde{v}_p \left( |\bar{r}_1 - \bar{r}_2| \right) . \quad \rho^2 \, g^{(2)}(r_1, r_2)$$

[Note: $\rho^2 = \rho \cdot \rho$

$\rho^{(2)} =$ two-body correlation

$\frac{\rho^{(2)}(r_1, r_2)}{\rho_0^2} = g(r_1, r_2)$

$$= \frac{1}{2} \rho^2 \int d\bar{r}_1 \, d\bar{r}_2 \, \tilde{v}_p \left( |\bar{r}_1 - \bar{r}_2| \right) g^{(2)} \left( |\bar{r}_1 - \bar{r}_2| \right)$$

Introducing the center-of-mass co-ordinates, we can write,

$(r_1, r_2) \Longrightarrow (R_c + r, R_c - r)$

vary $r$ only, since $R_c$ is fixed

Because of $d\bar{R}_c$ or $d\vec{r}_2$

$$= \frac{1}{2} \rho^2 \cdot \frac{V}{\cancel{\phantom{V}}} \int d\bar{r} \, \tilde{v}_p(r) \, g^{(2)}(r) = \frac{\rho^2 \cdot V}{2 \cancel{\phantom{V}}} \int \underbrace{4\pi r^2 dr}_{= d\bar{r}} \cdot \tilde{v}_p(|\bar{r}|) \, g^{(2)}(|\bar{r}|)$$

$$= \frac{2 \rho^2 \pi . V}{\cancel{\phantom{V}}} \int r^2 dr \, v_p(r) \, g(r) = 2\pi \rho . N \int r^2 dr \, v_p(r) \, g(r) \qquad \left[ \rho = \frac{N}{V} \right]$$

Thus,

$$\langle E \rangle = \frac{3}{2} K_B T N + 2\pi N \rho \int dr\, r^2 g(r) \cdot V_p(r)$$

or

$$\frac{\langle E \rangle}{N} = \frac{3}{2} K_B T + 2\pi \rho \int_0^{r_{max}} dr . \underbrace{\left[ r^2 g(r) \right]}_{\text{Structural information}} \underbrace{V_p(r)}_{\text{Pair potential}}$$

The above relation is exact for pair potential only!!