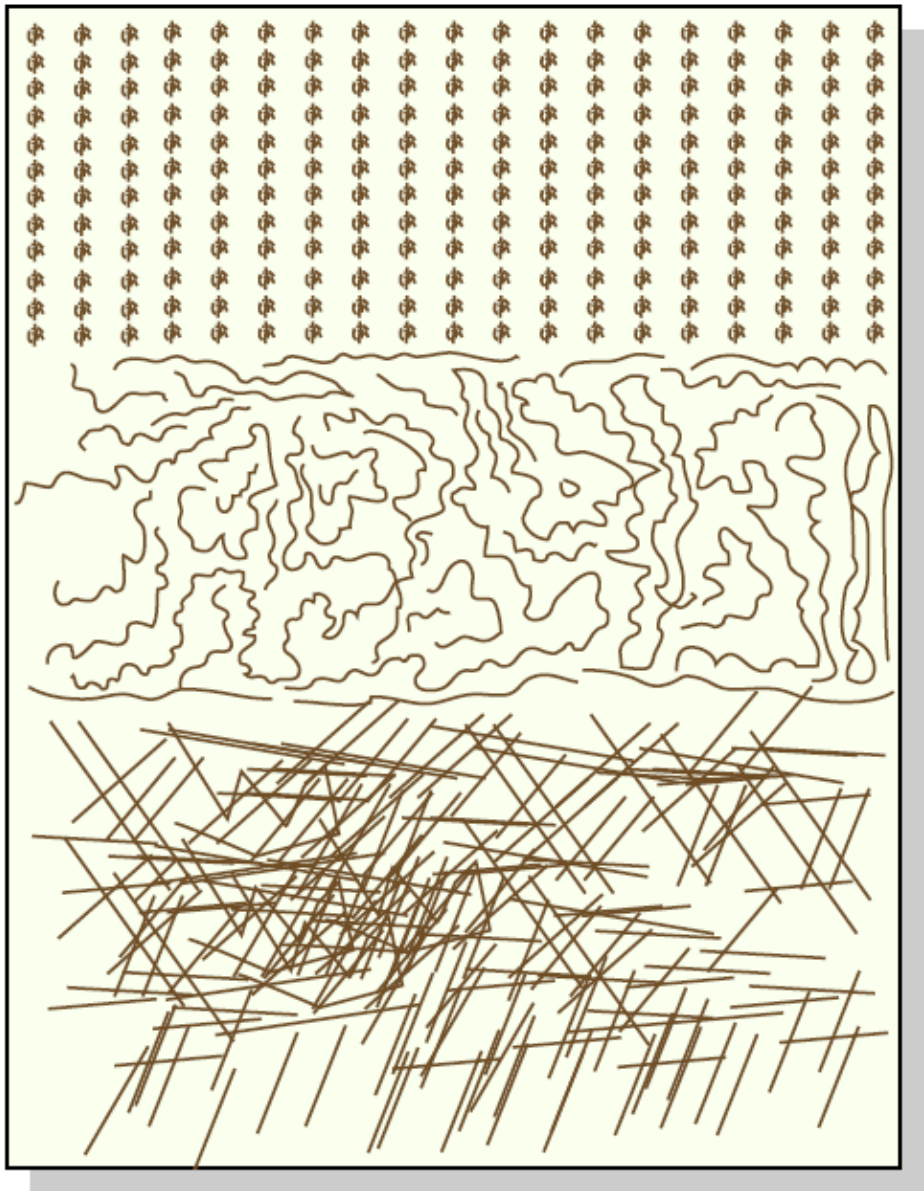
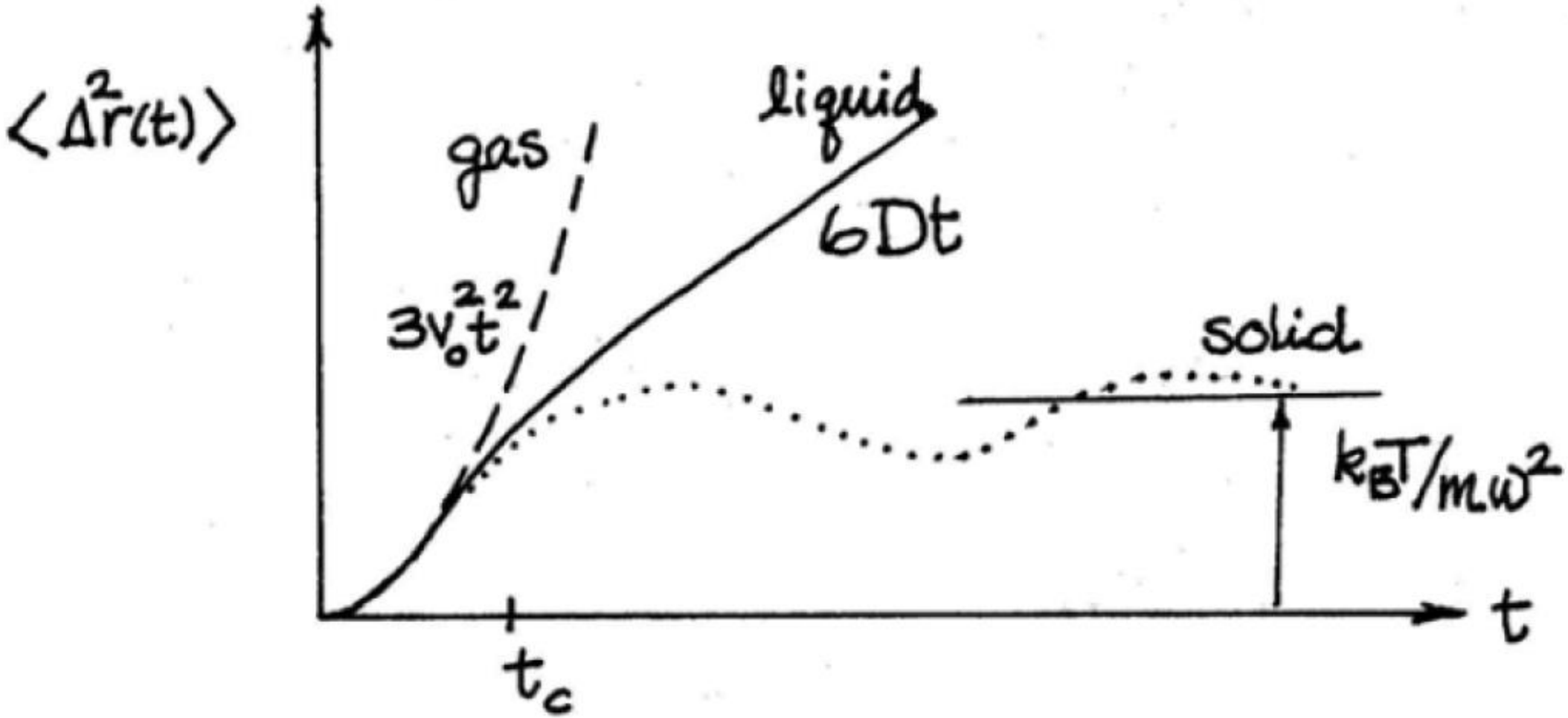
# Pair correlation

# MD modeling of crystals – solid, liquid, gas phase

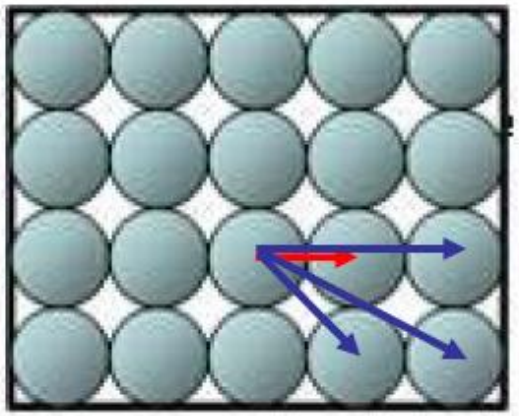
- Crystals:  Regular, ordered structure
- The corresponding particle motions are small-amplitude vibrations about the lattice site, diffusive movements over a local region, and long free flights interrupted by a collision every now and then.
- Liquids: Particles follow Brownian motion (collisions)
- Gas: Very long free paths



# Atomistic trajectory – through MSD

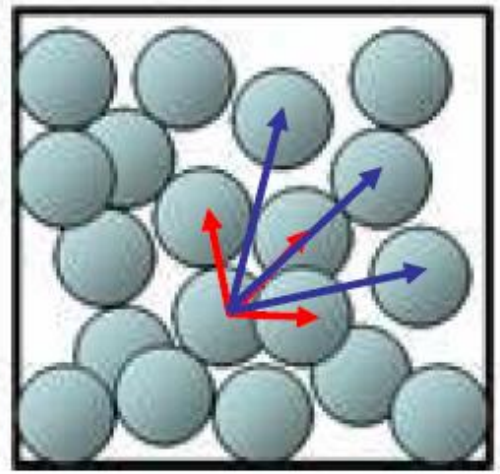


# How to characterize material state (solid, liquid, gas)



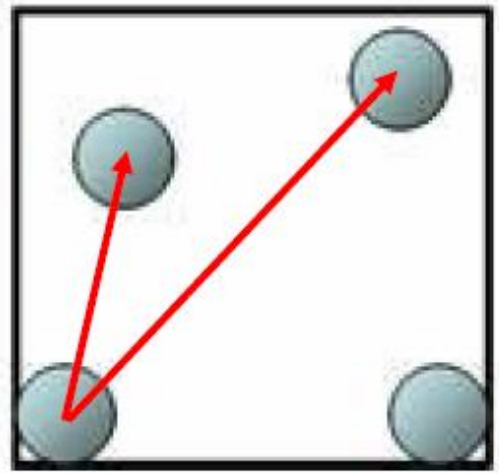
**Regular spacing**

Neighboring particles found at characteristic distances



**Irregular spacing**

Neighboring particles found at approximate distances (smooth variation)



**More irregular spacing**

More random distances, less defined

# Definitions:

At atomic level the density distribution in a system of N particles can be described as

$$\rho(\vec{r}) = \sum_{j}^{N} \delta(\vec{r} - \vec{r}_j)$$

Then, by definition, the density – density autocorrelation function is

$$C(\vec{r}) = \langle \rho(\vec{r}_i)\rho(\vec{r}_i + \vec{r}) \rangle \quad \text{where} \quad \rho(\vec{r}_i) = \sum_{j}^{N} \delta(\vec{r}_i - \vec{r}_j) = 1$$

$$\text{and} \qquad \rho(\vec{r}_i + \vec{r}) = \sum_{\cdot}^{N} \delta(\vec{r}_i + \vec{r} - \vec{r}_j) = \sum_{\cdot}^{N} \delta(\vec{r} - \vec{r}_{ij})$$

Therefore

$$C(\vec{r}) = \langle \rho(\vec{r}_i)\rho(\vec{r}_i + \vec{r}) \rangle = \left\langle \sum_{j}^{N} \delta(\vec{r} - \vec{r}_{ij}) \right\rangle = \frac{1}{N} \sum_{i}^{N} \sum_{j}^{N} \delta(\vec{r} - \vec{r}_{ij})$$

To relate the probability to find a particle at **r** to what is expected for a uniform random distribution of particles of the same density, we can normalize to the average density in the system, $\rho_0 = N/V$:

$$c(\vec{r}) = \frac{C(\vec{r})}{\rho_0} = \frac{V}{N^2} \sum_{i}^{N} \sum_{j}^{N} \delta(\vec{r} - \vec{r}_{ij})$$

For isotropic system c(**r**) can be averaged over angles and calculated from MD data by calculating an average number of particles at distances r – r+Δr from any given particle:

$$N_r(r) = \langle c(\vec{r}) \rangle_{angle}$$

To define the probability to find a particle at a distance r from a given particle we should divide $N_r$ by the volume of a spherical shell of radius r and thickness Δr:

$$g(r) = N_r/(4\pi r^2 \Delta r)$$

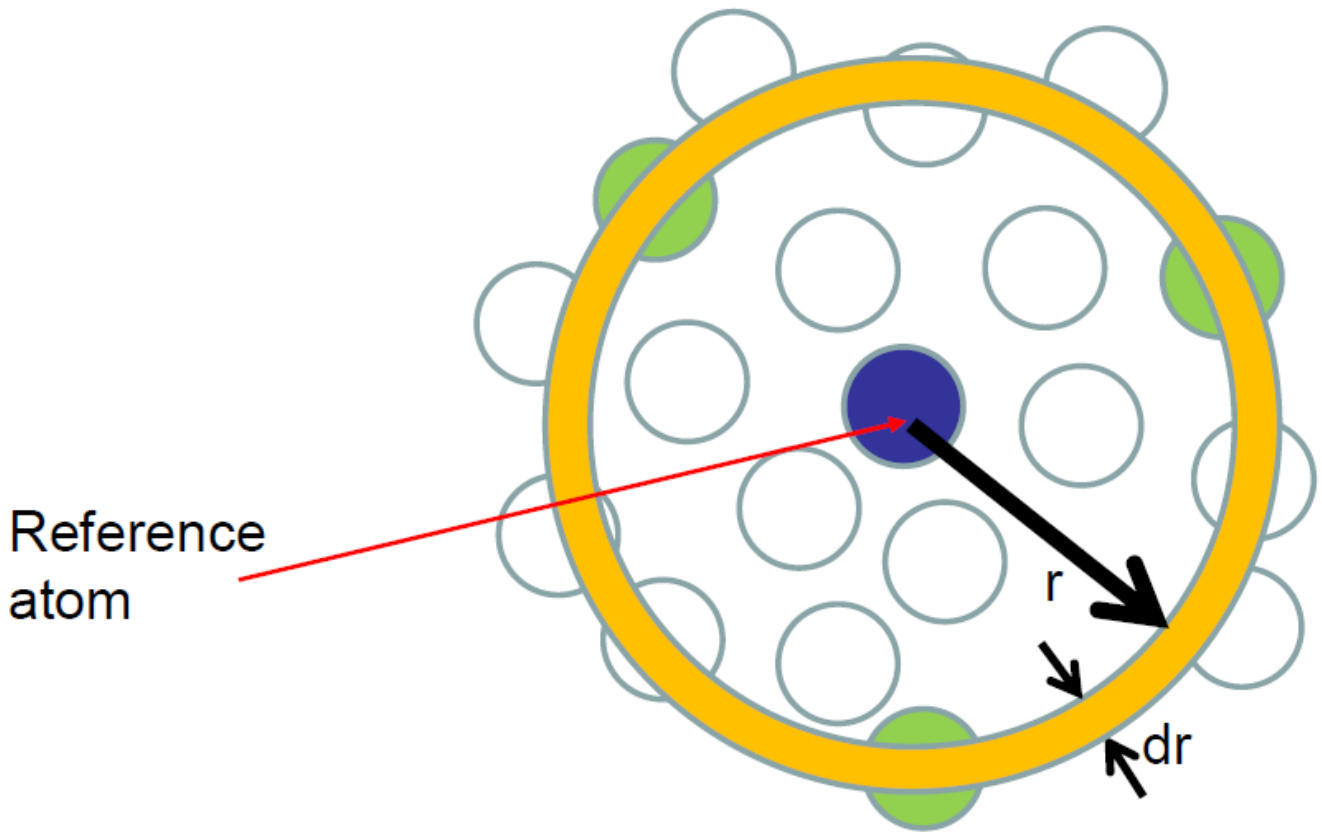
Thus, we can define the **pair distribution function**, which is a real-space representation of correlations in atomic positions:

$$g(r) = \frac{1}{4\pi N r^2 \rho_0} \sum_{j=1}^{N} \sum_{\substack{i=1 \\ i \neq j}}^{N} \delta(r - r_{ij}) = \frac{1}{2\pi N r^2 \rho_0} \sum_{j=1}^{N} \sum_{i>j}^{N} \delta(r - r_{ij})$$

g(r) can be calculated up to the distance $r_g$ that should not be longer than the half of the size of the computational cell.

# Formal approach: Radial distribution function (RDF)

Ratio of density of atoms at distance $r$ (in control area $dr$) by overall density = relative density of atoms as function of radius




$$g(r) = \rho(r) / \rho$$

# Formal approach: Radial distribution function (RDF)

The radial distribution function is defined as

Overall density of atoms (volume)

$$g(r) = \rho(r) / \rho$$

Local density

Provides information about the density of atoms at a given radius $r$; $\rho(r)$ is the local density of atoms

**Discrete:**

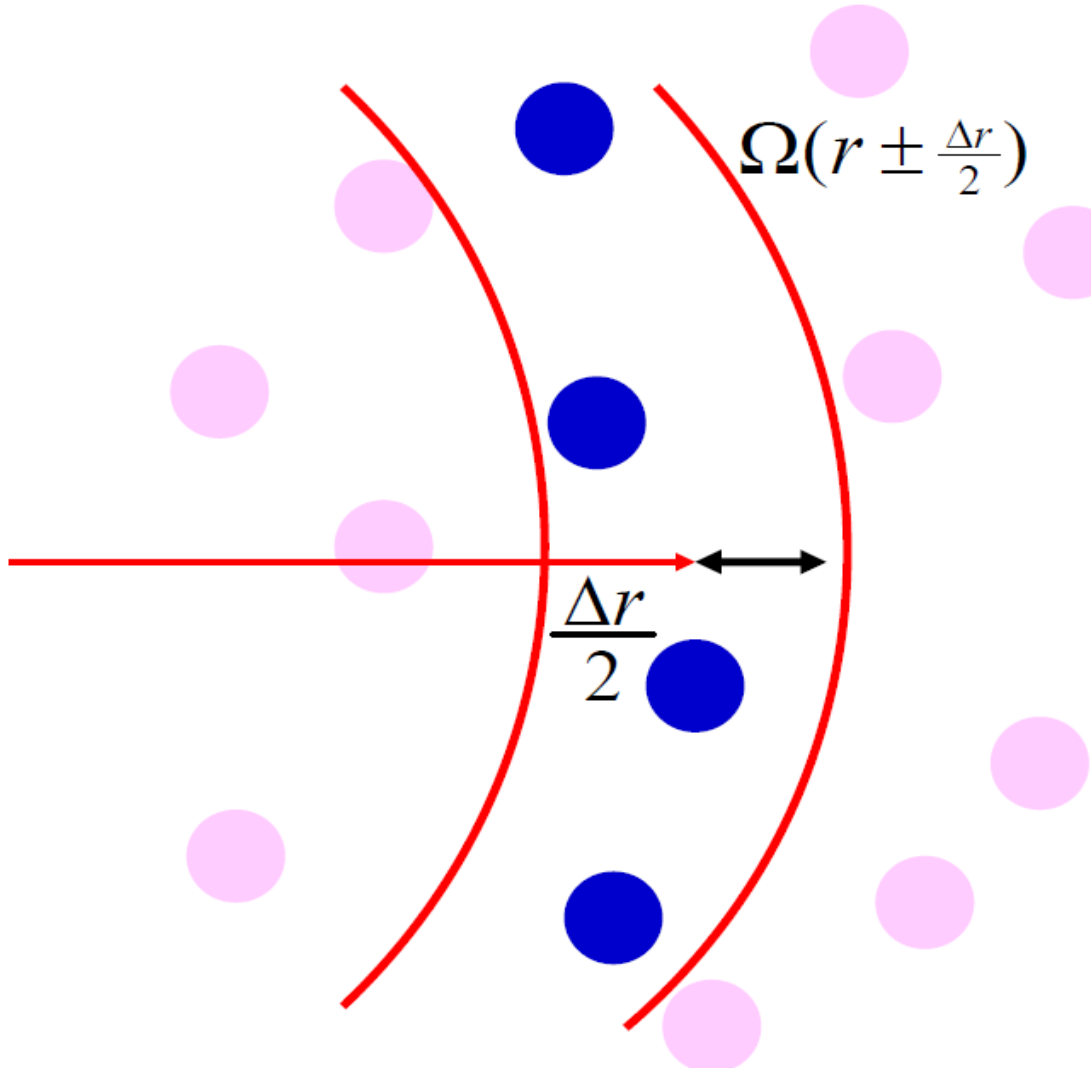
Number of atoms in the interval $r \pm \frac{\Delta r}{2}$

$$g(r) = \frac{< N(r \pm \frac{\Delta r}{2}) >}{\Omega(r \pm \frac{\Delta r}{2})} \frac{1}{\rho}$$

Volume of this shell $(dr)$

$g(r)2\pi r^2 dr =$ Number of particles that lie in a spherical shell of radius *r* and thickness *dr*

# Radial distribution function




considered volume

$$g(r) = \frac{N(r \pm \frac{\Delta r}{2})}{\Omega(r \pm \frac{\Delta r}{2})\rho}$$

Density

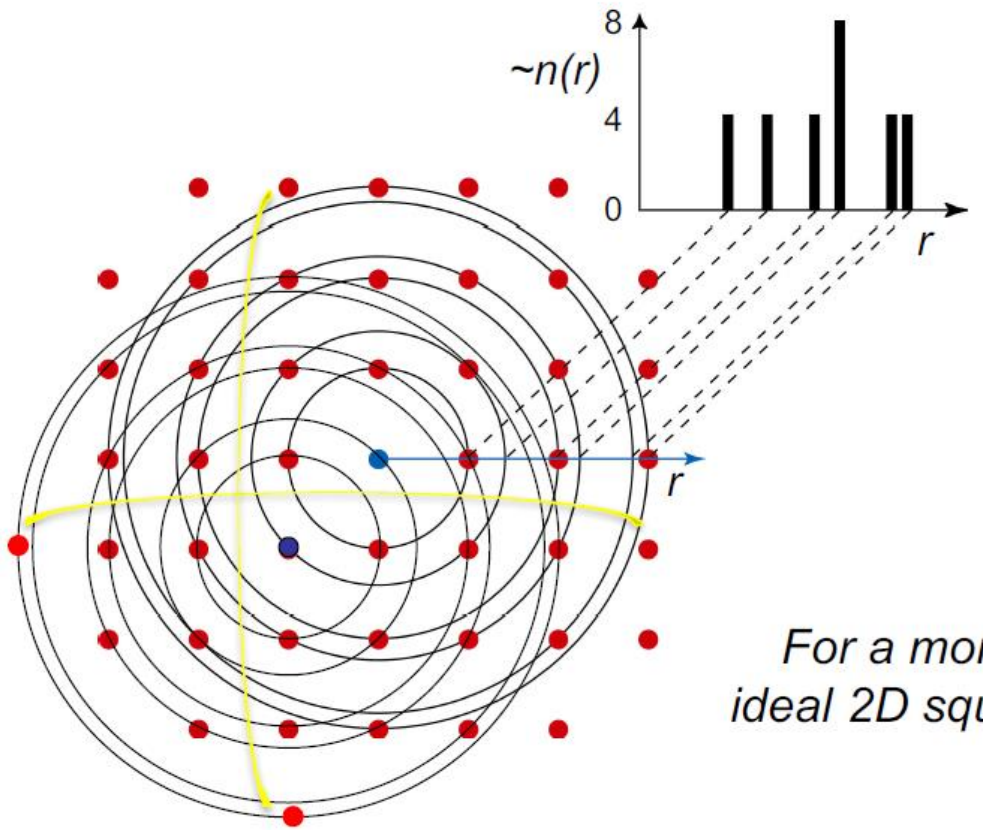
$$\rho = N / V$$

**Note:** RDF can be measured experimentally using x-ray or neutron-scattering techniques

• For a multicomponent material, the partial pair distribution function, $g_{ij}(r)$ is given by:

$$g_{ij}(r) = \frac{n_{ij}(r)}{4\pi r^2 \mathrm{d}r \rho_j}$$

where $n_{ij}(r)$ is the number of atoms $j$ between $r$ and $r$+d$r$ from an atom $i$, averaged over all atoms $i$ as centres and $\rho_j$ is the average atomic density $\rho$ multiplied by the proportion of atoms $j$




*For a monatomic ideal 2D square lattice*