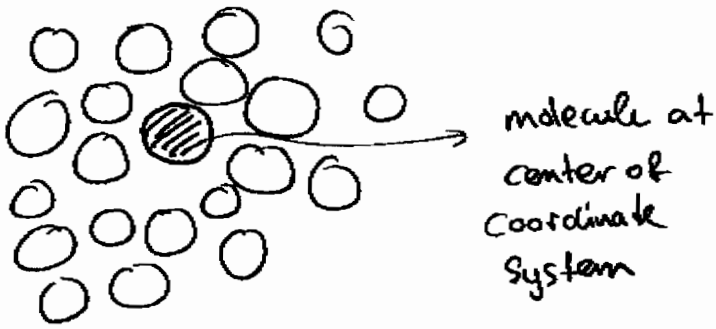
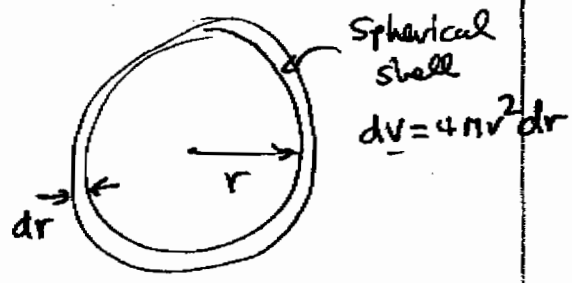
Distribution functions

When particles are no longer independent of each other, description of a system must be in "statistical" terms. Distribution functions serve this purpose. Most theories of liquids are developed based on these functions.

Pair correlation function: $g(r)$

Consider a system of molecules in a liquid or solid. Look at the environment around a given molecule:



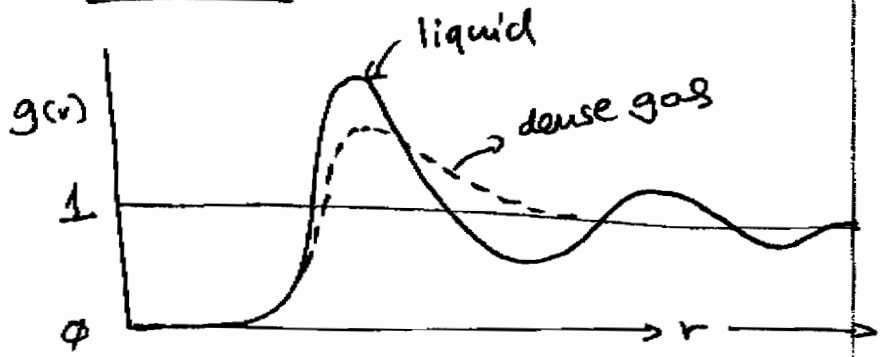


The pair correlation function $g(r)$ (also known as radial distribution function) is defined as:

$$g(r) = \frac{\text{average number of particles in shell between } r, r+dr}{\text{number of particles in random system} = 4\pi r^2 \rho\, dr}$$

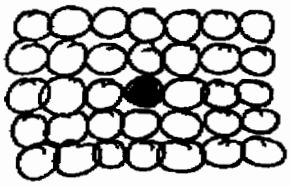
where $\rho = \frac{N}{V}$ (macroscopic density)

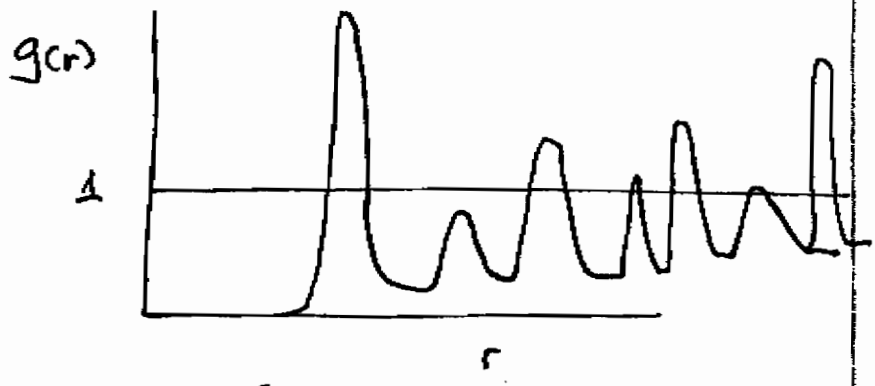
Typical $g(r)$ for dense monoatomic liquid:



The function starts at ϕ because molecules cannot penetrate each other. First, second etc peaks correspond to "coordination shells".

For a solid,





→ discrete peaks at specific distances (depending on crystallographic system)

→ long-range structure

The radial distribution function can be determined experimentally – X-ray scattering (small molecules)

– neutron scattering (macromolecules)

<u>Relationships of thermodynamic quantities to g(r)</u>

For the energy,

$$\underline{u} = \underbrace{\underline{u}_{\text{kinetic}}}_{\frac{3}{2}NkT \text{ for monoatomic system}} + \underbrace{\underline{u}_{\text{potential}}}_{\text{due to interactions between molecules}}$$

$$\frac{\mathcal{U}_{\text{potential}}}{N} = \frac{1}{2} \int_0^\infty u(r) \cdot 4\pi r^2 \bar{N}(r) \cdot dr = \frac{1}{2} \int_0^\infty 4\pi r^2 u(r) g(r) dr$$

$\downarrow$

factor to avoid double-counting of interaction between pairs of particles.

$u(r)$ is the intermolecular potential between particles at a distance r.

For the pressure, the derivation is a bit more involved, but uses the fact that the <u>force</u> between two particles: $F = -\frac{\partial u(r)}{\partial r}$

The final result is $$\frac{P}{kT} = \rho - \frac{\rho^2}{6kT} \int_0^\infty \frac{du(r)}{dr} g(r) \cdot 4\pi r^3 dr \quad (1)$$

Now, consider the virial expansion:

$$\frac{P}{kT} = \rho + B_2(T) \cdot \rho^2 + B_3(T) \cdot \rho^3 + \cdots \Rightarrow$$

$$\frac{P}{\rho kT} = 1 + B_2(T) \cdot \rho + B_3(T) \cdot \rho^2 + \cdots$$

For O_2 @ $T = 300\,K$,

P (atm)	$\frac{P}{\rho kT}$	$+ B_2 \rho$	$+ B_3 \rho^2$
1	1	-0.00064	$+ 0.$
10	1	-0.00648	$+0.00020$
100	1	-0.06754	$+0.02127$
1000	1	-0.384	$+0.687$

From (1) $\Rightarrow$ $$\frac{P}{\rho kT} = 1 - \frac{\rho}{6kT} \int_0^\infty \frac{du(r)}{dr} g(r) 4\pi r^3 dr = 1 + B_2(T) \cdot \rho$$

$$\Rightarrow B_2(T) = -\frac{1}{6kT}\int_0^\infty \frac{du(r)}{dr}\, g(r)\, 4\pi r^3 dr \quad \Big\} \text{ for } \rho \to 0 \qquad (2)$$

For low densities, the probability of observing a pair at a distance r must be proportional to $\exp[-\beta u(r)] = g(r)$, since $g(r)$ is a measure of that probability (and goes to 1 at long distances), we get from (2)

$$B_2(T) = -\frac{4\pi}{6kT}\cdot \int_0^\infty \underbrace{\frac{du(r)}{dr}\cdot \exp(-\beta u(r))}_{f'}\, \underbrace{r^3}_{g}\, dr$$

$$\{f = e^{-\beta u(r)} - 1\}$$

$$= \frac{2\pi}{3}\cdot\left[r^3\left(e^{-\beta u(r)} - 1\right)\Big|_0^\infty - \int_0^\infty \left[e^{-\beta u(r)} - 1\right]\cdot 3r^2 dr\right]$$

First term must be zero, since @ $r = \rho$ $r^3 = \phi$,

@ $r \to \infty$ $\beta u(r) \to 0$

$\Rightarrow r^3\left(e^{-\beta u(r)} - 1\right) \to$

$-r^3 \beta u(r) \to \phi$ {why?}

$$\Rightarrow \boxed{B_2(T) = -2\pi \int_0^\infty \left[e^{-\beta u(r)} - 1\right] r^2 dr}$$

The second virial coefficient is simply related to the intermolecular forces!

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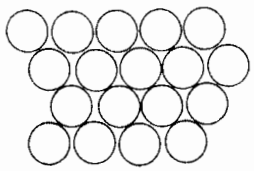


Fig. 7.3. Two-dimensional crystalline array of spherical particles.

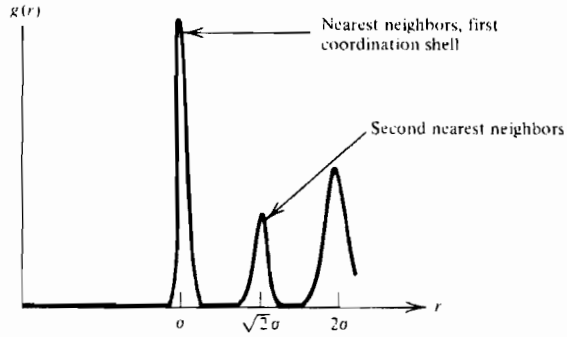


Fig. 7.4. Radial distribution function for a highly ordered solid.

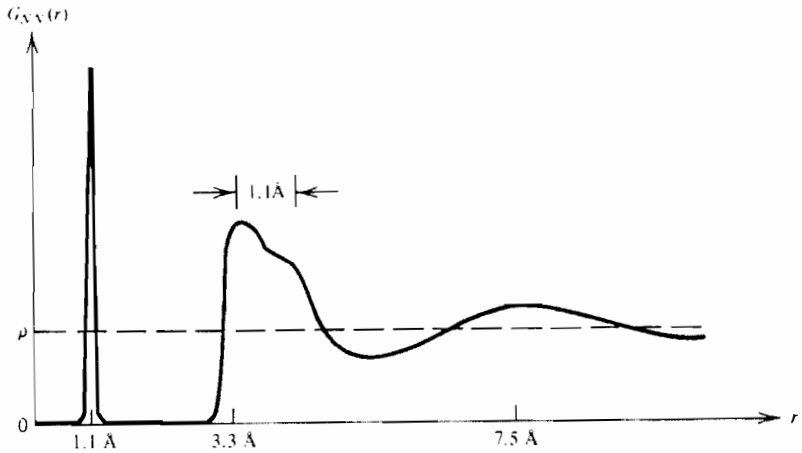


Fig. 7.9. Pair distribution function for liquid nitrogen.

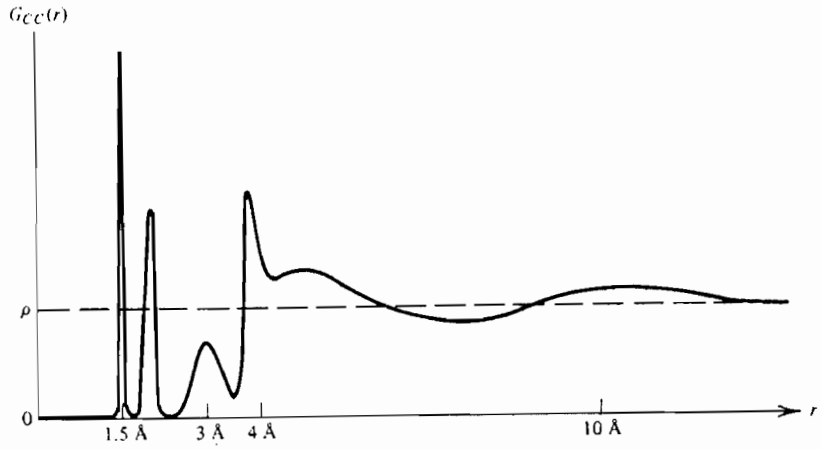
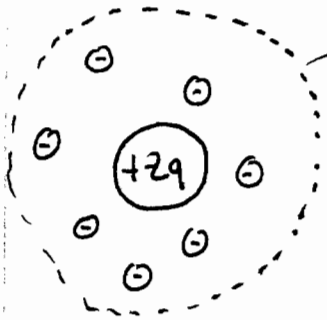


Fig. 7.11. Pair distribution function for liquid *n*-butane.

A simple application: Poisson-Boltzmann Distribution

How can we describe distributions of counterions around a fixed central charge? (e.g. colloids, DNA)?

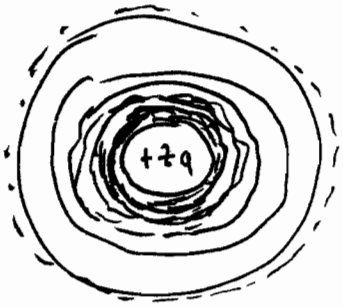


System boundary - radius R; central ion radius σ

Coulombic interactions:

$$U_{ij}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$$

Assume: * point counterions * no correlations of counterion positions



Mean density of counterions at distance r prop. to $g(r)$

Effective potential felt by counterions at spherical shell of distance r has two contributions

$$U_{eff}(r) = \underbrace{-\frac{Q_{in}\, q}{4\pi\epsilon_0 r}}_{\text{interaction with charge in sphere of radius } r} + \underbrace{\int_r^R \frac{4\pi r'^2 g(r')\,dr'\, q^2}{4\pi\epsilon_0 r'}}_{\text{potential due to charge at dist. greater than } r} \quad (1)$$

$$Q_{in} = Z - \int_\sigma^r 4\pi r'^2 g(r')\,dr'$$

But we also must have $g(r) \propto \exp(-\beta U_{eff}(r))$ (2)

The normalization condition for equation (2) is

that $\int_{\sigma}^{R} 4\pi r^2 g(r)\, dr = Z$ (3), since there must be Z counterions in the gap between σ and R.

Equations (1) (2) and the normalization condition (3) can be solved self-consistently e.g. in Excel or Matlab (see problem 2)

Once $g(r)$ is known, the energy of the system can be calculated from

$$E = -\int_{\sigma}^{R} \frac{Q_{in}\, 4\pi r^2 g(r)\, dr}{4\pi\epsilon\epsilon_0 r} \qquad (4)$$

In eq. (4) only interactions with ions at distances less than σ are taken into account, to avoid double-counting.