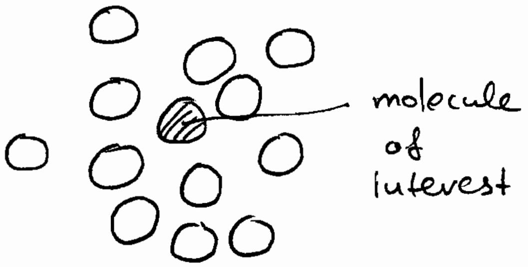
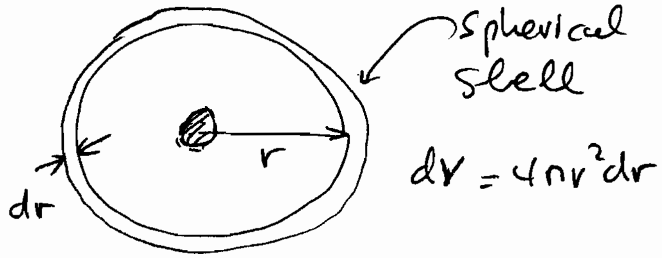
Distribution functions

When particles are no longer independent of each other, description of a system must take into account their correlations. Distribution functions describe these correlations. Most theories of liquids are based on these functions.

Pair correlation function: $g(r)$

Consider a system of molecules in a liquid or a solid. We focus on one molecule considered to be at the origin of the coordinate system:





$dV = 4\pi r^2 dr$

If there are no correlations between particle positions, the average number to be found in the shell at r is

$$N_{random} = 4\pi r^2 \rho dr \quad \text{where } \rho = \frac{N}{V} \left(\begin{matrix}\text{macro.}\\ \text{density}\end{matrix}\right)$$

The function $g(r)$, A.K.A. radial distribution function, is:

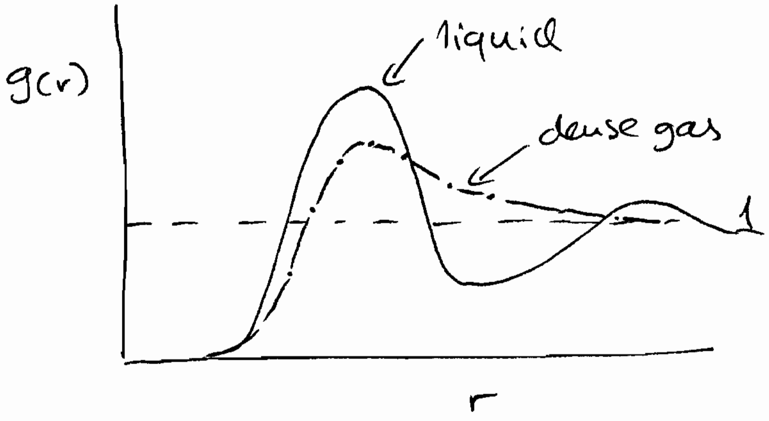
$$g(r) = \frac{\text{mean number of particles between } r \text{ and } r+dr}{N_{random}}$$

At short distances, electonic repulsions prevent molecular overlaps, so $g(r \to 0) = 0$

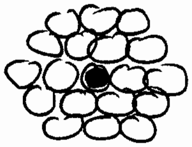
At long distances, random distribution prevails:

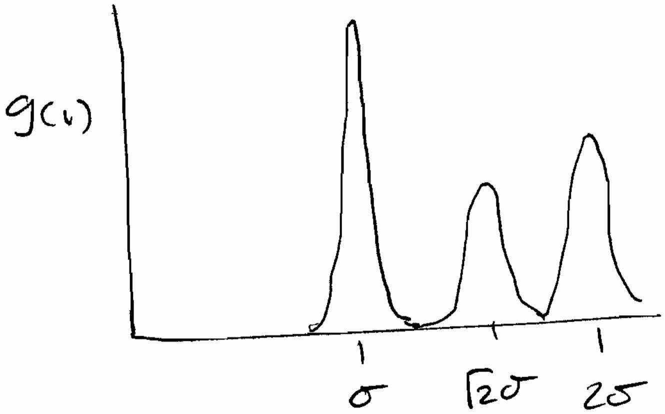
$$g(r \to \infty) = \underline{1}$$

Typical $g(r)$ for dense monoatomic fluids e.g. Ar

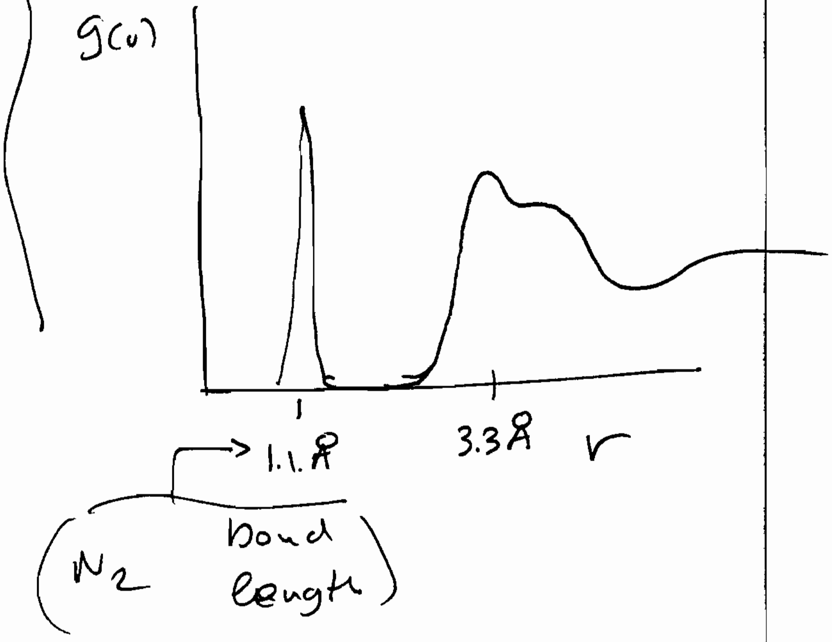


For Solids, $g(r)$ is much more structured





For molecular fluids, Convolution of intra- and inter-molecular correlations, E.g. N_2



pair correlation functions can be measured by x-ray or neutron scattering methods.

Relationships of thermodynamic quantities to $g(r)$

$$E = \underbrace{E_{kin}}_{\frac{3}{2}Nk_BT} + \underbrace{E_{pot}}_{\text{due to intermolecular interactions}}$$

for monoatomic

E_{pot} is usually assumed to be pair-wise additive:

$$E_{pot} = \sum_{i=1}^{N} \sum_{j>i}^{N} u_{ij}(r_{ij})$$

} good approximation if using effective potentials.

Assuming pair-wise additivity,

$$\frac{E_{pot}}{N} = \overset{\uparrow}{\frac{1}{2}}\, \rho \int_0^\infty u(r)\, 4\pi r^2 g(r)\, dr$$

to prevent double-counting

For the pressure, we will soon (see "classical Systems" page 6) derive the relationship:

$$+ \frac{1}{3V} \langle \sum_i \vec{F}_i \cdot \vec{r}_i \rangle =$$

$$P = \frac{Nk_BT}{V} + \frac{1}{3V} \underbrace{\int \cdots \int \left(\sum_i \vec{F}_i \cdot \vec{r}_i \right) \mathcal{P}(\vec{r}^N)\, d\vec{r}^N}_{\textcircled{A}}$$

The integral Ⓐ can be expressed in terms of pair correlation functions between particles, if we assume pair-wise additive interactions:

$$Ⓐ = \underset{\text{all } N \text{ particles identical}}{\frac{N}{\underset{\text{to avoid double-counting}}{2}}} \cdot \int_0^\infty \underbrace{-\frac{du(r)}{dr}}_{\text{force on central particle}} \cdot r \cdot \underbrace{g(r) 4\pi r^2 \rho}_{\text{\# of particles at } r} \cdot dr$$

$$\Rightarrow \frac{P}{k_BT} = \rho - \frac{4\pi\rho^2}{6k_BT} \int_0^\infty \frac{du(r)}{dr} g(r) r^3 dr \quad ①$$

for low densities, the probability of finding two particles at distance r is just the Boltzmann factor of the potential:

$$g(r) \simeq \exp[-\beta u(r)] \quad ②$$

Substituting ② in ①:

$$\frac{P}{k_BT} \simeq \rho - \frac{2\pi\rho^2}{3} \int_0^\infty \underbrace{\beta \frac{du(r)}{dr} e^{-\beta u(r)}}_{-f'} \underbrace{r^3}_{g} dr \quad ③$$

$$\text{Consider} \left\{ \begin{array}{l} f = e^{-\beta u(r)} - 1 \\ g = r^3 \end{array} \right\}$$

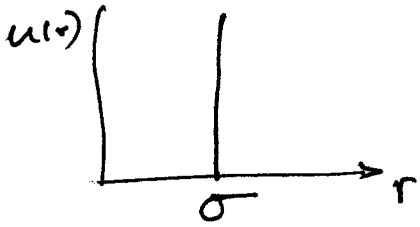
Integrate by parts: $\int f'g = fg - \int fg' \Rightarrow$

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

$$③ \Rightarrow \frac{P}{k_BT} \simeq \rho \underbrace{-\left(2\pi \int_0^\infty \left[e^{-\beta u(r)} - 1\right] r^2 dr\right)}_{B(T)\text{: second virial coeff.}} \cdot \rho^2$$

Example - hard spheres

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma \end{cases}$$

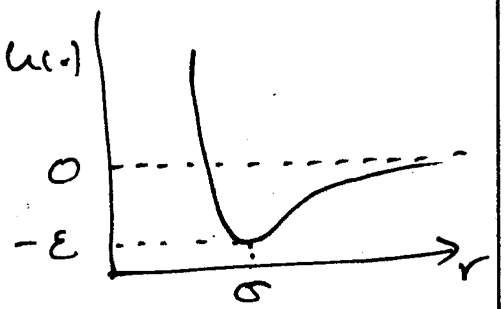


$$B = -2\pi \int_0^\infty \left[e^{-\beta u(r)} - 1 \right] r^2 dr = +2\pi \int_0^\sigma r^2 dr = \frac{2\pi\sigma^3}{3}$$

- independent of T
- always positive - physical interpretation?

Example - Lennard-Jones (LJ)

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

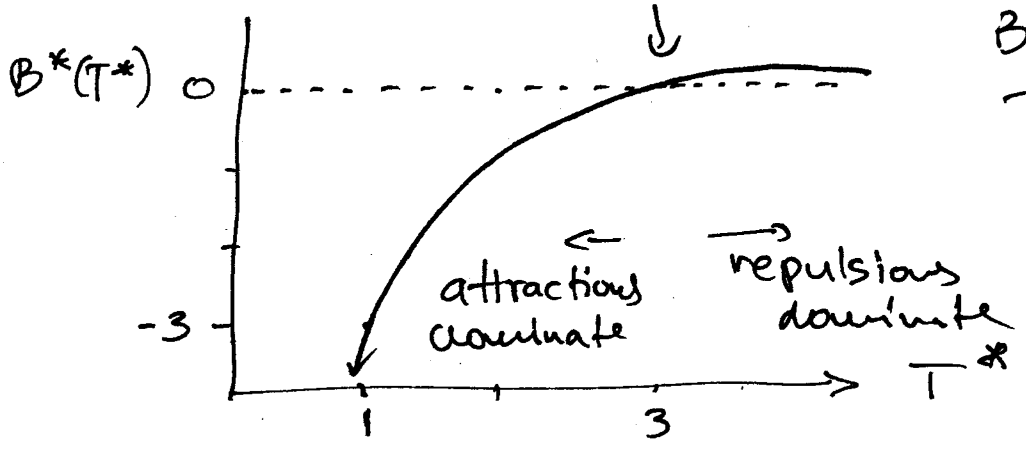


$$B(T) = -2\pi \int_0^\infty \left[e^{-\beta u(r)} - 1 \right] r^2 dr$$

no simple analytical solution

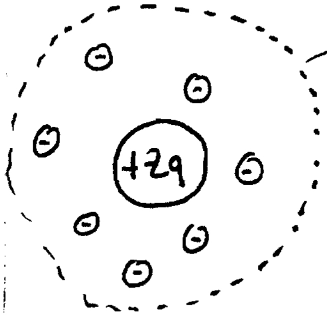
$$\left.\begin{aligned} B^* &= B/\sigma^3 \\ T^* &= k_B T/\varepsilon \end{aligned}\right\} \text{dimensionless units for LJ}$$

B(T) = 0 at Boyle Temp. T_B –



A simple application: Poisson-Boltzmann Distribution

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

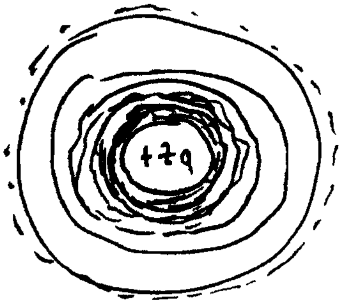


System boundary - radius R; central ion radius σ

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 $g(r)\cdot\rho$ $\left[\rho = \frac{Z}{V_{gap}}\right]$ where

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

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

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

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

The normalization condition for equation (2) is that $\rho \int_{\sigma}^{R} 4\pi r^2 g(r)\, dr = Z$ (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.

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

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

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