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:

![Diagram of a molecule of interest and a spherical shell with differential volume $dr$.]

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

$$N_{\text{random}} = 4\pi r^2 \rho dr$$

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

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

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

At short distances, electronic repulsions prevent molecular overlaps, so $g(r \to 0) = 0$. 
At long distances, random distribution prevails:
\[ g(r \rightarrow \infty) = 1 \]

Typical \( g(r) \) for dense monatomic fluids, e.g. Ar

For solids, \( g(r) \) is much more structured

For molecular fluids, convolution of intra- and inter-molecular correlations, e.g. \( \text{N}_2 \)

\( r \rightarrow 1.1 \alpha \)
\( r \rightarrow 3.3 \alpha \)

\( \text{Bond length} \)
Pair correlation functions can be measured by x-ray or neutron scattering methods.

Relationships of thermodynamic quantities to $g(r)$

$$E = E_{\text{kin}} + E_{\text{pot}}$$

$$= \frac{3}{2}Nk_BT$$ due to intermolecular interactions

For monoatomic

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

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

Good approximation is using effective potentials.

Assuming pair-wise additivity,

$$\frac{E_{\text{pot}}}{N} = \frac{1}{2} \int_{0}^{\infty} u(r) 4\pi r^2 g(r) \, dr$$

To prevent double-counting.

For the pressure, we have previously (see "classical systems" page 6) derived the relationship:

$$P = \frac{Nk_BT}{V} + \frac{1}{3V} \int \int \int (z \delta_i \cdot \vec{r}_i) \rho(r_1) \, dr_1 \, dr_2$$

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

\[ \Pi = \frac{N}{2} \int_0^\infty -\frac{du(r)}{dr} \cdot r \cdot g(r) 4\pi r^2 \rho \cdot dr \]

all \( N \) particles identical to avoid double-counting particle at \( r \)

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

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

\[ g(r) = \exp [-B u(r)] \quad (2) \]

Substituting (2) in (1):

\[ \frac{P}{k_B T} = \rho - \frac{2 \pi \rho^2}{3} \int \frac{du(r)}{dr} e^{-B u(r)} r^3 dr \quad (3) \]

Consider:

\[
\begin{cases}
  f = e^{-B u(r)} - 1 \\
g = r^3
\end{cases}
\]

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

\[ -\int \frac{du(r)}{dr} e^{-B u(r)} r^3 dr = \left[ e^{-B u(r)} - 1 \right] r^3 \bigg|_0^\infty - 3 \int [e^{-B u(r)} - 1] r^2 dr \]

\[ \Rightarrow \frac{P}{k_B T} = \rho - \left( 2n \int [e^{-B u(r)} - 1] r^2 dr \right) \cdot \rho^2 \]

\( B(T) \) : second virial coefficient.
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 \( \sigma \);
- Coulombic interactions:

\[
U_{ij}(r_{ij}) = \frac{q_i q_j}{4 \pi \varepsilon_0 r_{ij}}
\]

Assume:
- Point counterions;
- No correlations of counterion positions;

Mean density of counterions at zero distance \( r \) proportional to \( g(r) \).\( \rho \left[ \rho = \frac{\varepsilon}{V_{gap}} \right] \)

Effective potential felt by counterions at spherical shell of distance \( r \) has two contributions:

\[
U_{\text{eff}}(r) = -\frac{Q_{\text{in}} q}{4 \pi \varepsilon_0 r} + \int \frac{4 \pi r^2 g(r') dr'}{4 \pi \varepsilon_0 r'} \tag{1}
\]

- Interaction with change in sphere of radius \( r' \);
- Potential due to charge at distance greater than \( r' \);

\[
Q_{\text{in}} = \left[ 2 - \beta \int \frac{4 \pi r' g(r') dr'}{6} \right] q \tag{2}
\]

But we also must have \( g(r) \propto \exp(-B \text{eff}(r)) \).

The normalization condition for equation (2) is
that \( \int_0^R 4\pi r^2 g(r) \, dr = z \), since there

(3)
must be \( z \) counterions in the gap between \( \sigma \) and \( R \).

Equations (1) (2) and the renormalization 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

\[
E = -\int_0^R \frac{Q^2}{4\pi} 4\pi r^2 g(r) \, dr \, \phi(r)
\]

(4)

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