1.3: Excluded Volume

Excluded Volume

One of the key concepts that arises from a particulate description of matter is excluded volume. Even in the absence of attractive interactions, at short range the particles of the fluid collide and experience repulsive forces. These repulsive forces are a manifestation of excluded volume, the volume occupied by one particle that is not available to another. This excluded volume gives rise to the structure of solvation shells that is reflected in the short-range form of $g(r)$ and $W(r)$. Excluded volume also has complex dynamic effects in dense fluids, because one particle cannot move far without many other particles also moving in some correlated manner.

The excluded volume can be related to $g(r)$ and $W(r)$, making note of the virial expansion. If we expand the equation of state in the density of the fluid (ρ):

$$\frac{p}{\rho k_B T} = 1 + B_2(T)\rho + \cdots$$

The second virial coefficient B_2 is half of the excluded volume of the system. This is the leading source of non-ideality in gasses reflected in the van der Waals equation of state.

$$\begin{aligned} 2B_2(T) &= \int_0^\infty r^2(1-g(r))dr \\ &= \int_0^\infty r^2\left(1-\exp[-W(r)/k_BT]\right)dr \end{aligned}$$