A

HMSA closure

The structure factor is essentially the Fourier transform of the radial distribution function $g(r)$, which gives the relative conditional probability of finding a particle at a distance $r$ apart from another particle [9]. The pair distribution function is related to the direct correlation function $c(r)$ by the Ornstein-Zernike equation [69]:

$$h(r) = c(r) + nh(r) \ast c(r), \quad (A.1)$$

where $h(r) = g(r) - 1$ is the total correlation function, $n$ the particle number density, and the symbol $\ast$ denotes a convolution product. To calculate $g(r)$ [and therefore $S(q)$] for a given potential, eq. A.1 has to be closed by an additional relation. We will employ the so-called HMSA closure here, proposed by Zerah and Hansen [112]. This closure relation reads

$$g(r) = \exp\{-u_1(r)/k_B T\} \left(1 + \exp\{f(r)[h(r) - c(r) - u_2(r)/k_B T]\}/f(r) - 1\right), \quad (A.2)$$

where $u_1(r)$ is the repulsive part of the interparticle potential and $u_2(r)$ the attractive part. The “switching function” $f(r)$ is parameterized by

$$f(r) = 1 - \exp\{-\zeta r\}. \quad (A.3)$$

For a given potential, the parameter $\zeta$ is varied until thermodynamic consistency is achieved, that is, until the isothermal compressibility obtained from the Ornstein-Zernike equation is equal to the one obtained from the virial
The closure A.2 interpolates between the hypernetted-chain closure \([f(r) = 1]\) and the soft mean spherical approximation \([f(r) = 0]\), which are both thermodynamically inconsistent [112]. For a purely repulsive potential \([u_2(r) = 0]\), the soft mean spherical approximation reduces to the well-known Percus-Yevick closure and, consequently, the HMSA scheme to the thermodynamically consistent Rogers-Young (RY) closure [9]. Since the DLVO potential is purely repulsive, the closure A.2 is identical to the RY-closure. The accuracy of the RY closure in conjunction with the DLVO potential has been demonstrated by D'Aguanno and Klein by comparison with computer simulation results [113]. The particular numerical scheme we use has successfully been applied to Lennard-Jones systems [112, 114]. We tested the scheme for the case of a DLVO potential by comparison with published computer simulation data [113, 115] and found agreement to better than 5 \%.

\[^{1}\chi_T^{-1} = n(\partial P/\partial n)_T,\] where \(P\) is the pressure.