The Random Phase Approximation

for Binary Hard-Core Mixture

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Abstract

Expressions of the Ashcroft-Langreth partial structure factors for an arbitrary two-component hard-core fluid in the random phase approximation are presented.

Keywords: Hard-core mixture, random phase approximation, partial structure factor

In general case, the random phase approximation (RPA) for classical binary fluid is formulated as follows:

\[ c_{ij}^{\text{RPA}}(r) = c_{ij}(r) - \beta \varphi_{ij}(r), \]

where \( c_{ij}(r) \) is the partial direct correlation function, \( \varphi_{ij}(r) \) - partial pair interatomic potential, \( \beta = (k_B T)^{-1} \), \( k_B \) - Boltzmann constant, \( T \) - temperature, symbols “0” and “1” are attributes of a reference system and perturbation, respectively, \( i, j = 1, 2 \).

For any hard-core (HC) \( \varphi_{ij}(r) \),

\[ \varphi_{ij}^{\text{HC}}(r) = \begin{cases} \infty, & r < \sigma_{ij} \\ \phi_{ij}(r), & r \geq \sigma_{ij} \end{cases}, \]

where \( \sigma_{ij} \) is the partial HC diameter,

\[ c_{ij}^{\text{RPA-HC}}(r) = c_{ij}^{\text{HS}}(r) - \beta \phi_{ij}(r). \]

Here, “HS” denotes the hard-sphere model, which for a mixture is described by the following \( \varphi_{ij}(r) \):
In the wave space Eq. (3) is being rewritten as
\[ c_{ij}^{\text{RPA-HC}}(q) = c_{ij}^{\text{HS}}(q) - \beta \phi_j(q). \] (5)

The Lebowitz exact solution [1] obtained for the additive HS binary mixture in the Percus-Yevick approximation [2] can be used to calculate \( c_{ij}^{\text{HS}}(r) \) and \( c_{ij}^{\text{HS}}(q) \).

The Ashcroft-Langreth (AL) partial structure factors [3] are expressed as follows \( i \neq j \):
\[ S_i(q) = \prod_{k=1,2} \left( 1 - c_i \rho c_j(q) - c_i c_j \rho^2 c_j^2(q) \right), \] (6)
\[ S_j(q) = \prod_{k=1,2} \left( 1 - c_i \rho c_k(q) - c_i c_j \rho^2 c_j^2(q) \right), \] (7)
where \( c_j \) is the concentration of the \( i \)-th component, \( \rho \) - mean atomic density of a mixture. Combining Eqs. (6) and (7) with Eq. (5) one can obtain after some transformations the expressions of AL partial structure factors within the RPA for an arbitrary \( \phi_j(r) \) in a general form:
\[ S_{ij}^{\text{RPA-HC}}(q) = \frac{1 - c_i \rho c_j^{\text{HS}}(q) + c_i c_j \rho^2 \phi_j(q)}{Z(q)}, \] (8)
\[ S_{ji}^{\text{RPA-HC}}(q) = \frac{\sqrt{c_j} c_i \rho c_j^{\text{HS}}(q) - \sqrt{c_j} c_j c_i \rho \phi_j(q)}{Z(q)}, \] (9)
\[ Z(q) = \prod_{k=1,2} \left( 1 - c_k \rho c_k^{\text{HS}}(q) \right) - c_i c_j \rho^2 c_j^{\text{HS2}}(q) + \prod_{k=1,2} \left( 1 + c_k \rho \phi_j(q) \right) - c_i c_j \rho^2 \phi_j^2(q) - \left[ -1 - c_i c_j \rho^2 \beta \sum_{i,j} c_{ij}^{\text{HS}}(q) \phi_j(q) - 2 c_j^{\text{HS}}(q) \phi_j(q) \right]. \] (10)

Expressions obtained can be used to describe the square-well, triangular-well, hard-core-Yukawa, charged-hard-sphere and other model binary mixtures.

References


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