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Static structure factor for a fluid with interaction of hard spheres plus two Yukawa tails

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ABSTRACT

We determine the static structure factor $S(k)$ for a fluid of hard spheres with two-Yukawa interactions through the application of the mean spherical approximation (MSA) to a multi-component system composed of hard-spheres plus double Yukawa interactions (HSDY). This $S(k)$ depends on scaling parameters Γ_n that satisfy a system of nonlinear equations. We report explicit results for a mono-dispersed HSDY fluid and show that the hard-sphere contributions control the main peak of the $S(k)$, while for wave vectors approaching zero, we predict a cluster peak which could be identified with that of recent experimental results of Liu et al. [Y. Liu, W.-R. Chen, S.H. Chen, J. Chem. Phys. 122 (2005) 044507-1].

1. Introduction

The classical statistical mechanics of fluids requires an effective interaction potential, associated with the potential of the mean force, to be able to represent adequately a real system and, consequently, to be able to predict its structure and thermodynamic behavior [1]. One useful effective potential is represented by the sum of two contributions, i.e., a hard sphere plus a linear combination of attractive and repulsive interactions [2]. The linear combination of a hard-sphere and a double Yukawa interaction (HSDY) results in one of the most useful potential models. This model has already been applied to the study of colloids, polymers, and membranes [2–6].

The static structure factor $S(k)$ of this system has been determined by Hoye et al. [7], who developed an analytical expression involving a system of non-linear equations for the coefficients of the correlation functions. Recently, Liu et al. applied Hoye's approach and reduced the solution of the system of non-linear equations to a numerical one involving a polynomial equation of order 27, [2]. In addition, Blum et al. [8] calculated the static structure factor in terms of $\tilde{g}(s)$ for a multi-Yukawa fluid, and discussed the limitation of the MSA [8,9]. Blum also tackled the study of a general multi-Yukawa fluid without considering an interaction satisfying the Lorentz Berthelot rules [10].

Some recent work indicates that the MSA can be used to develop perturbation theories around the reference model system described by a Yukawa potential, that predict results in very good agreement with those from molecular simulations [11].

In this work, we focus on the study of model fluids with an effective HSDY potential obeying the Lorentz–Berthelot rules in the MSA. We present a straightforward formulation that has the advantage of allowing us to extend it to treat mixtures with an arbitrary number of Yukawa terms and with the same range of validity of the aforementioned approaches [7–10].

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The main result of our work is the determination of the static structure factor for a HSDY model fluid under the MSA and a Multi-Yukawa closure involving a scaled matrix to solve the set of coupled linear equations [12–15]. In addition, we use an iterative numerical method to determine the physically-meaningful roots of the scaling parameters [13,14]. In Section 2 we present the methodology used to extract the static structure factor in terms of the scaling parameters Γ_n for a multicomponent HSDY fluid, while in Section 3 we display explicitly the expression for the corresponding $S(k)$. Some results for the $S(k)$ of monodispersed HSDY fluids, involving either equal or dissimilar relative sizes of the attractive and repulsive amplitudes, are displayed in Section 4. Finally, in the appendix, we summarize the relevant expressions involved in the calculation of the reported results.

2. Methodology

The static structure factor $S(k)$ is an important quantity in the physics of fluids since it is related to the radial distribution function through the corresponding Fourier transform of the Ornstein–Zernike (OZ) equation [16]. This quantity is also experimentally accessible using diffraction of electromagnetic radiation or scattering of slow neutrons. However, its experimental determination is complex and costly, since it requires the use of particle accelerators or neutron sources. For that reason, it is important to have available an analytical expression allowing the comparison between theoretical predictions and experimental data.

For a homogeneous mixture of R components, the OZ equation can be written as [16]:

$$h_{ij}(r_{12}) = c_{ij}(r_{12}) + \sum_{n=1}^{R} \rho_n \int \mathrm{d}^3 r_3 c_{in}(r_{13})\, h_{nj}(r_{32})\,, \tag{1}$$

where $h_{ij}(r)$ and $c_{ij}(r)$ are the total and direct correlation functions, respectively, ρ_n is the number density of component n. By Fourier transforming of the OZ equation we can define the partial structure factors $S_{ij}(k)$ as follows,

$$S_{ij}(k) = \left[\delta_{ij} + \sqrt{\rho_i \rho_j}\tilde{h}_{ij}(k)\right] = \left[\mathbf{C}^{-1}(k)\right]_{ij} \tag{2}$$

where $\mathbf{C}(k)$ is the matrix with elements $\delta_{ij} - \sqrt{\rho_i \rho_j}\tilde{c_{ij}}(k)$, $\tilde{c}_{ij}(k)$ and $\tilde{h}_{ij}(k)$ are the Fourier transforms of the direct and total correlation function, respectively. To solve the OZ equation we use the Baxter factorization method, which can be written in terms of the direct correlation matrix as [17],

$$\delta_{ij} - \sqrt{\rho_i \rho_j}\tilde{c}_{ij}(k) = \sum_{l=1}^{R} \tilde{Q}_{il}(k)\tilde{Q}_{jl}(-k) \tag{3}$$

with $\tilde{Q}(-k) = \tilde{Q}^*(k)$; and * indicates the complex conjugate of the Baxter matrix, whose components are calculated from the expression:

$$\tilde{Q}_{mn}(k) = \delta_{mn} - \sqrt{\rho_m \rho_n} \int_{\lambda_{nm}}^{\infty} \mathrm{e}^{\mathrm{i}kr} Q_{mn}(r)\, \mathrm{d}r \tag{4}$$

where $\lambda_{nm} = \frac{1}{2}(\sigma_n - \sigma_m)$ and σ_i is the molecular diameter of component i. On the other hand, Blum and Hoye solved the OZ equation for a Multi-Yukawa plus a hard-sphere potential [18], by writing the closure as follows,

$$c_{ij}(r) = -\beta u_{ij}(r) = \sum_{n=1}^{M} \frac{K_{ij}^{(n)}}{r} \mathrm{e}^{-z_n r} \quad r > \sigma_{ij} = \frac{1}{2}\left(\sigma_i + \sigma_j\right) \tag{5}$$

where M is the number of Yukawa terms. In this case we need to apply the exact condition, $h_{ij}(r) = -1$, for short distances ($r < \sigma_{ij}$). Eq. (7) considers an interaction potential of the following form,

$$u_{ij}(r) = \sum_{n=1}^{M} A_{ij}^{(n)} \frac{\mathrm{e}^{-z_n r}}{r} \tag{6}$$

where z_n governs the potential range while $A_{ij}^{(n)}$ are related to the strength of the interactions. Therefore, according to Eq. (6), the Baxter function becomes

$$Q_{ij}(r) = Q_{ij}^{0}(r) + \sum_{n=1}^{M} D_{ij}^{(n)} \mathrm{e}^{-z_n r} \tag{7}$$

with,

$$Q_{ij}^{0}(r) = \frac{1}{2}\left(r - \sigma_{ij}\right)\left(r - \lambda_{ij}\right) A_j + \left(r - \sigma_{ij}\right)\beta_j + \sum_{n=1}^{M} C_{ij}^{(n)}\left(\mathrm{e}^{-z_n r} - \mathrm{e}^{-z_n \sigma}\right) \quad \sigma_{ij} > r > \lambda_{ij}$$