Classical density functional calculation of radial distribution functions of liquid water

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A B S T R A C T

We have calculated the radial distribution functions (RDFs) of liquid water on the basis of the classical density functional theory combined with the reference interaction site model for molecular liquids. The density expansion for the Helmholtz free energy functional is retained up to the third order in order to take into account the effects of the bridge functions beyond the hypernetted-chain (HNC) approximation. The ternary direct correlation functions in the expression of the bridge functions are then given by a factorization approximation in terms of the site–site pair correlation functions, thus leading to a closed set of integral equations for the determination of the RDFs. We have obtained a numerical result in which a poor description by the HNC approximation for the second peak of the oxygen–oxygen RDF at room temperature has been improved to some extent by incorporating the oxygen–oxygen bridge function. Some directions toward more satisfactory agreement with computer simulation results are addressed as well.

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1. Introduction

Integral equation approach provides an efficient tool to calculate the correlation functions and the thermodynamic properties of liquids with high accuracy and mild cost of computation [1]. This analytical approach often gives fair results on par with those by extensive Monte Carlo or molecular dynamics (MD) simulations, and combined with the reference interaction site model (RISM) [1–3], can comprehensively describe the equilibrium properties of molecular liquids such as liquid water [4]. Recent developments in the methods, algorithms and benchmarks [5–9] indicate that the RISM-based integral equation approach can provide an alternative route for theoretical analyses on water and related aqueous systems with comparable reliability to more expensive, computer simulation approaches. However, it has also been observed [5–9] that the descriptions of intermolecular correlations of water become less accurate at room temperature in comparison with at higher temperatures.

Among the RISM-based integral equation formalisms for molecular liquids, the density functional theory (DFT) approach due to Chandler, McCoy and Singer [10,11] is one of the most sophisticated and dependable methods. Donley, Curro and McCoy (DCM) [12] then extended this DFT scheme for the calculations of pair correlation functions of molecular liquids, and later, Reddy et al. [6] and Sumi et al. [13] applied this method to the calculations of the radial

distribution functions of fluid water. Their calculated results demonstrated that the DCM scheme provides accurate descriptions at high temperatures, but the deviations from the computer simulation results are observed at room temperature, e.g., in the description of the location of the second peak of oxygen–oxygen (O–O) radial distribution function, which may be associated with the formation of tetrahedral structure of condensed water. Considering that the DCM theory is based on the density expansion of free energy functional up to the second order, which corresponds to the hypernetted-chain (HNC) approximation [1,14] in liquid theory, the present authors [15] have recently developed an extended DCM theory for molecular liquids in which the density expansion of free energy functional is retained up to the third order, thus taking into account the effect of the bridge functions [1,14] beyond the HNC approximation. Their preliminary test calculation in which a simple Gaussian approximation is employed in the factorization [16] for the ternary direct correlation functions has, however, failed to appropriately reproduce the simulation results for liquid water at room temperature, suggesting the importance of incorporation of detailed structures of correlation functions in the representation of ternary direct correlation functions. The purpose of the present study is thus to examine the validity and accuracy of another factorization approximation to the ternary direct correlation functions in the bridge functions,
in which the site–site pair correlation functions are employed in the factorization according to a scheme [17] that worked well in the one-component plasma system [14]. We will address the theoretical methods and the numerical results in the following sections.

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2. DFT–RISM method

Let us consider a liquid water system consisting of rigid H_2O molecules whose average number density and temperature are ρ and T, respectively. We then assume the site–site interaction potentials $v_{\alpha\beta}(\mathbf{r})$ between the atomic sites α and β (α, β = O, H, H, i.e., one oxygen and two hydrogens) on two water molecules. According to the prescription given by Donley et al. [12], the radial distribution function (RDF) between the sites α and β is given by

$$g_{\alpha\beta}(\mathbf{r}_\alpha - \mathbf{R}_\beta) = \left\langle\left\langle \exp\left\{\sum_\eta \left[\psi_{0\eta}(\mathbf{r}_\eta) - \psi_{0L\eta}\right]\right\}\right\rangle\right\rangle^{\mathcal{P}}_{\mathbf{r}_\alpha, \mathbf{R}_\beta}, \tag{1}$$

where $\langle\langle\ \ \rangle\rangle^{\mathcal{P}}_{\mathbf{r}_\alpha, \mathbf{R}_\beta}$ represents the average over the relative orientation of two (system and external) molecules whose αth and βth sites are fixed at $\mathbf{r}_\alpha$ and $\mathbf{R}_\beta$, respectively.

$$\psi_\eta(\mathbf{r}_\eta) = -U_\eta(\mathbf{r}_\eta) + \psi_{L\eta} = -\beta\sum_\gamma v_{\eta\gamma}(\mathbf{r}_\eta - \mathbf{R}_\gamma) + \psi_{L\eta} \tag{2}$$

with $\beta = 1/k_BT$ and k_B being the Boltzmann constant means the field at the ηth site, $\mathbf{r}_\eta$, produced by an inserted, external molecule [18] situated at $\{\mathbf{R}\} = \{\mathbf{R}_\gamma\}$, and its deviation from the homogeneous (liquid L) part is expressed as

$$\psi_{0\eta}(\mathbf{r}) - \psi_{0L\eta} \simeq -U_\eta(\mathbf{r}) + \sum_\sigma \int d\mathbf{r}' c_{\eta\sigma}(\mathbf{r}, \mathbf{r}')\Delta\rho_\sigma(\mathbf{r}')$$
$$+ \frac{1}{2}\sum_{\mu,\nu}\int d\mathbf{r}' \int d\mathbf{r}'' c^{(3)}_{\eta\mu\nu}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')\Delta\rho_\mu(\mathbf{r}')\Delta\rho_\nu(\mathbf{r}'') \tag{3}$$

for the fictitious, noninteracting system denoted by the subscript "0" whose density profile $\rho_\alpha(\mathbf{r})$ is identical to that of the real, interacting system. Here, $\Delta\rho_\alpha(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho$ refers to the induced density around the unperturbed, homogeneous liquid (L) state, and the expansion with respect to $\Delta\rho_\alpha(\mathbf{r})$ has been carried out up to the third order for the Helmholtz potential [15]. $c_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ and $c^{(3)}_{\alpha\beta\gamma}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ refer to the two-body and three-body direct correlation functions in the liquid state [1], respectively.

We thus obtain an expression for the RDF as [15]

$$g_{\alpha\beta}(\mathbf{r}_\alpha - \mathbf{R}_\beta)$$
$$= \left\langle\left\langle \exp\left[-\beta\sum_{\eta,\gamma} v_{\eta\gamma}(\mathbf{r}_\eta - \mathbf{R}_\gamma) + \Lambda(\{\mathbf{r}\}, \{\mathbf{R}\}) + B(\{\mathbf{r}\}, \{\mathbf{R}\})\right]\right\rangle\right\rangle^{\mathcal{P}}_{\mathbf{r}_\alpha, \mathbf{R}_\beta}. \tag{4}$$

Here, the two-body part is expressed as

$$\Lambda(\{\mathbf{r}\}, \{\mathbf{R}\}) = \rho\sum_{\eta,\gamma}\sum_{\sigma,\xi}\int d\mathbf{r}_\sigma \int d\mathbf{r}_\xi c_{\eta\sigma}(\mathbf{r}_\eta - \mathbf{r}_\sigma)h_{\sigma\xi}(\mathbf{r}_\sigma - \mathbf{r}_\xi)\omega^{-1}_{\xi\gamma}(\mathbf{r}_\xi - \mathbf{R}_\gamma)$$
$$= \sum_{\eta,\gamma}\sum_{\sigma,\xi}\int d\mathbf{r}_\sigma \int d\mathbf{r}_\xi c_{\eta\sigma}(\mathbf{r}_\eta - \mathbf{r}_\sigma)S_{\sigma\xi}(\mathbf{r}_\sigma - \mathbf{r}_\xi)c_{\xi\gamma}(\mathbf{r}_\xi - \mathbf{R}_\gamma) \tag{5}$$

with the aid of a site–site pairwise approximation for the induced density [12], and

$$\omega_{\alpha\beta}(\mathbf{r}) = \delta_{\alpha\beta}\delta(\mathbf{r}) + (1 - \delta_{\alpha\beta})\delta(r - L_{\alpha\beta})/4\pi L^2_{\alpha\beta} \tag{6}$$

with $L_{\alpha\beta}$ being the distance between sites α and β means the intramolecular correlation functions. The site–site pair correlation functions $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$ and the two-body direct correlation functions $c_{\alpha\beta}(r)$ are related to each other via the site–site Ornstein–Zernike or RISM equation [1,2],

$$h_{\alpha\beta}(r) = \sum_{\eta,\sigma}\left[\omega_{\alpha\eta} * c_{\eta\sigma} * \omega_{\sigma\beta}(r) + \rho\omega_{\alpha\eta} * c_{\eta\sigma} * h_{\sigma\beta}(r)\right], \tag{7}$$

where $*$ means the convolution, and

$$S_{\alpha\beta}(r) = \rho\omega_{\alpha\beta}(r) + \rho^2 h_{\alpha\beta}(r) \tag{8}$$

refers to the density–density correlation functions.

If we neglect the higher-order contribution $B(\{\mathbf{r}\}, \{\mathbf{R}\})$ in Eq. (4), we are led to a two-body approximation that is equivalent to the HNC approximation [1]. The effective many-body potential

$$\Lambda(\{\mathbf{r}\}, \{\mathbf{R}\}) = \sum_{\eta,\gamma}X_{\eta\gamma}(\mathbf{r}_\eta - \mathbf{R}_\gamma) \tag{9}$$

with

$$X_{\eta\gamma}(\mathbf{r}_\eta - \mathbf{R}_\gamma) = \frac{1}{(2\pi)^3}\int d\mathbf{k}\ \exp[-i\mathbf{k}\cdot(\mathbf{r}_\eta - \mathbf{R}_\gamma)]\hat{X}_{\eta\gamma}(\mathbf{k}) \tag{10}$$

and its Fourier transform are expressed as

$$\hat{X}_{\eta\gamma}(\mathbf{k}) = \rho\sum_{\sigma,\xi}\hat{c}_{\eta\sigma}(\mathbf{k})\hat{h}_{\sigma\xi}(\mathbf{k})\hat{\omega}^{-1}_{\xi\gamma}(\mathbf{k}) = \sum_{\sigma,\xi}\hat{c}_{\eta\sigma}(\mathbf{k})\hat{S}_{\sigma\xi}(\mathbf{k})\hat{c}_{\xi\gamma}(\mathbf{k}), \tag{11}$$

or compactly by

$$\hat{\mathbf{X}} = \rho\hat{\mathbf{c}}\hat{\mathbf{h}}\hat{\omega}^{-1} = \hat{\mathbf{c}}\hat{\mathbf{S}}\hat{\mathbf{c}}. \tag{12}$$

We then rewrite this expression as

$$\hat{\mathbf{X}}_s = \hat{\omega}^{-1}\hat{\mathbf{h}}\hat{\omega}^{-1} - \hat{\mathbf{c}}_s = \hat{\omega}^{-1}(1 - \rho\hat{\omega}\hat{\mathbf{c}})^{-1}\hat{\omega}\hat{\mathbf{c}} - \hat{\mathbf{c}}_s \tag{13}$$

with the aid of Eq. (7), where the subscript s means that the long-range contributions have analytically been subtracted [19]. Thus, for given $\hat{\mathbf{c}}(\mathbf{k})$, one can calculate $\hat{\mathbf{X}}(\mathbf{k})$, $\mathbf{X}(\mathbf{r})$, $\Lambda(\{\mathbf{r}\}, \{\mathbf{R}\})$, $\mathbf{h}(\mathbf{r})$ and $\hat{\mathbf{h}}(\mathbf{k})$. An updated $\hat{\mathbf{c}}(\mathbf{k})$ is then given by

$$\hat{\mathbf{c}}_s = \hat{\omega}^{-1}\hat{\mathbf{h}}\hat{\omega}^{-1} - \hat{\mathbf{X}}_s, \tag{14}$$

leading to a closed set of self-consistent equations.

We numerically solved the integral equations in the HNC approximation addressed above for the correlation functions of liquid water. We employed the SPC/E model [20] for the (rigid) structure and intermolecular potentials for water molecules, thus assuming a three-site (one oxygen and two hydrogens) model in which the Lennard–Jones potential works only between the oxygen (O) sites. The computational details are found in the literature [15], where it is noted that the present DFT scheme is free from the difficulty of divergence encountered in the usual RISM–HNC approach when the SPC-like model potentials without the additional O–H repulsion are employed [4–6,21]. The results for the RDFs $g_{\alpha\beta}(r)$ obtained by the second-order, HNC scheme are illustrated in Fig. 1 for liquid water system at $\rho = 0.0334\ \text{Å}^{-3}$ and $T = 300$ K. For comparison, we have also depicted the results by 10 ns MD simulation [15] for the SPC/E water performed with AMBER 12 software [22], as well as those by a neutron diffraction experiment [23]. In contrast to successful descriptions at higher temperatures [6,13,15], one observes a significant discrepancy between the HNC and MD results at room temperature, in particular concerning the location of the second peak of $g_{OO}(r)$ that is situated at $r \simeq 4.5$ Å in the MD and experimental results. This observation indicates that the O–O tetrahedral ordering in dense, low-temperature water systems is not appropriately described by the second-order, HNC approximation for the intermolecular correlations.

3. Third-order correction

Next, we proceed to an incorporation of the triplet correlation term in Eq. (4). According to Eqs. (1) and (3), the three-body, bridge contribution is expressed as [15]

$$B(\{\mathbf{r}\}, \{\mathbf{R}\}) = \frac{1}{2}\rho^2\sum_\eta\sum_{\gamma,\lambda}\sum_{\mu,\nu}\int d\mathbf{r}_\mu \int d\mathbf{r}_\nu \sum_{\xi,\sigma}\int d\mathbf{r}_\xi \int d\mathbf{r}_\sigma c^{(3)}_{\eta\mu\nu}(\mathbf{r}_\eta, \mathbf{r}_\mu, \mathbf{r}_\nu)$$
$$\times h_{\mu\xi}(\mathbf{r}_\mu - \mathbf{r}_\xi)\omega^{-1}_{\xi\gamma}(\mathbf{r}_\xi - \mathbf{R}_\gamma)h_{\nu\sigma}(\mathbf{r}_\nu - \mathbf{r}_\sigma)\omega^{-1}_{\sigma\lambda}(\mathbf{r}_\sigma - \mathbf{R}_\lambda)$$
$$= \frac{1}{2}\sum_\eta\sum_{\gamma,\lambda}\sum_{\mu,\nu}\int d\mathbf{r}_\mu \int d\mathbf{r}_\nu \sum_{\xi,\sigma}\int d\mathbf{r}_\xi \int d\mathbf{r}_\sigma c^{(3)}_{\eta\mu\nu}(\mathbf{r}_\eta, \mathbf{r}_\mu, \mathbf{r}_\nu)$$
$$\times S_{\mu\xi}(\mathbf{r}_\mu - \mathbf{r}_\xi)c_{\xi\gamma}(\mathbf{r}_\xi - \mathbf{R}_\gamma)S_{\nu\sigma}(\mathbf{r}_\nu - \mathbf{r}_\sigma)c_{\sigma\lambda}(\mathbf{r}_\sigma - \mathbf{R}_\lambda), \tag{15}$$