Effects of Bridge Functions on Radial Distribution Functions of Liquid Water

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1 Introduction

Integral equation approach provides an efficient tool to calculate the correlation and thermodynamic functions of liquids with high accuracy and mild cost of computation [1, 2]. This analytical approach often gives fair results on a par with those by extensive Monte Carlo or molecular dynamics (MD) simulations, and combined with the reference interaction site model (RISM) method [1, 3, 4], can comprehensively describe the equilibrium properties of molecular liquids such as liquid water [5], which plays essential roles in a variety of biochemical processes. Recent developments in the methods, algorithms and benchmarks [6, 13, 15–17, 19] 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 [6–11] 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 et al. [12, 13] is one of the most sophisticated and dependable methods. Donley, Curro and McCoy (DCM) [14] then extended this DFT scheme for the calculations of pair correlation functions of molecular liquids, and later, Reddy et al. [8] and Sumi et al. [11] applied this method to the calculations of the radial distribution functions (RDFs) 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) RDF, 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, 2] in liquid theory, the present authors [15] have recently extended the DCM approximation beyond the HNC functional up to the third order, thus taking into account the theory so as to retain the density expansion of free energy functional up to the third order, which corresponds to the hypernetted-chain (HNC) approximation [1, 2] in liquid theory, the present authors [15] have recently extended the DCM approximation beyond the HNC functional. Their preliminary test calculation in which a simple Gaussian approximation is employed in the factorization for the ternary direct correlation functions in the bridge 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 present work then investigates another factorization approximation for 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 [2].

2 Methods

Let us consider a liquid water system consisting of rigid H2O molecules whose average number density and temperature are ρ and T, respectively. We then assume the site–site interaction potentials v_αβ(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 DFT scheme [14, 15], the RDF between the sites α and β is given by

\[ g_{αβ}(r_α - r_β) = \left\langle \exp \left[ -β \sum_{η,γ} v_{ηγ}(r_η - r_γ) + \Lambda(\{r\}, \{R\}) + B(\{r\}, \{R\}) \right] \right\rangle_{r_α, r_β} \]

with β = 1/k_BT and k_B being the Boltzmann constant, where \( \left\langle \langle \rangle \right\rangle_{r_α, r_β}^{p} \) refers to the average over the relative orientation of two water molecules whose αth and βth sites are fixed at \( r_α \) and \( r_β \), respectively, and whose coordinates are represented by \( \{r\} = \{r_α\} \) and \( \{R\} = \{r_β\} \), respectively. In this expression, the two-body part is given by

Then, we proceed to an incorporation of the triplet correlation term in Eq. (1). In a preceding DFT study [15] we derived an explicit expression for \( B(\{r\}, \{R\}) \) in terms of ternary direct correlation functions, and employed, as a first attempt, a simple Gaussian approximation for the factorized, three-body direct correlation functions. However, the calculated result for \( g_{αβ}(r) \) failed to quantitively...
reproduce the MD or experimental results. In the present study we instead consider another factorization approximation according to Iyetomi and Ichimaru [17], which took relevant account of the lowest-order contribution and worked well in the case of strongly coupled, one-component plasma [2]. It is expected that this approximation would provide a good description for hard and soft sphere systems as well as for Coulombic system, considering the universality in strongly correlated systems [1, 2]. Taking into account only the O–O contribution, which would play a primary role, the bridge function can then be given by

$$B_{oo}(r) = \frac{1}{2} \rho^2 \int dr \int dr' h_{oo}(r - r') \times h_{oo}(r' - r'') h_{oo}(r'' - r) h_{oo}(r''') h_{oo}(r'''')$$

with $r = |r| = |r_o - R_o|$ for $B(r, \{ R \})$ in Eq. (1), which is symmetric with respect to $r_o$ and $R_o$ due to the exclusive consideration of O–O correlation.

However, there is a drawback in the expression of Eq. (5) that this form of bridge function does not reproduce the correct short-range behavior due to $h_{oo}(r) \to -1$ at $r \to 0$ [16, 17]. We hence renormalize the bridge function as [15]

$$\tilde{B}(r) = f(r) B_{oo}(r)$$

by introducing a short-range enhancement function [17] as

$$f(r) = (C - 1) \exp \left[ -\left( \frac{r}{a} \right)^2 \right] + 1. \quad (7)$$

The parameters in Eq. (7) are roughly fixed as $a = 4.5$ Å and $C = 30.0$ in the following analysis, considering the location of the second peak of $g_{oo}(r)$ for the former and the typical magnitude of the short-range renormalization for $h_{oo}(r)$ [16, 17] for the latter. In addition, to reduce the computational cost, we use the experimental results [18] for $h_{oo}(r)$ to evaluate $B_{oo}(r)$ in terms of Eq. (5). The behavior of $\tilde{B}(r)$ at $\rho = 0.0334$ Å$^{-3}$ and $T = 300$ K is depicted in Fig. 1.

**3 Results and Discussion**

We have employed the SPC/E model [19] 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. We have thus carried out the calculation of the RDFs of liquid water at $\rho = 0.0334$ Å$^{-3}$ and $T = 300$ K, where the renormalized bridge function, $\tilde{B}(r)$, above was employed in Eq. (1). The computational details are found in the literature [15]. The calculated results for $g_{oo}(r)$ are shown in Fig. 2, in which we have also depicted the results by 10 ns MD simulation [15] for the SPC/E water performed with AMBER 12 software [20] as well as those by a neutron diffraction experiment [18] for comparison.

It is shown in Fig. 2b, c that the present DFT scheme with inclusion of $\tilde{B}(r)$ reproduces the behaviors of $g_{oo}(r)$ and $g_{HH}(r)$ obtained in the MD simulation fairly well. Concerning the description of $g_{OO}(r)$ shown in Fig. 2a, on the other hand, the present DFT scheme slightly improves the behavior of the second peak of $g_{OO}(r)$ over the HNC result [8, 11, 15], yielding the (weak) peak at $r \approx 4.7$ Å in comparison with that at $r \approx 4.5$ Å in the MD result and $r \approx 5.5$ Å in the HNC result. It should be remarked, however, that the agreement between the DFT and MD results is still unsatisfactory, especially concerning the quantitative description of the oscillatory behavior of $g_{OO}(r)$, e.g., the location of the third peak, thus needing further improvement on the theoretical scheme beyond the factorization approximation in terms of $h_{oo}(r)$; for instance, the contributions other than the O–O correlation may play some roles in $B(r, \{ R \})$. In addition, there is a
possibility that the fourth- and higher-order terms contribute to the bridge functions to some extent.

In this context, we have attempted to correct $\tilde{B}(r)$ in an ad hoc way by

$$
\delta \tilde{B}(r) = D \left\{ \exp \left[ -\frac{(r - r_1)^2}{\Delta_1} \right] - \exp \left[ -\frac{(r - r_2)^2}{\Delta_2} \right] \right. \\
\left. - \exp \left[ -\frac{(r - r_3)^2}{\Delta_3} \right] \right\} 
$$

(8)

with $D = 0.1$, $r_1 = 4.5 \text{ Å}$, $r_2 = 3.5 \text{ Å}$, $r_3 = 5.5 \text{ Å}$, and $\Delta_1 = \Delta_2 = \Delta_3 = 0.5 \text{ Å}$, considering the discrepancy between the DFT and MD results for $g_{OO}(r)$ shown in Fig. 2. We have thus performed the calculation of RDFs with the corrected bridge function,

$$
\tilde{B}_c(r) = \tilde{B}(r) + \delta \tilde{B}(r).
$$

(9)

While the correction $\delta \tilde{B}(r)$ is very minor as shown in Fig. 1a (indiscernible between $\tilde{B}(r)$ and $\tilde{B}_c(r)$ at the full scale), we have found that this correction substantially improves the agreement between the DFT and MD results as shown in Fig. 2, which indicates a delicate manner (see Fig. 1b at the zoomed scale) to quantitatively describe the RDFs with the bridge functions at medium to long distances. More accurate descriptions of the RDFs for liquid water would thus be a challenging task in the framework of many-body theory.

4 Conclusion

In summary, we calculated the RDFs of liquid water at ambient temperature and density on the basis of the third-order DFT method, in which the ternary direct correlation functions were expressed by the factorization with the pair correlation functions and the O–O bridge function was taken into account beyond the HNC approximation in the expression for the RDFs. Improvement on the HNC scheme was thus achieved with the use of the proposed bridge function and its corrected one, especially concerning the behavior of $g_{OO}(r)$, while some future tasks still remain for better theoretical description.

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