



# Triplet correlations and bridge functions in classical density functional theory for liquid water

Shigenori Tanaka<sup>a,\*</sup>, Miki Nakano<sup>b</sup>

<sup>a</sup> Graduate School of System Informatics, Department of Computational Science, Kobe University, 1-1 Rokkodai, Nada-ku, Kobe 657-8501, Japan

<sup>b</sup> Frontier Institute for Biomolecular Engineering Research (FIBER), Konan University, 7-1-20 Minatojima-minamimachi, Chuo-ku, Kobe 650-0047, Japan

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## ABSTRACT

Density functional theory for molecular fluids developed by Donley et al. (J. Chem. Phys. 101 (1994) 3205) is extended to include the effects of orientation-dependent bridge functions associated with the interparticle, triplet correlations. Resultant integral equations for the pair and direct correlation functions are solved for water, where the three-body direct correlation functions are approximated in terms of two-body functions. A test calculation employing a simple Gaussian form for the two-body function between the oxygen sites then provides a promising result to improve the description of the oxygen–oxygen correlations in liquid water at room temperature.

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## 1. Introduction

Theoretical elucidation of structural and thermodynamic properties of water has attracted much attention, since water is one of the most important and fascinating compounds in nature. In addition to microscopic computer simulations based on the Monte Carlo [1] and the molecular dynamics (MD) [2] methods employing reliable force fields between water molecules, there have been a number of analytical attempts to develop molecular theories for the structure of bulk water. In this context, the reference interaction site model (RISM) [3–5] has provided a useful theoretical framework to describe the correlational and thermodynamic properties of molecular fluids including water. Combined with standard closure relations such as the hypernetted-chain (HNC) approximation [3,6] developed for simple liquids, the RISM theory was implemented [7] for the MSPC model of water, where the SPC model [8] was modified to include a repulsive potential between the oxygen (O) and hydrogen (H) sites to avoid the divergence in solution to the integral equations. Later, a diagrammatically proper theory proposed by Chandler et al. [9] was also applied [10] to the MSPC model of water, thus leading to moderately successful descriptions [11] of structural and thermodynamic properties of water fluids as well as the original RISM approach did [7]. Further, as an alternative approach, the molecular Ornstein–Zernike (MOZ) theory where the two molecule correlation functions are expanded in terms of spherical harmonics and the resulting coefficient equations are solved along with the HNC and reference HNC closures [12,13] was also applied to water fluids. Employing the SPC/E mod-

el of water [14] in which the O–H repulsion is not needed, the numerical calculations [12,13] on the basis of the MOZ theory appropriately reproduced the computer simulation results for the correlational and thermodynamic properties of water fluids at high temperatures, while they did not give satisfactory results at room temperature concerning the description of ice-like tetrahedral structures.

Another theoretical formalism for describing the structure of molecular fluids is based on the density functional theory (DFT) for classical-mechanical systems [3,6,15,16]. In the framework of DFT one begins with an expression for (grand) free energy as a functional of density profile in an external field. A minimization of this functional with respect to the density profile gives the density distribution of system at equilibrium. If the external field is due to an inserted molecule at the origin, then the density profile of the fluid in the field is related to the pair distribution functions in a uniform fluid [17]. By extending the DFT for molecular fluids developed by Chandler et al. [15,16], Donley, Curro and McCoy (DCM) [18] derived a set of integral equations for obtaining the two-point intermolecular correlation functions, where the radial distribution functions were expressed as two-molecule averages over a Boltzmann factor involving bare site–site interactions and pairwise additive, medium-induced potentials which mimicked the remaining molecules in the system. DCM then demonstrated that their DFT method gave a good agreement with a simulation of homonuclear diatomic molecules. Later, Reddy et al. [11] and Sumi et al. [19] applied the DCM theory to the SPC and SPC/E models of water, respectively, thus finding the superiority of the DCM theory over other theories above in the descriptions of intermolecular correlations in high-temperature water fluids. However, as in the MOZ theory, the results for the oxygen–oxygen correlations

\* Corresponding author. Fax: +81 78 803 6621.

E-mail address: [tanaka2@kobe-u.ac.jp](mailto:tanaka2@kobe-u.ac.jp) (S. Tanaka).

were found to be poor at room temperature, which may be attributed to the importance of three-body correlations missing in the DCM theory [11,19].

In order to improve the DFT-based DCM theory for the description of correlational properties of liquid water, we here reformulate the DCM theory so that the triplet density correlations neglected in the HNC-like, second-order truncation of free energy functional [18] are taken into account through higher-order density expansions. A factorization ansatz [20,21] for the triplet direct correlation functions is then employed to derive improved, DFT-based integral equations for the pair correlation functions, in which the contributions of the bridge functions [3,6,20,21] beyond the HNC approximation are appropriately incorporated. In the following section we illustrate a formulation of the present theory for expressing anisotropic bridge functions that depend on molecular orientations in terms of two-body functions. A preliminary, test calculation in which a dominant, O–O pair correlation is considered for the bridge functions is then attempted in Section 3 to investigate a possibility of improvement over the HNC scheme in the O–O radial distribution function at room temperature. Summary is given in Section 4.

## 2. Theory

Let us consider a fluid system consisting of one-component rigid molecules whose average density and temperature are  $\rho$  and  $T$ , respectively. We rely on the classical DFT [3,6,15,16,18] for the description of many-body correlations, and insert an additional molecule of the same type into the system [17] whose configuration is represented by  $\{\mathbf{R}\} = \{\mathbf{R}_\gamma\}$ , where  $\mathbf{R}_\gamma$  refers to the coordinate of the  $\gamma$ th site ( $\gamma = 1, 2, \dots, s$ ) of the inserted molecule. The field at the  $\eta$ th site,  $\mathbf{r}_\eta$  ( $\eta = 1, 2, \dots, s$ ), of a system molecule is then expressed as

$$\begin{aligned} \psi_\eta(\mathbf{r}_\eta) &= -U_\eta(\mathbf{r}_\eta) + \psi_{L\eta} \\ &= -\beta \sum_{\gamma=1}^s v_{\eta\gamma}(\mathbf{r}_\eta - \mathbf{R}_\gamma) + \psi_{L\eta} \end{aligned} \quad (1)$$

in terms of the external field  $U_\eta(\mathbf{r}_\eta)$  composed of site–site interaction potentials  $v_{\eta\gamma}(\mathbf{r})$  and the site chemical potential  $\psi_{L\eta}$  in the unperturbed state, where  $\beta = 1/k_B T$  with  $k_B$  being the Boltzmann constant and the subscript ‘L’ symbolically represents the homogeneous, liquid state.

According to a recipe of the DFT, we suppose a virtual, noninteracting molecular system represented by a subscript ‘0’ whose density distribution  $\rho_\eta(\mathbf{r})$  of the system molecules is identical to that of the actual, interacting system in the presence of external field. The radial distribution function of the actual system can then be given by [18]

$$g_{\alpha\beta}(\mathbf{r}_\alpha - \mathbf{R}_\beta) = \left\langle \left\langle \exp \left\{ \sum_\eta \left[ \psi_{0\eta}(\mathbf{r}_\eta) - \psi_{0L\eta} \right] \right\} \right\rangle \right\rangle_{\mathbf{r}_\alpha, \mathbf{R}_\beta}^P \quad (2)$$

in terms of the field  $\psi_{0\eta}(\mathbf{r}_\eta)$  of the noninteracting system, where  $\langle \langle \rangle \rangle_{\mathbf{r}_\alpha, \mathbf{R}_\beta}^P$  represents the orientational average of the system and external (inserted) molecules with the  $\alpha$ th site of the system molecule and the  $\beta$ th site of the external molecule held fixed at  $\mathbf{r}_\alpha$  and  $\mathbf{R}_\beta$ , respectively. The site–site pair correlation function is accordingly given by  $h_{\alpha\beta}(\mathbf{r}) = g_{\alpha\beta}(\mathbf{r}) - 1$ .

In order to calculate the right-hand side of Eq. (2), we consider the dimensionless (measured in units of  $k_B T$ ) Helmholtz potential  $A$  of the system and the corresponding, noninteracting one  $A_0$ . When we introduce the grand potential through the Legendre transformation as

$$W = A - \sum_\alpha \int d\mathbf{r} \psi_\alpha(\mathbf{r}) \rho_\alpha(\mathbf{r}), \quad (3)$$

the variational principle to determine the equilibrium density is expressed as

$$\frac{\delta W}{\delta \rho_\alpha(\mathbf{r})} = 0. \quad (4)$$

The functional derivative of  $A$  by the site density  $\rho_\alpha(\mathbf{r})$  gives the field at the site  $\alpha$ :

$$\frac{\delta A}{\delta \rho_\alpha(\mathbf{r})} = \psi_\alpha(\mathbf{r}). \quad (5)$$

We then expand the Helmholtz potential with respect to the density deviation  $\Delta\rho_\alpha(\mathbf{r}) = \rho_\alpha(\mathbf{r}) - \rho$  around the unperturbed, homogeneous state ( $L$ ). In order to take into account the intermolecular correlation effects beyond the HNC approximation, we retain the expansion up to the third-order as

$$\begin{aligned} A[\rho] &= A_L + \sum_\alpha \int d\mathbf{r} \frac{\delta A}{\delta \rho_\alpha(\mathbf{r})} \Big|_L \Delta\rho_\alpha(\mathbf{r}) \\ &+ \frac{1}{2!} \sum_{\alpha, \beta} \int d\mathbf{r} \int d\mathbf{r}' \frac{\delta^2 A}{\delta \rho_\alpha(\mathbf{r}) \delta \rho_\beta(\mathbf{r}')} \Big|_L \Delta\rho_\alpha(\mathbf{r}) \Delta\rho_\beta(\mathbf{r}') \\ &+ \frac{1}{3!} \sum_{\alpha, \beta, \gamma} \int d\mathbf{r} \int d\mathbf{r}' \int d\mathbf{r}'' \frac{\delta^3 A}{\delta \rho_\alpha(\mathbf{r}) \delta \rho_\beta(\mathbf{r}') \delta \rho_\gamma(\mathbf{r}'')} \Big|_L \Delta\rho_\alpha(\mathbf{r}) \Delta\rho_\beta(\mathbf{r}') \Delta\rho_\gamma(\mathbf{r}'') \\ &+ \Delta^{(4)}, \end{aligned} \quad (6)$$

where  $A_L$  and  $\Delta^{(4)}$  represent the Helmholtz potential in the liquid state and the contribution of higher-order terms beyond the third order of  $\Delta\rho$ , respectively.

The functional derivative of Eq. (6) with respect to the site density thus provides

$$\begin{aligned} U_\alpha(\mathbf{r}) + \sum_\beta \int d\mathbf{r}' \frac{\delta^2 A}{\delta \rho_\alpha(\mathbf{r}) \delta \rho_\beta(\mathbf{r}')} \Big|_L \Delta\rho_\beta(\mathbf{r}') \\ + \frac{1}{2!} \sum_{\beta, \gamma} \int d\mathbf{r}' \int d\mathbf{r}'' \frac{\delta^3 A}{\delta \rho_\alpha(\mathbf{r}) \delta \rho_\beta(\mathbf{r}') \delta \rho_\gamma(\mathbf{r}'')} \Big|_L \Delta\rho_\beta(\mathbf{r}') \Delta\rho_\gamma(\mathbf{r}'') \\ + \frac{\delta \Delta^{(4)}}{\delta \rho_\alpha(\mathbf{r})} = 0 \end{aligned} \quad (7)$$

with the aid of Eqs. (1) and (5). These relations stand in the case of noninteracting (0) system as well. Here we employ an approximate truncation as

$$\Delta^{(4)} - \Delta_0^{(4)} \simeq 0, \quad (8)$$

that is our primary approximation in the present work. We thus find an approximate equation from Eq. (7),

$$\begin{aligned} \psi_{0\alpha}(\mathbf{r}) - \psi_{0L\alpha} \simeq -U_\alpha(\mathbf{r}) + \sum_\beta \int d\mathbf{r}' c_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \Delta\rho_\beta(\mathbf{r}') \\ + \frac{1}{2} \sum_{\beta, \gamma} \int d\mathbf{r}' \int d\mathbf{r}'' c_{\alpha\beta\gamma}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') \Delta\rho_\beta(\mathbf{r}') \Delta\rho_\gamma(\mathbf{r}''), \end{aligned} \quad (9)$$

where the two-body and three-body direct correlation functions,  $c_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$  and  $c_{\alpha\beta\gamma}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}'')$ , have been introduced as [3,6,20,21]

$$\frac{\delta^2 (A - A_0)}{\delta \rho_\alpha(\mathbf{r}) \delta \rho_\beta(\mathbf{r}')} \Big|_L = -c_{\alpha\beta}(\mathbf{r}, \mathbf{r}'), \quad (10)$$

$$\frac{\delta^3 (A - A_0)}{\delta \rho_\alpha(\mathbf{r}) \delta \rho_\beta(\mathbf{r}') \delta \rho_\gamma(\mathbf{r}'')} \Big|_L = -c_{\alpha\beta\gamma}^{(3)}(\mathbf{r}, \mathbf{r}', \mathbf{r}''). \quad (11)$$

Combining Eq. (9) with Eq. (2), we can thus evaluate the radial distribution functions of the system as

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