An analytical expression for the direct correlation function of a hard-sphere liquid derived from the extended scaled particle theory

Takuya Fukudome, Daiki Mitarai, Masayuki Irisa *

Department of Bioscience and Bioinformatics, Kyushu Institute of Technology, Iizuka 820-8502, Japan

ARTICLE INFO

ABSTRACT

Integral equation methods based on the Ornstein–Zernike equation have been widely used for calculations of the radial distribution functions, $g(r)$, of simple liquids. The closure that connects a direct correlation function, $c(r)$, with a total correlation function, $h(r)$, is necessary for solving the integral equation. In this work, we propose an analytical expression of the direct correlation function for a hard-sphere liquid through the solvation free energy for a pair of hard-spheres as a solute derived from the extended version of scaled particle theory (XSPT) instead of using iterative calculations with some closure. The solvation free energy has an analytical expression given by the XSPT that treats solvation of an arbitrary shaped particle into a hard-sphere liquid. In the case of a hard-sphere liquid, our new expression for the direct correlation function gives an analytical expression of the radial distribution function in Fourier Transform k-space. In addition, the radial distribution function in real-space quantitatively agrees with the Monte Carlo simulation results better than the Percus–Yevick equation method under equivalent numerical conditions. Our method with the proposed direct correlation function in this work is expected to be applied to estimation of the contributions from hydrophobic hydration in the hydration free energy of two associated molecules, which is a key to understanding the mechanism for association of proteins.

1. Introduction

Hard-sphere liquid is a widely used model system that is applied to neat liquids composed of spherical small and large molecules such as proteins in aqueous solutions [1–4]. The association of molecules is a key element for investigating reaction constants of molecules in liquids. For example, the first step of protein filament formation as a series of reactions involves the association of two molecules. A subject of intensive study is the calculation of radial distribution functions of hard-sphere liquids [1]. The contact value, which is the location of the first peak of the radial distribution function of a hard-sphere liquid, is directly related to the pressure or osmotic pressure of the system, depending on the adopted model. Analytical expressions of the equation of the state of a hard-sphere liquid have been obtained using the scaled particle theory (SPT) [5] and the integral equation method based on the Ornstein–Zernike (OZ) equation using the Percus–Yevick (PY) closure independently [6]. Analytical expressions of radial distribution functions and direct correlation functions for hard-sphere liquids have also been obtained using the integral equation method with the PY closure [7]. On the other hand, SPT only gives an analytical expression for the contact value of the system. The integral equation methods based on the OZ equation have been widely used for calculations of the radial distribution

functions, $g(r)$, of simple liquids. The closure that connects a direct correlation function, $c(r)$, with a total correlation function, $h(r)$, is necessary for solving the OZ integral equation. In addition to the PY closure, other closures, including the famous hyper-netted-chain (HNC) closure are used in numerical calculations involving the OZ equation. However, in most cases, the physical meaning of a closure is ambiguous even if radial distribution functions are quantitatively reproduced. The PY closure can be explained as a truncated approximation of the exponential function appearing in the HNC closure, but the results of the OZ equation method for a hard-sphere liquid using the PY closure are better than those using the HNC closure in comparison with Monte Carlo simulation results. The HNC closure is an approximation of the exact expression of the solvation free energy of a pair of hard-spheres which is composed of the direct correlation function ($c(r)$), the total correlation function ($g(r)-1$), and the bridge function ($b(r)$). The HNC closure neglects the function $b(r)$. The estimation of $b(r)$ is difficult even when using the mathematical technique of diagrammatic representation as a power series of number density. Numerical calculation of the OZ equation requires iterative calculation to solve the integral equation. These situations require an analytical expression of the direct correlation function that has concrete physical meaning. In this work, we propose an analytical expression of the direct correlation function for a hard-sphere liquid based on the solvation free energy derived from the extended version of scaled particle theory (XSPT) [8,9] instead of using some closure and iterative calculations. The morphometric approach [10], which also uses geometric

* Corresponding author.
  E-mail address: irisa@bio.kyutech.ac.jp (M. Irisa).

measures like the XSPT, gives quantitative results for solvation free energies of hard-sphere liquids. However, the physical meaning of the parameters used in this approach has not yet been clarified yet because of its use of semi-empirical parameters such as weights for geometric measures, which are treated as constants. If the scale of a solute size is macroscopic, the weights for geometric measures correspond to the generalized surface tensions composed of four types tensions acting through zero, one, two and three dimensional geometric measures, respectively in thermodynamics. On the other hand, if the scale of a solute size is microscopic, the original version of the scaled particle theory (SPT) [5] gives the analytical expression for these weights of a hard-sphere liquid in statistical mechanics. Correspondences between the morphometric approach and the XSPT are described in Section 2.3. The analytical expression of the direct correlation function proposed here will aid in understanding the semi-empirical estimation of solvation free energy with the morphometric approach.

2. Methods

2.1. The OZ integral equation for pair distribution functions

The two equations which are shown below, a closure equation and the OZ equation, are used to derive two unknown distribution functions, $h(r)$: the radial distribution function minus one, $g(r) - 1$, and $c(r)$: the direct correlation function. An exact closure equation in statistical mechanics is of the following form

$$y(r) = \exp(h(r) - c(r) + b(r)), \tag{1}$$

where $b(r)$ is the bridge function, for which estimation remains elusive even now, and $y(r)$ is the cavity function. The cavity function $y(r)$ satisfies the following equation

$$g(r) = \exp(-\beta u(r)) y(r), \tag{2}$$

where $u(r)$ is the pair interaction potential, which, for a hard core potential, has values of either zero or infinity. Thus, this equation is usually approximated to avoid the precise estimation of the bridge function in existing closures (e.g., the HNC and PY closures). Eq. (1) has a physical meaning related to the relative value of the solvation free energy of paired particles, $w(r)$, with a distance of r. The value of $w(r)$ is regularized by setting $w(\infty)$ equal to zero. The function $w(r)$ is expressed as

$$\beta w(r) = -h(r) + c(r) - b(r). \tag{3}$$

The OZ equation, which connects the radial distribution function with the direct correlation function, is expressed as

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13}) h(r_{32}) d\vec{r}_3, \tag{4}$$

where $h(r)$ is identical to the radial distribution function, $g(r)$, minus one. After applying three-dimensional Fourier transform, which is denoted by ˆ in this work, to the OZ equation using the uniformity of the hard-sphere fluid, the equation is expressed as follows in the Fourier transform k-space:

$$\hat{h}(k) = \hat{c}(k) + \rho \hat{c}(k) \hat{h}(k), \tag{5}$$

where k is scalar because of the uniformity,

$$\hat{h}(k) = \frac{\hat{c}(k)}{1 - \rho \hat{(k)}}, \tag{6}$$

$$\hat{t}(k) = \frac{\rho \hat{c}(k)^2}{1 - \rho \hat{c}(k)}, t(r) = h(r) - c(r). \tag{7}$$

The reason Eq. (7) is used as the target function of three-dimensional Fourier transform for solving the OZ equation is because the profile of $(h(r) + 1)$ demonstrates a steep incline from zero to the contact value at r, which is equal to the hard-sphere diameter. In this work, numerical calculations for solving the OZ equation mostly use Eq. (7). The HNC closure approximates Eq. (1) as

$$h(r) - c(r) = \ln \ y(r), \tag{8}$$

thus the values of $g(r)$ are directly derived from $h(r) - c(r)$ in the HNC closure method. The notation "type-2" of the calculated results in this work denotes that the $g(r)$ values are calculated through $y(r)$ using Eq. (8) at only the final estimation of the $g(r)$ values. On the other hand, the notation "type-1" indicates that the values of $h(r)$ or $g(r)$ are calculated without using Eq. (8).

2.2. An analytical expression for the direct correlation function, c(r)

A new method, which is called the XSPTH, adopts the analytical expression of the direct correlation function proposed by us

$$c(r) = \begin{cases} \beta w(r) - 1 & (r < \sigma) \\ \beta w(r) + \exp(-\beta w(r)) - 1 & (\sigma < r < r') \\ 0 & (r > r') \end{cases} \tag{9}$$

where σ is the diameter of a hard-sphere and r' is the smallest value of radial coordinate that satisfies the condition $\beta w(r)$ equal to zero. The expression of $w(r)$ is derived from the analytical expression of a solute for the solvation free energy $W(r)$ in the XSPT. The value of $W(r)$ of a pair of hard-spheres is considered as the solvation free energy of one solute particle having a dumbbell-shaped excluded region. Even when a pair of hard-spheres is disconnected ($r > \sigma$), the excluded region is still connected if r is smaller than twice the diameter, as shown in Fig. 1.

The relative value of solvation free energy of pair particles, $w(r)$, and the cavity function $y(r)$ is expressed as

$$w(r) = -k_B T \ln y(r) = W(r) - W(\infty), \tag{10}$$
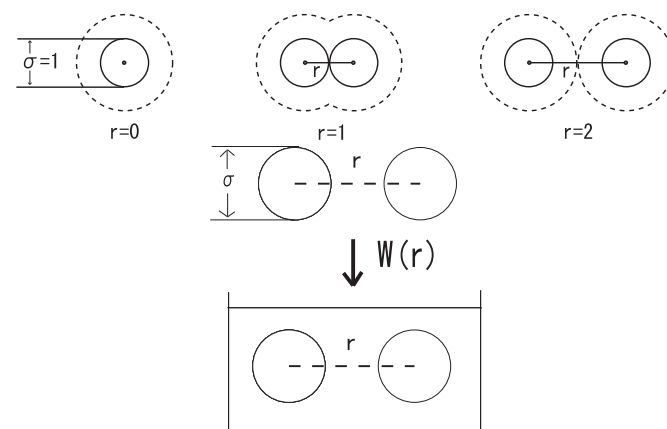
$$W(\infty) = 2W(0). \tag{11}$$

Fig. 1. Schematic illustration of the solvation free energy of a pair of hard-spheres, W(r). The dashed curves represent envelopes of the excluded regions.