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Exact site–site bridge functions for dielectric consistent reference interaction site model: A test for ambient water

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ABSTRACT

We develop a method to extract site–site bridge functions from simulations of molecular liquids with the use of dielectric consistent reference interaction site model (DRISM). We reduce the problem to evaluations of short-range parts of direct correlation functions, providing consistent corrections to the DRISM integral equations. We reconstruct site–site bridge functions with the use of the corrected DRISM equations and Fourier transforms of simulated radial distribution functions. The performance of the algorithm has been tested for the SPC/E water model. The obtained bridge functions are quite close to those obtained with the use of the RISM approach. We evaluate structural properties of ambient water within the DRISM framework, using the bridge functions. All the calculated structural properties are in a good agreement with available experimental data.

1. Introduction

Hydration of ions has been in focus of many theoretical and experimental studies during the last century due to its importance in various chemical and biological processes. Integral equations theory (IET) offers a fast way to compute the solvent structure around a solute immersed in a liquid. The theory has been intensively applied for various physicochemical systems during the last decades (see, for example, [1–12]). The main area of the applications is simple liquids (see, for example, [12]), whereas the IET treatment of molecular liquids remains to be a challenge and is much more complicated, because it requires evaluations of six-dimensional integrals. The interaction site model (ISM) is an alternative to the full molecular IET, since it treats the liquid structure only in terms of distance-dependent site–site correlation functions, and therefore avoids the expensive computation of high-dimensional integrals. There is a plethora of methods based on the ISM formalism such as the reference interaction site model (RISM) [13], extended RISM [14,15], proper ISM [16], and dielectric consistent RISM [17]. The RISM approach has been applied extensively to investigate various features of solvation processes (see, for example, [18–26]). At the same time, the original [13] as well as extended [14,15] RISM approaches lead to inconsistencies when finite concentrations of ions were considered, due to an underestimate of the dielectric constant of the bulk solvent. This deficiency has motivated the development of dielectric consistent RISM (DRISM) [17]. The latter theory has been successfully applied to a number of bulk systems, for instance, saline solutions [17,27–29], water–alcohol [30,31] and water–acetone [32] mixtures, protein [33–37] and DNA [38,39] solvation in aqueous solutions. Various properties have been investigated with the use of the DRISM such as solubility of noble gases [40], frequency-dependent conductivity [41], partial molar volumes [42] and Kirkwood–Buff integrals [43] of ions.

The DRISM and RISM can provide semi-quantitative estimates for certain cases, however an accurate treatment of molecular liquids by the methods requires data on the so-called bridge functions whose exact expressions are not known. In spite of numerous attempts to apply empirical bridge functions, a progress has been recorded only for certain classes of the molecular solvents and solutes [44–49]. For simple liquids there is a possibility to extract bridge functions from simulations [50–53]. However, the extraction of site–site bridge functions is an ill-posed problem within the ISM framework; it could have multiple solutions and be strongly affected by the quality of data obtained from simulations [54].

Recently, we have developed a method to obtain site–site bridge functions from simulations [55]. The method is based on the inverse solution of the RISM. Using the exact long-range asymptotics of site–site direct correlation functions, we regularize the ill-posed inverse problem, and then calculate site–site bridge functions and effective pair potentials for ambient water, methanol, and ethanol [54]. Our study has revealed various peculiarities of the site–site bridge functions, such as long-range behavior and strong dependence on the electrostatic

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interactions. We should mentioned that the obtained long-range behavior of the bridge functions is a consequence of the long-range asymptotics of the RISM direct correlation functions which are different from site–site Coulomb interaction potential. In contrast to it, the DRISM approach prescribes the asymptotics to be equal site–site Coulomb potential. Whether and to which extent the prescribed asymptotics alter the short-range part of the bridge functions is not clear up to now. To provide an insight into the behavior of the bridge functions, it would therefore be helpful to obtain the site–site bridge functions from simulations using the DRISM approach. Therefore, the goal of our paper is to extend our approach [55,54] and obtain exact site–site functions from simulations with the use of the DRISM. We will evaluate the site–site bridge functions for the ambient water. We consider a special class of rigid water models, i.e. two nonequivalent interaction sites (TNIS) model and test the bridge functions for the SPC/E [56] model. Our choice is motivated by the fact that among the rigid water models this model is best fitted experimental structural data [57–59].

We note that the accuracy of calculations of site–site bridge functions depends strongly on the quality of evaluations of Fourier transformed RDFs at low wave vectors. To provide reasonable estimates in our previous studies [55,54] we have approximated the Fourier transformed radial distribution functions (RDFs) by low-order polynomials. Although such methodology provides a success for certain molecular liquids [54], unfortunately it does not guarantee accurate estimates for more complicated cases. Moreover, the method yields an unphysical solution to long-range parts of site–site DCFs for solvents consisting of molecules including more than 4 nonequivalent sites. In the current version, we will modify the algorithm of the bridge extraction. For this purpose we will renormalize site–site DCFs and derive the integral equations which involve only short-range parts of the DCFs. In the case of TNIS model, it allows us to avoid the polynomial approximation and to reduce the problem to accurate evaluations of static dielectric response function via a well-documented procedure [60–62].

2. Theory

2.1. Inverse problem of DRISM

The site–site bridge functions can be expressed in terms of relevant site–site total correlation (TCF) and direct correlation (DCF) functions as:

$$b_{ij}(r) = ln\left[h_{ij}(r)+1\right] + \beta u_{ij}(r) - h_{ij}(r) + c_{ij}(r), \tag{1}$$

here $u_{ij}(r)$ is the site–site interaction potential, $\beta = 1/k_BT$ is the inverse temperature, while $c_{ij}(r)$ is the site–site DCF and $h_{ij}(r)$ is the site–site TCF related with the corresponding radial distribution function $g_{ij}(r)$ as $h_{ij}(r) = g_{ij}(r) - 1$. We note that $u_{ij}(r)$ and β are the input parameters as usual, while the data on $g_{ij}(r)$ can be easily obtained from molecular simulations. Thus, to evaluate the site–site bridge functions we have to calculate the relevant DCF $c_{ij}(r)$. If the DCFs are found, relation (1) defines the site–site bridge functions at distances for which $ln[g_{ij}(r)]$ can be evaluated, i.e. beyond a site core $r > \sigma_{ij}$ where σ_{ij} is the relevant Lennard–Jones diameter.

At the same time the DCFs and TCFs are related via the DRISM integral equations. They can be written in the matrix form for the corresponding Fourier transforms:

$$\hat{\mathbb{H}}(k) = \rho^{-1}\hat{\zeta}(k) + \left[\hat{\mathbb{W}}(k) + \hat{\zeta}(k)\right]\hat{\mathbb{C}}(k)\left[\hat{\mathbb{W}}(k) + \rho\hat{\mathbb{H}}(k)\right], \tag{2}$$

where ρ is the solvent density, $\hat{\mathbb{W}}(k)$ is the matrix of intramolecular correlation functions, whose elements are $\omega_{ij}(k) = \delta_{ij} + [1 - \delta_{ij}]sin(kd_{ij})/kd_{ij}$, where d_{ij} denotes the intramolecular distances between the sites. In the above relation $\hat{\mathbb{C}}(k)$ is the matrix of Fourier transformed DCFs $\hat{c}_{ij}(k)$, while $\hat{\mathbb{H}}(k)$ is comprised of the Fourier transformed TCFs $\hat{h}_{ij}(k)$. The matrix $\hat{\zeta}(k)$ in Eq. (2) is the input data which are related with dielectric constant, the elements $\hat{\zeta}_{ij}(k)$ are defined as [17]

$$\hat{\zeta}_{ij}(k) = j_0(kx_i)j_0(ky_i)j_1(kz_i)j_0\left(kx_j\right)j_0\left(ky_j\right)j_1\left(kz_j\right)h_c(k), \tag{3}$$

where $j_0(a)$ and $j_1(a)$ are the zero- and first-order spherical Bessel functions, while $\{x_i, y_i, z_i\}$ and $\{x_j, y_j, z_j\}$ are the relevant coordinates of the i-th and j-th sites, and $h_c(k)$ is a function to provide dielectric consistency, it is given by the following relation for pure solvent:

$$h_c(k) = \left[\frac{\epsilon - 1}{y} - 3\right] exp\left[-\frac{\eta^2 k^2}{4}\right], \tag{4}$$

where ϵ is the static dielectric constant, $y = 4\pi\beta\rho m^2/9$, and m is the absolute value of the dipole moment of solvent molecule, and η is a damped parameter.

Formally, the DCFs involved in Eq. (2) can be calculated by an 'inverse solution' of the DRISM equations, which can be written in the matrix form as

$$\rho\hat{\mathbb{C}}(k) = \left[\hat{\mathbb{W}}(k) + \hat{\zeta}(k)\right]^{-1} - \left[\hat{\mathbb{W}}(k) + \rho\hat{\mathbb{H}}(k)\right]^{-1}. \tag{5}$$

Thus, we have to solve Eq. (5), then using the inverse Fourier transform of $\hat{\mathbb{C}}(k)$ we can evaluate bridge functions by Eq. (2). However, the direct inversion of matrices $\hat{\mathbb{W}}(k) + \rho\hat{\mathbb{H}}(k)$ and $\hat{\mathbb{W}}(k) + \hat{\zeta}(k)$ are problematic, because they are almost singular at low wave vectors, i.e. their determinants tend to zero. The inverse DRISM problem is ill-posed. The obtained solutions diverge, i.e. $\hat{\mathbb{C}}(k) \propto k^{-2n}$, moreover it can be easily checked that index n exceeds unity in the general case, whereas the elements of the DCF matrix are not proportional to site charges. Special methods are required to evaluate accurately the divergent part of $\hat{\mathbb{C}}(k)$. We have developed such methods within the framework of RISM [55,54]. They are based on the regularization of the inverse problem by imposing additional constraints. The methods can be extended to the DRISM, however their modifications are required to be applicable to arbitrary solvent models. Leaving aside consideration for the general case of arbitrary molecules, in this article we apply the methods to the special class of solvents, namely, to the TNIS model. As we will indicate below (see Appendix), the regularization of the inverse problem is simplified in this case, because the long-ranged DCFs coincide with the Coulomb asymptotics within the DRISM framework.

2.2. Regularization of the inverse problem

For the TNIS model the long-range asymptotics of $c_{ij}(r \to \infty)$ is equal to $-\beta e^2 q_i q_j / r$ (see Appendix A), where q_i is the relevant site charge (in electron units), and e is the electron charge. That means the site–site bridge functions to be short-ranged within the DRISM treatment. To evaluate the bridge functions, we split the site–site interaction potential into the long- and short-range parts:

$$u_{ij}(r) = u^s_{ij}(r) + u^l_{ij}(r) = u^s_{ij}(r) + \frac{e^2 q_i q_j}{r} erfc\left(\frac{r}{\tau}\right), \tag{6}$$

where τ is a charge smearing parameter. Then, we can rewrite relation for the bridge functions in terms of short-ranged DCFs $c^s_{ij}(r) = c_{ij}(r) + \beta u^l_{ij}(r)$ as:

$$b_{ij}(r) = ln\left[h_{ij}(r)+1\right] + \beta u^s_{ij}(r) - h_{ij}(r) + c^s_{ij}(r). \tag{7}$$

Then, using the recursive relations between the DCFs and TCFs [63], we can regularize matrices (see details in Appendix A) and express the short-range DCFs via these matrices as:

$$\rho\hat{\mathbb{C}}^s(k) = \left[\hat{\mathbb{W}}(k) + \hat{\zeta}(k) + \Delta_s(k)\right]^{-1} - \left[\hat{\mathbb{W}}(k) + \rho\hat{\mathbb{H}}(k) + \Delta_t(k)\right]^{-1}, \tag{8}$$

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