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Research paper

# Performance of Kobryn-Gusarov-Kovalenko closure from a thermodynamic viewpoint for one-component Lennard-Jones fluids

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ABSTRACT

The performance of Kobryn-Gusarov-Kovalenko (KGK) closure was examined in terms of the thermodynamics for one-component Lennard-Jones fluids. The result was compared to molecular dynamics simulation as well as to hypernetted chain, Kovalenko-Hirata (KH), Percus-Yevick and Verlet-modified closures. As the density increases, the error of KGK closure shows a turnover, regarding the excess internal energy, pressure and isothermal compressibility. On the other hand, it was numerically confirmed that the energy and the virial equations are consistent under both KH and KGK closures. The accuracies of density-derivative and temperature-derivative of the radial distribution function are also discussed.



## 1. Introduction

A family of Ornstein-Zernike (OZ) theory has been developed to describe the structure and thermodynamics of liquids composed not only of monatomic molecules [1] but also of complex polyatomic molecules [2]. One of the typical examples is the reference interaction site model (RISM) theory [2]. The extension of the RISM theory to its three-dimensional version, i.e. 3D-RISM theory [2,3], has enabled us to study solvation around a protein molecule [4–8].

On the other hand, a certain necessity concerning the numerical convergence of the theory had arisen through the experience of its application to a complicated system. After the appearance of 3D-RISM theory, the modified method of direct inversion in iterative subspace (MDIIS) was proposed [9], by which the technique for the numerical convergence of the theory was made powerful. In the early studies using 3D-RISM theory [3,4], it was combined with hypernetted chain (HNC) closure, which is referred to, hereafter, as 3D-RISM/HNC. Even if we use the MDIIS method, it is generally impossible to obtain a numerically converged solution of 3D-RISM/HNC theory for the issue of hydration around a protein, which was pointed out, for example, in Ref. [10]. Instead of HNC, Kovalenko-Hirata (KH) closure has begun to be used when complementing the 3D-RISM equation (i.e. 3D-RISM/KH) [5–7]. 3D-RISM/KH theory does not suffer from a failure of numerical convergence when we apply the theory to the hydration around a complicated solute molecule: at least, one of the authors (T. M.) has never experienced such a failure when applying, for example, the combination method between molecular dynamics (MD) simulation and 3D-RISM/KH theory to the hydration-related problem [11–13]. In fact, KH closure possesses such a feature that it is numerically much more stable than HNC closure. The superior feature of KH closure in terms of the numerical stability must have played an important role in many applications of 3D-RISM theory.

Recently, an ambitious attempt has been reported by Kobryn et al. [14], in which the RISM theory was applied to very complicated solvent systems such as oligomeric polyelectrolytes at a finite concentration in electrolyte solution. Even KH closure often fails to provide a numerically converged solution for such a system. To resolve this problem, Kobryn-Gusarov-Kovalenko (KGK) closure was proposed in Ref. [14]. It was pointed out in Ref. [14] that KGK closure is numerically more stable than KH closure. On the other hand, the performance of KGK closure in terms of its accuracy has not been fully studied yet. Aside the article by Kobryn et al. [14], only one paper has been reported concerning this issue [15], focusing only on the solvation free energy. When we discuss the applicability of KGK closure to a certain model system, the knowledge of its performance is indispensable. It is to be noted that the RISM theory involves another approximation in addition to the closure: i.e., the molecular direct correlation function is assumed to be described by the summation of site-site direct correlation functions [2]. Therefore, it is desirable to study the behavior of KGK closure for fluids composed of monatomic molecules, if we intend to reveal the *unpolluted* property of KGK closure. Regarding the above circumstances, we mainly examine the performance

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of KGK closure in terms of the thermodynamics for one-component Lennard-Jones (LJ) fluids here.

This article studies the accuracies of the excess internal energy, virial pressure and isothermal compressibility obtained from KGK closure. The isothermal compressibility is evaluated via two routes: one is from the compressibility equation, and the other from the differentiation of the virial equation with respect to the fluid density. The accuracy of KGK closure is discussed through the comparison with the MD simulation. It is also compared to the results obtained from HNC, KH, Percus-Yevick (PY) and Verlet modified (VM) closures. Furthermore, we investigate in this article whether the KGK approximation is thermodynamically consistent or not between the energy equation and the virial equation. While it is known that HNC closure possesses this type of thermodynamic consistency irrespective of the potential [16], Santos rigorously proved that the mean spherical approximation (MSA) closure also exhibits this consistency for soft potentials [17]. Since KGK closure adopts the MSA almost everywhere except only for the repulsive core (see Eq. (4)), it would be interesting to check the energy-virial consistency for KGK approximation. The MSA is partially used also in the KH closure: hence, KH may be interpreted as a hybridized closure between HNC and MSA (see Eq. (6)). Therefore, this article examines also the KH closure in terms of the energy-virial thermodynamic consistency. Such a consistency is checked numerically in this article, using both the temperature-derivative [18,19] and the density-derivative of the radial distribution function (RDF).

## 2. Theory and computational methods

Throughout this study, we focus only on a one-component LJ fluid, the potential of which is written as

$$\varphi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{1}$$

### 2.1. Ornstein-Zernike theory

This section describes an outline of OZ theory briefly. The OZ equation reads [1,2]

$$h(r) = c(r) + \rho\, c * h(r), \tag{2}$$

where $h(r)$, $c(r)$, and $\rho$ represent the total correlation function, the direct correlation function, and the fluid density, respectively. The asterisk * stands for the convolution integral. We consider the following five closure equations to complement OZ theory, where $\beta$ is $(k_B T)^{-1}$ ($k_B$ and $T$ denote the Boltzmann constant and temperature, respectively). Let us define $d(r)$ as

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

The closure equations we consider are as follows.

(I) KGK closure [14]:

$$1 + h(r) = \begin{cases} 0 & \text{for } d(r) \leqslant -1 \\ 1 + d(r) & \text{for } d(r) > -1 \end{cases}. \tag{4}$$

(II) HNC closure [1,2]:

$$1 + h(r) = exp[d(r)]. \tag{5}$$

(III) KH closure [2,20]:

$$1 + h(r) = \begin{cases} exp[d(r)] & \text{for } d(r) \leqslant 0 \\ 1 + d(r) & \text{for } d(r) > 0 \end{cases}. \tag{6}$$

(IV) PY closure [1]:

$$1 + h(r) = exp[-\beta\varphi(r)]\,\{1 + h(r) - c(r)\}. \tag{7}$$

(V) VM closure [21]:

$$1 + h(r) = exp[d(r) + b(r)], \tag{8}$$

where

$$b(r) = \begin{cases} -\frac{s(r)^2}{2\,\{1+\alpha_{VM}\,s(r)\}} & \text{for } s(r) \geqslant 0 \\ -\frac{1}{2}s(r)^2 & \text{for } s(r) < 0\,. \end{cases} \tag{9}$$

In Eq. (9), s(r) is defined by

$$s(r) = h(r) - c(r) - \beta\varphi_2(r), \tag{10}$$

where

$$\varphi_2(r) = -4\varepsilon\left(\frac{\sigma}{r}\right)^6 exp\left[-\frac{1}{\rho\sigma^3}\left(\frac{\sigma}{r}\right)^{6\rho\sigma^3}\right], \tag{11}$$

and $\alpha_{VM}$ is given by

$$\alpha_{VM} = 1.0175 - 0.275\rho\sigma^3. \tag{12}$$

The RDF $g(r)$ is related to $h(r)$ as

$$g(r) = h(r) + 1. \tag{13}$$

### 2.2. Equations for density-derivative of RDF

This section describes the equations for the density-derivative of RDF, which are solved numerically. We simply follow the method by Yu et al. [18]. A Fourier transformed form of Eq. (2) differentiated by $\rho$ is expressed as

$$\frac{\partial\, h(k)}{\partial\rho} = \frac{\{\partial\, c(k)/\partial\rho\}\left\{1 + \rho\;\, h(k)\right\} + c(k)\, h(k)}{1 - \rho\;\, c(k)}, \tag{14}$$

where $k$ is the wave number, and the hat denotes the Fourier transform. The density-derivatives of closure equations (Eqs. (4)–(8)) are as follows:

(I) KGK closure

$$\frac{\partial c(r)}{\partial\rho} = \begin{cases} -\frac{\partial h(r)}{\partial\rho} + \frac{\partial c(r)}{\partial\rho} & \text{for } d(r) \leqslant -1 \\ 0 & \text{for } d(r) > -1. \end{cases} \tag{15}$$

(II) HNC closure:

$$\frac{\partial c(r)}{\partial\rho} = h(r)\left[\frac{\partial h(r)}{\partial\rho} - \frac{\partial c(r)}{\partial\rho}\right]. \tag{16}$$

(III) KH closure:

$$\frac{\partial c(r)}{\partial\rho} = \begin{cases} h(r)\left[\frac{\partial h(r)}{\partial\rho} - \frac{\partial c(r)}{\partial\rho}\right] & \text{for } d(r) \leqslant 0 \\ 0 & \text{for } d(r) > 0. \end{cases} \tag{17}$$

(IV) PY closure:

$$\frac{\partial c(r)}{\partial\rho} = (exp[-\beta\varphi(r)] - 1)\left[\frac{\partial h(r)}{\partial\rho} - \frac{\partial c(r)}{\partial\rho}\right]. \tag{18}$$

(V) VM closure:

$$\frac{\partial c(r)}{\partial\rho} = h(r)\left[\frac{\partial h(r)}{\partial\rho} - \frac{\partial c(r)}{\partial\rho}\right] + g(r)\frac{\partial b(r)}{\partial\rho}, \tag{19}$$

where

$$\frac{\partial b(r)}{\partial\rho} = \begin{cases} -\frac{2\partial s(r)/\partial\rho + \alpha_{VM} s(r)\partial s(r)/\partial\rho - s(r)^2\partial\alpha_{VM}/\partial\rho}{2\,\{1+\alpha_{VM}\,s(r)\}^2}s(r) & \text{for } s(r) \geqslant 0 \\ -s(r)\frac{\partial s(r)}{\partial\rho} & \text{for } s(r) < 0\,. \end{cases} \tag{20}$$

$\partial s(r)/\partial\rho$ in Eq. (20) is given by

$$\frac{\partial s(r)}{\partial\rho} = \frac{\partial h(r)}{\partial\rho} - \frac{\partial c(r)}{\partial\rho} - \beta\frac{\partial\varphi_2(r)}{\partial\rho}, \tag{21}$$