Pressure consistency for binary hard-sphere mixtures from an integral equation approach

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ABSTRACT

The site-site Ornstein-Zernike equation combined with the Verlet-modified bridge function has been applied to the binary hard sphere mixtures and pressure consistency has been tested. An equa tion of state has been computed for the case where a packing fraction is $\eta = 0.49$, diameter ratios are $\sigma_2/\sigma_1 = 0.3$ and 0.6, and the mole fractions are $x_1 = 0.125, 0.5, 0.75,$ and 1. An excess chemical potential for each component has been obtained as well. Our findings for thermodynamic properties are in good agreement with available data in literature.

Keywords: *site-site Ornstein-Zernike, hard-sphere, pressure consistency, excess chemical potential*

1. INTRODUCTION

Nowadays, an integral equation (IE) theory which was first introduced by Ornstein and Zernike [1] for a simple one-component system has expanded to more complex systems of soft matter, including atomic/molecular liquids, plasma, polymers and liquid crystals and so on [2] . In IE theory an integral equation, such as the Ornstein-Zernike (OZ) equation which is basically a relation between total correlation function and direct correlation function describing physical systems can be solved self-consistently with an additionally introduced equation. A solution of the IE gives directly the correlation functions which can be used to obtain thermodynamic properties.

In classical statistical physics, a soft matter–liquid and its constituent particles interaction can be described as the model potentials, such as, a hard-sphere and Lennard-Jones potentials [4], [3]. For hard-sphere system, a solution of the IE can be found in a closed-form within a Percus-Yevick bridge approximation [5] and a pressure from both virial and compressibilty routes can be computed via analytical expressions as well. However, the former approach gives a high value of it, and the latter one underestimates it [6], [7]. Based on values obtained from these two routes, the Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) technique [8] can correct the value [7]. Along with this technique, there can be a more direct way to get rid of this ambiguous result in which one would obtain unambiguous value by performing thermodynamically consistent calculation that can be done in terms of the free-parameterized bridge approximations, such as the Verlet-modified [9], [11], [10] or Tsednee-Luchko [12] approximations.

Therefore, in this work our goal is to carry out a pressure consistent calculation using the Verlet-modified (VM) [10] bridge function for a binary hard-sphere mixture for which the site-site Orsntein-Zernike equation is solved [6], [7]. We will then compute a virial equation of state for the system at equilibrium and obtain an excess chemical potential for each component using approximate analytical expression. We note that a pressure consistent calculation for this system had been previously performed with the VM-type bridge function with nine free-parameters [13], which in turn may make a computation a large. However, in our calculation we attempt to employ the VM bridge function with three free-parameters only and use a rather different expression in evaluating the excess chemical potential as well. Note that to our knowledge, so far this type of implementation has not been tested for this system, yet. We will compare our findings for thermodynamic properties with those obtained in Ref. [13] and other available BMCSL [7] and Monte-Carlo (MC) [14] data.

In Section 2 we will discuss about theoretical formulations for the site-site Ornstein-Zernike equation and pressure consistency. In Section 3 we present numerical results and their discussions. In Section 4 the conclusion is given.

U. Vandandoo et al. (eds.), *Proceedings of the International Conference on Applied Sciences and Engineering (ICASE 2023)*,
Atlantis Highlights in Engineering 22,
https://doi.org/10.2991/978-94-6463-330-6_15

2. THEORY

2.1. *The site-site Ornstein-Zernike equation*

A relation between the total and direction correlation functions for a multicomponent atomic fluid can be defined as the site-site Orsntein-Zernike equation (SSOZ), which should be written for a binary system in the matrix form in the momentum-space as:

$$\hat{H}(k) = \hat{C}(k) + \hat{C}(k)R\hat{H}(k). \tag{1}$$

Here $\hat{H}(k)$, $\hat{C}(k)$ and R are the matrices based on the site-site total correlation functions, the direct correlation functions and densities of the components, namely, their forms are

$$\hat{H}(k) = \begin{bmatrix} \hat{h}_{11}(k) & \hat{h}_{12}(k) \\ \hat{h}_{21}(k) & \hat{h}_{22}(k) \end{bmatrix}, \tag{2}$$

$$\hat{C}(k) = \begin{bmatrix} \hat{c}_{11}(k) & \hat{c}_{12}(k) \\ \hat{c}_{21}(k) & \hat{c}_{22}(k) \end{bmatrix}, \quad R = \begin{bmatrix} \rho_1 & 0 \\ 0 & \rho_2 \end{bmatrix}.$$

The total number density of the system is $\rho = \sum_i x_i \rho_i$, where $\sum_i x_i = 1$, $(i = 1, 2)$ is a mole fraction defined as component i. In above expressions a caveat defines the Fourier transform of the function.

In the SSOZ Equation (1), the total and direct correlation functions, $\hat{h}_{ij}$ and $\hat{c}_{ij}$ are both unknown, therefore it cannot be solved directly. In order to solve it, an another equation is required, with which the SSOZ equation can be solved in self consistent way. This additional equation is called a *closure equation*, which is usually given in the form

$$h_{ij}(r) = \exp[-\beta u_{ij}(r) + \gamma_{ij}(r) + B_{ij}(r)] - 1 \tag{3}$$

where $u_{ij}(r), (i, j = 1, 2)$ is a pair potential defining an interaction of interparticles in the system; $\gamma_{ij}(r) = h_{ij}(r) - c_{ij}(r)$ is an indirect correlation function; $B_{ij}(r)$ is a bridge function; $\beta = 1/k_B T$, where k_B is the Boltzmann's constant and T is a temperature of the system.

An interaction potential for the binary hard-sphere system is defined as

$$u_{ij} = \begin{cases} 0, & r \le \sigma_{ij} \\ \infty, & r > \sigma_{ij}, \quad (i, j = 1, 2) \end{cases} \tag{4}$$

where $\sigma_{ij} \equiv (\sigma_i + \sigma_j)/2$ and $\sigma_{ii} = \sigma_i$ is given as σ_i, the diameter of the hard-sphere component i.

The Verlet-modified [10], [13] bridge function in our calculation has a form

$$B_{ij}(r) = -\frac{\phi\gamma_{ij}^2}{2} - \frac{\varphi}{2}\frac{\gamma_{ij}^2}{(1 + \alpha\gamma_{ij})}, \quad (i, j = 1, 2) \tag{5}$$

where (ϕ, φ, α) are free parameters to be determined by an imposed condition.

2.2. *Pressure consistency*

For the hard-sphere mixture the virial (v) pressure, p^v can be obtained with an analytical expression

$$\frac{\beta p^v}{\rho} = 1 + \frac{2\pi}{3}\rho \sum_{i,j} \sigma_{ij}^3 x_i x_j g_{ij}(\sigma_{ij}), \quad (i, j = 1, 2), \tag{6}$$

where $g_{ij}(\sigma_{ij})$ are the contact values of the radial distribution function, defined as $g_{ij} = h_{ij} + 1$, at σ_{ij}.

The isothermal compressibility (c) for the mixture is defined as

$$\frac{\partial \beta p^c}{\partial \rho} = 1 - \frac{1}{\rho}\sum_{ij} \rho_i \rho_j \int c_{ij}(r) d\mathbf{r}, \quad (i, j = 1, 2). \tag{7}$$

In the pressure consistency, the pressure obtained from the virial route would be equal to that obtained from the compressibility route [11], [13], [12]. In this work we use $dp^v - dp^c$ consistency discussed in Refs. [11], [13], [12] in which, we need to compute the density derivative of the virial pressure (Equation (6)) and make it be equal to the isothermal compressibility dp^c (Equation (7)) with a help of an optimized free parameters given in the bridge function [11], [13], [12], that is, we will check $\partial\beta p^v/\partial\rho = \partial\beta p^c/\partial\rho$ relation.

2.3. *An excess chemical potential*

For a hard-sphere system, an excess chemical potential is another essential thermodynamic quantity along with a pressure since the system has no internal energy. In this work we compute an excess chemical potential for a component i using a closed-form expression [6], [12]

$$\begin{aligned} \beta\mu_i \;&\approx\; \sum_{i=1}^{2} \rho_j \int d\mathbf{r} \Big[\Big(\frac{1}{2}h_{ij}^2 - c_{ij} - \frac{1}{2}h_{ij}c_{ij} \Big) \\ &+\; \Big(B_{ij} + \frac{2h_{ij}}{3}B_{ij} \Big) \Big]. \end{aligned} \tag{8}$$

3. RESULTS AND DISCUSSION

In our calculation we choose a component 1 as a reference particle which is a larger component ($\sigma_1 > \sigma_2$), and all calculations can be done with respect to this component. In this work in all calculations the diameter ratios of hard spheres are $\sigma_2/\sigma_1 = 0.3$ and 0.6; the mole fractions are $x_1 = 0.125, 0.5, 0.75$ and 1; and the packing fraction (volume density) defined as $\eta = (\pi/6)\sum_i \rho_i \sigma_i^3$ is $\eta = 0.49$ at which the hard-sphere system may exist in a fluid-like state [3].

We used the Picard iterative method in the calculation in which the SSOZ Equation (1) is solved in the Fourier space, while a closure Equation (3) is computed in a coordinate space and an in-house MATLAB [15] code is employed. The numerical tolerance for the root mean squared residual of the indirect correlation functions during a successive iterations was set 10^{-8}. A number of grid points for all calculations 2^{14} and a length interval $L = 16\,\sigma_1$. In pressure consistency test calculation a density derivative is computed with a finite difference with $\Delta\rho = 10^{-3}$. Note that our all results are independent on these numerical parameters. In our all calculations we set $\varphi = 1$, so that we have only two parameters (ϕ, α) to be found.

Table 1 presents an optimal values of free parameters (ϕ, α) in the VM bridge function (5) at which $dp^v - dp^c$ consistency condition is satisfied. An optimization calculation with a criterion of $|dp^v - dp^c|^2$ has been done using the 'fminsearch' multidimensional unconstrained nonlinear minimization routine of the MATLAB [15]. Last two columns of Table 1 show the pressure consistency checks.

Table 1. An optimal values of free parameters (ϕ, α) and pressure $dp^v - dp^c$ consistency checks for the binary hard sphere mixtures.

σ_2/σ_1	x_1	ϕ_{opt}	α_{opt}	$\frac{\partial\beta p^v}{\partial\rho}$	$\frac{\partial\beta p^c}{\partial\rho}$
0.3	0.125	0.01030	0.7760	25.20	25.20
	0.5	0.00999	0.7800	36.36	36.36
	0.75	0.01050	0.7855	42.00	42.00
	1.0	0.01024	0.7860	50.67	50.67
0.6	0.125	0.01000	0.7847	45.33	45.33
	0.5	0.00998	0.7830	44.75	44.75
	0.75	0.00985	0.7832	47.36	47.36
	1.0	0.00986	0.7843	50.67	50.67

Table 2 shows the numerically obtained values of equation of state $(Z \equiv \beta p^v/\rho)$ and an excess chemical potential for each components at fixed $\sigma_2/\sigma_1 = 0.3$ which indicates a system is totally asymmetric, and the comparisons of our values with those from the VM [13], MC [14] and BMCSL [7] calculations.

Table 3 displays our results obtained for $\sigma_2/\sigma_1 = 0.6$ and their comparisons with those of the VM [13], MC [14] and BMCSL [7] calculations. From the comparisons shown in two tables, it has been seen that our pressure values have been slightly underestimated, however, values for excess chemical potential are mostly better than those from the similarly implemented VM bridge calculations [13] and close to the accurate MC [14] and BMCSL [7] values. We note that the first term with free parameter ϕ in the bridge function (5) can enable us to obtain comparable value of the excess chemical potential. When $\phi = 0$, the bridge function (5) becomes the commonly used VM bridge forms [10], [12] and in this case the excess chemical potential for each component is usually high (such as, $(\beta\mu_1 = 23.4, \beta\mu_2 = 2.7)$ at $\sigma_2/\sigma_1 = 0.3$ and $x_1 = 0.5$), however, values of the compressibility factor are comparable ($Z = 8.69$ at $\sigma_2/\sigma_1 0.3$ and $x_1 = 0.5$) with accurate ones. Therefore, we note that the ϕ-free parameter term in the VM bridge function (5) is essential in the calculation. We also note that the excess chemical potential obtained in Ref. [13] had been computed with an analytical-type expression, which is different from what is given in (8), however, results from them show a reasonable agreements.

Table 2. Thermodynamic properties for the binary hard sphere mixtures and $\eta = 0.49$.

Method	σ_2/σ_1	x_1	Z	$\beta\mu_1$	$\beta\mu_2$
	0.3	0.125			
This work			6.58	39.8	3.93
MC [14]			6.77	41.22	3.77
BMCSL [7]			6.70	39.28	3.76
		0.5			
This work			8.44	20.3	2.62
VM [13]			8.72	18.00	2.50
MC [14]			8.69	19.67	2.52
BMCSL [7]			8.67	19.17	2.55
		0.75			
This work			10.1	17.9	2.47
MC [14]			10.42	17.20	2.37
BMCSL [7]			10.41	17.12	2.41
		1.0			
This work			11.8	16.7	2.40
BMCSL [7]			12.19	15.70	2.32

Table 3. The same as shown in table 2, however, for $\sigma_2/\sigma_1 = 0.6$.

Method	σ_2/σ_1	x_1	Z	$\beta\mu_1$	$\beta\mu_2$
	0.6	0.125			
This work			10.7	35.7	12.1
VM [13]			11.16	33.00	11.10
MC [14]			11.10	34.97	11.53
BMCSL [7]			11.04	33.93	11.33
		0.5			
This work			10.6	21.7	7.93
MC [14]			10.93	20.95	7.51
BMCSL [7]			10.91	20.47	7.45
		0.75			
This work			11.1	18.5	6.94
MC [14]			11.48	17.81	6.58
BMCSL [7]			11.47	17.45	6.54
		1.0			
This work			11.8	16.7	6.38
BMCSL [7]			12.19	15.70	6.02

4. CONCLUSION

In this we have applied the free-parameterized Verlet-modified bridge function for the binary hard-sphere mixture in terms of the site-site Orsntein-Zernike integral equation method. The pressure consistency test for the system at a high density has been performed, by which a pressure have been obtained unambiguously. It has been shown that the Verlet-modified bridge function with less free parameters than that was used in Ref. [13] could have worked and given comparable values for a pressure. An excess chemical potential for each component has been computed with an closed form expression. In general, the numerically obtained findings for pressure and excess chemical potential present good agreements with available accurate data.

5. ACKNOWLEDGEMENT(S)

This research work has been supported by the Mongolian Foundation for Science and Technology (Project No. ShUTBIKhKhZG-2022/167).

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