

ARTICLE

Equilibrium thermodynamic properties of binary hard-sphere mixtures from integral equation theory

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Abstract: The binary additive hard-sphere mixtures have been studied by the Ornstein-Zernike integral equation coupled with the Martynov-Sarkisov (MS) closure approximation. Virial equation of state is computed in the MS approximation. The excess chemical potential for the mixture is evaluated with a closed-form expression based on correlation functions. The excess Helmholtz free energy is obtained using the Euler relation of thermodynamics. Moreover, these thermodynamic quantities are obtained by the Boublík-Mansoori-Carnahan-Starling-Leland (BMCSL) formulas. Our findings for pressure and excess chemical potential for the number of binary sets of the mixtures from the MS approximation show good agreements with those findings obtained by the BMCSL formulas and available data in literature, having a maximum deviation of 5% for a packing fraction up to 0.5. The maximum deviation of the excess free energy obtained for the mixtures is shown to be ~16% for a packing fraction of 0.5. Note that this work presents an initial calculation of an excess chemical potential of the system in the MS approximation.

Keywords: *Ornstein-Zernike equation, Martynov-Sarkisov closure, Pair correlation functions;*

INTRODUCTION

The hard-sphere (HS) model plays a major role in the theoretical development of the modern theory of liquids [1]. This system is often used as a standard reference system in the perturbation approach of the liquids for studying the liquid-state properties [1, 2]. The HS mixtures of various size distributions can be employed to model the colloidal suspensions, which play an important role in chemical and bioengineering fields [3, 4].

The binary HS mixture is the simplest model of multicomponent systems. Computer simulations for its thermodynamic and structural properties began in the mid-1960s. Alder [5] used the molecular dynamic (MD) simulation to

solve the equation of state (EOS) for the binary mixture. Rotenberg [6] performed the Monte-Carlo (MC) EOS calculation for hard-sphere mixtures. An alternative approach to studying a liquid is the integral equation (IE) method, in which the IE combined with an approximate closure is solved to predict the structure and to obtain thermodynamic properties. Lebowitz [7] obtained an exact solution of the Percus-Yevick (PY) integral equation for a multicomponent additive mixture. Mansoori *et al.* [8] investigated the EOS for the HS mixture using the MC and MD simulations and proposed an analytical expression for the EOS using the solution the PY integral equation [9].

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Barošová *et al.* [10] applied a test particle insertion method to obtain the excess chemical potential of the binary HS mixtures. Santos and his co-workers have investigated extensively thermodynamic properties and structural nature for multicomponent HS fluids in terms of the analytical approaches from the IE method [11, 12] and MD simulation [13]. Moreover, Ballone *et al.* [14] tested the PY approximation for the HS mixtures. Schmidt [15] and Malijevský *et al.* [16] applied the Martynov-Sarkisov (MS) [17] closure for the binary mixtures as well.

Through this work, hoped to obtain thermodynamic properties for binary additive HS mixture using the Ornstein-Zernike equation method coupled with the MS closure approximation. We will compute pressure using a virial route in the MS approximation. The excess chemical potential has been computed by an approximate expression based on correlative functions. The excess free energy will be obtained from thermodynamic relation. Moreover, we computed these thermodynamic quantities using the Boublík -Mansoori-Carnahan-Starling-Leland (BMCSL) [8, 18] approach, which is based on closed-form

formulas obtained in the virial and compressibility routes from the PY integral equation theory. We compared some of our findings for pressure, excess free energy and chemical potential with those obtained by MC method [10] and MD simulation [12] and will present other new findings as well. To our knowledge, this is the first attempt to calculate the excess chemical potential for the mixture in the MS approximation. Therefore, we hope that it can be considered as a contribution in this field. The organization of this paper is as follows. Introduction is presented in the first section. The next two sections discuss about theoretical formulation of the IE method for multicomponent mixture and thermodynamic quantities, which we compute, and of our numerical results and their discussions, respectively. Then a conclusion follows.

THEORY

Integral equation theory

For binary system with the total number density ρ , the Ornstein-Zernike (OZ) equation, which establishes a relation between the total correlation function and the direct correlation function, has the following formula:

$$h_{ij}(\mathbf{r}) = c_{ij}(\mathbf{r}) + \rho \sum_{k=1}^2 x_k \int d\mathbf{r}' c_{ij}(\mathbf{r} - \mathbf{r}') h_{ij}(\mathbf{r}') \quad (1)$$

where $h_{ij}(\mathbf{r})$ and $c_{ij}(\mathbf{r})$ are the total and direct correlation functions, respectively, and $x_i = \rho_i/\rho$ is the mole fraction for the component i with $\sum_{i=1}^2 x_i = 1$.

Since the OZ Eq. (1) contains the unknown correlation functions, it cannot be

solved directly. In order to solve this equation, another equation, which is called a *closure relation*, must be introduced, that couples the total and direct correlation functions with the pair interaction potential. A general closure equation for the mixture may be written in the following formula:

$$h_{ij}(\mathbf{r}) = \exp[-\beta u_{ij}(\mathbf{r}) + \gamma_{ij}(\mathbf{r}) + B_{ij}(\mathbf{r})] - 1 \quad (i, j = 1, 2). \quad (2)$$

Here $u_{ij}(\mathbf{r})$ is an interaction potential between particles in the system; where $\gamma_{ij} \equiv h_{ij} - c_{ij}$ is an indirect correlation function; $B_{ij}(\mathbf{r})$ is the bridge function; $\beta = 1/k_B T$, and k_B is the Boltzmann constant and T is the temperature for the system.

Then the OZ Eq. (1) and closure Eq. (2) are solved in self-consistent manner, and the total and direct correlation functions can be found numerically. For HS mixture, a form of an interaction potential in this work is given by the following:

$$u_{ij}(r) = \begin{cases} \infty, & r < \sigma_{ij} \\ 0, & r \geq \sigma_{ij} \end{cases} \quad (3)$$

where $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$, and $\sigma_{ii} = \sigma_i$ is the hard sphere diameter for the component i . Since the exact analytic expression for the bridge function is unknown in the liquid

theories, its approximated form has been mostly employed. A bridge function in the Martynov-Sarkisov [17] approximation, which we are using in this work, has the following formula:

$$B_{ij}(r) = (1 + 2\gamma_{ij})^{1/2} - \gamma_{ij} - 1. \quad (4)$$

Thermodynamic properties

Once a solution of the integral equation is obtained, thermodynamic properties can be evaluated analytically as follows.

Pressure

For the binary HS mixture, in the MS approximation we compute a pressure using a virial (v) route, in which pressure is evaluated via the following:

$$\frac{\beta p_v^{MS}}{\rho} = 1 + \frac{2\pi}{3} \rho \sum_{i,j=1}^2 x_i x_j \sigma_{ij}^3 g_{ij}(\sigma_{ij}), \quad (5)$$

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

We also used the BMCSL pressure expression [13], which is obtained as an interpolation between pressures from virial and compressibility routes in the Percus-Yevick approximation:

$$\frac{\beta p^{BMCSL}}{\rho} = \frac{1}{1-\eta} + \frac{3\eta}{(1-\eta)^2} \frac{m_2}{m_3} + \frac{\eta^2(3-\eta)}{(1-\eta)^3} \frac{m_2^3}{m_3^2}. \quad (6)$$

In formula (6) m_n is the reduced moments given by $m_n \equiv M_n/M_1^n$, where M_n is the n th moment of the diameter

distribution, which is given by the following:

$$M_n \equiv \langle \sigma^n \rangle = \sum_{i=1}^2 x_i \sigma_i^n, \quad (7)$$

where $\eta = \pi \rho M_3/6$ is a packing fraction, and x_i is a mole fraction of the component i .

An excess chemical potential

In order to calculate the excess (e) chemical potential for the component i in the mixtures in the MS approximation, we used the following closed-form expression based on the correlation functions [19-22]

$$\beta \mu_i^e \approx \sum_{j=1}^2 \rho_j \int d\mathbf{r} \left[\left(\frac{1}{2} h_{ij}^2 - c_{ij} - \frac{1}{2} h_{ij} c_{ij} \right) + \left(1 + \frac{2h_{ij}}{3} \right) B_{ij} \right]. \quad (8)$$

Note that this approximated expression (8) for the excess chemical potential can be used for any bridge functions since it does not require the explicit forms of them. A derivation of an expression (8) was given in

the Appendix. Similarly to the BMCSL expression for pressure, one can employ the BMCSL expression for an excess chemical potential, which has the following formula [13]

$$\beta\mu_i^{eBMCSL} = -\ln(1-\eta) + \frac{3\eta}{(1-\eta)} \frac{m_2}{m_3} \frac{\sigma_i}{M_1} + \left[\frac{3\eta}{1-\eta} \frac{m_2}{m_3} + X_2(\eta) \frac{m_2^3}{m_3^2} \right] \frac{\sigma_i^2}{M_2} + \left[\frac{\eta}{1-\eta} + \frac{3\eta^2}{(1-\eta)^2} \frac{m_2}{m_3} + X_3(\eta) \frac{m_2^3}{m_3^2} \right] \frac{\sigma_i^3}{M_3} \quad (9)$$

where $X_2(\eta) = 3\eta/(1-\eta)^2 + 3\ln(1-\eta)$ and $X_3(\eta) = (5\eta^2 - 2\eta - \eta^3)/(1-\eta)^3 - 2\ln(1-\eta)$.

An excess free energy

Once we have the values of the

compressibility factor $Z \equiv \beta p_v^{MS}/\rho$ and the excess chemical potential $\beta\mu_i^e$, we can compute the excess Helmholtz free energy per particle using the following Euler equation of thermodynamics:

$$\beta a^e = \sum_{i=1}^2 x_i \beta \mu_i^e - Z + 1. \quad (10)$$

Moreover, we will use the BMCSL formula for an excess free energy per particle, which is given in Ref. [13]:

$$\beta a^{eBMCSL} = -\ln(1-\eta) + \frac{3\eta}{1-\eta} \frac{m_2}{m_3} + \left[\frac{\eta}{(1-\eta)^2} + \ln(1-\eta) \right] \frac{m_2^3}{m_3^2}. \quad (11)$$

RESULTS AND DISCUSSION

In our calculation we chose a component 1 with a diameter σ_1 as a reference particle. A simple Picard iterative method for solving the OZ Eq. (1) was employed, and the numerical tolerance for the root-mean-squared residual of the indirect correlation functions during successive was set at 10^{-8} . For all calculations the number of grid points is 2^{15} and the length parameter is $L = 16\sigma_1$.

We first did numerical calculations for binary mixtures at values of $\eta = 0.15, 0.25, 0.35$ and 0.45 , and for $\sigma_2/\sigma_1 = 0.5$ and $x_1 = 0.5$ values. Table 1 shows

numerical results for the equations of state and their comparisons with accurate MD values [12]. Values in columns 2 and 3 are obtained with Eqs. (5) and (6), respectively. For each density, the absolute relative deviation percentage (ARD%) error for the MS and BMCSL values is obtained by means of accurate MD values in column 4 and is shown in parenthesis. From this comparison, the BMCSL formula presents quite accurate value for both low and high densities. However, in the MS approximation, as density increases, the ARD% value increases as well.

Table 1. Values of pressure from the MS and BMCSL approximations at different values of a packing fraction η , and $x_1 = 0.5$, and $\sigma_2/\sigma_1 = 0.5$ and MD results [12].

η	$\beta p_v^{MS}/\rho$	$\beta p^{BMCSL}/\rho$	MD [12]
0.15	1.8 (1.3)	1.7761 (0.068)	1.7773
0.25	2.7 (2.3)	2.7588 (0.195)	2.7642
0.35	4.5 (0.8)	4.5216 (0.322)	4.5362
0.45	7.8 (2.0)	7.9320 (0.381)	7.9623

In Table 2, we compared numerical values of the excess chemical potential obtained in the MS and BMCSL approximations for each component with the MD values [12]. The MS and BMCSL

values were obtained with formulas (8) and (9), respectively. The corresponding ARD% value for each value of η is also shown in parenthesis.

Table 2. The same as shown in Table 1, but for the excess chemical potential.

η	$\beta\mu_1^e$	$\beta\mu_1^e(\text{BMCSL})$	MD [12]	$\beta\mu_2^e$	$\beta\mu_2^e(\text{BMCSL})$	MD [12]
0.15	2.1(0.3)	2.0953(0.555)	2.1070	0.7(5.1)	0.7338(0.542)	0.7378
0.25	4.5(0.7)	4.5279(0.095)	4.5322	1.5(2.2)	1.4736(0.354)	1.4684
0.35	8.6(0.8)	8.6287(0.472)	8.6696	2.6(0.3)	2.5819(0.405)	2.5924
0.45	16(0.9)	16.1394(0.006)	16.1404	4.5(2.0)	4.3843(0.581)	4.4099

Table 3 demonstrates numerical values of the excess Helmholtz free energy obtained by expressions (10) and (11) against the MD values [12]. In the MS approximation, the ARD% values for the excess free energy are somewhat larger than

those for pressure and excess chemical potential. The BMCSL values are comparable with the MD values, as well. Note that all the results obtained here are independent of number of grid points and a length parameter mentioned above.

Table 3. The same as shown in Table 1, but for the excess Helmholtz free energy.

η	$\beta a^e(\text{MS})$	$\beta a^e(\text{BMCSL})$	MD [12]
0.25	1.2(2.9)	1.2420(0.4777)	1.2361
0.35	2.1(0.3)	2.0837(0.487)	2.0939
0.45	3.6(8.7)	3.3298(0.510)	3.3129

We note that since the BMCSL formulas are based on an interpolation, which uses results obtained from both virial and compressibility routes, they enable more accurate values, which are quite close to the exact values obtained by the MD method, than what the MS approximation presents.

After these calculations, we continued our numerical experiments of thermodynamic quantities for the number of binary sets of mixtures, in which one of the

three parameters (diameter ratio σ_2/σ_1 , mole fraction of a larger sphere x_1 , and a packing fraction η) was varied, while the remaining two were kept constant. Numerical values of the MS and BMCSL approaches as a function of σ_2/σ_1 at $\eta = 0.3$ and $x_1 = 0.5$ are presented in Figure 1. Numerical values of thermodynamic quantities as functions of x_1 at $\eta = 0.3$ and $\sigma_2/\sigma_1 = 0.5$ are shown in Figure 2.

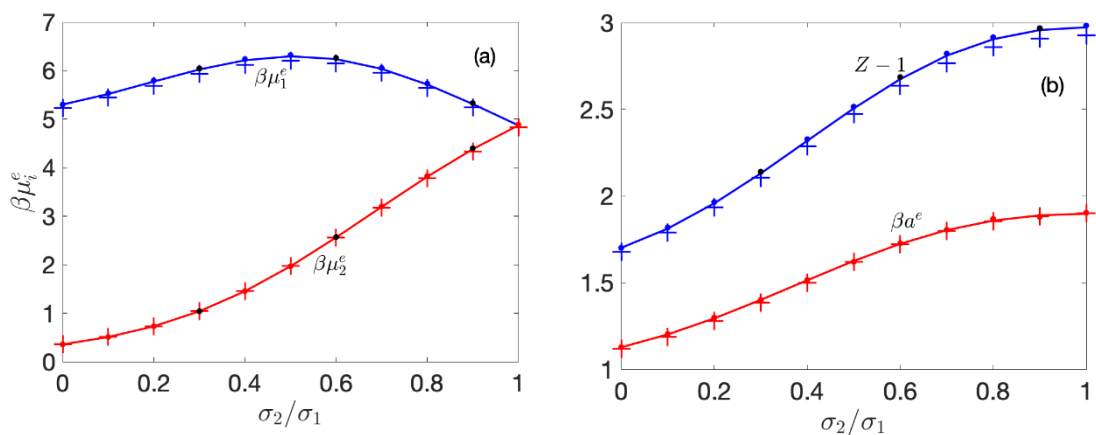


Figure 1. Results from the MS and BMCSL approaches are shown with crosses and solid curves, respectively. Plots of the excess chemical potential $\beta\mu_i$ (a), and the excess Helmholtz free energy (b) and the compressibility factor $Z - 1$ (b) as a function of a diameter ratio σ_2/σ_1 at $\eta = 0.3$ and $x_1 = 0.5$. Black and blue/red points show the MC [10] and MD [12] simulations, respectively.

Figure 3 presents thermodynamic quantities as a function of η at $\sigma_2/\sigma_1 = 0.5$ and $x_1 = 0.5$. In all plots of Figures 1-3 the cross and solid curve denotes the MS and BMCSL results respectively. Black point in the plot denotes the MC result [10], while blue/red point presents the MD data [12].

From the plots of Figures 1-3, it has been seen that the MD (blue/red points) and BMCSL (solid lines) are almost indistinguishable, and values of excess chemical potential from the MS approach follows more closely the curves than those of the pressure and excess free energy, especially for high values of η (Figure 3).

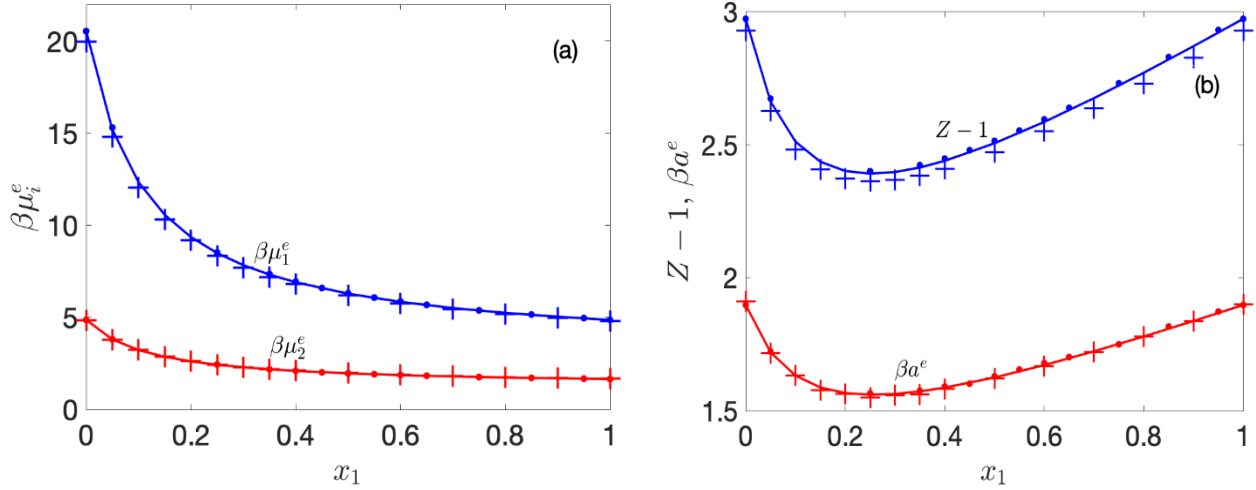


Figure 2. The same plots as shown in Figure 1, but for as a function of the mole fraction x_1 at $\eta = 0.30$ and $\sigma_2/\sigma_1 = 0.5$. Points show the MD [12] simulations.

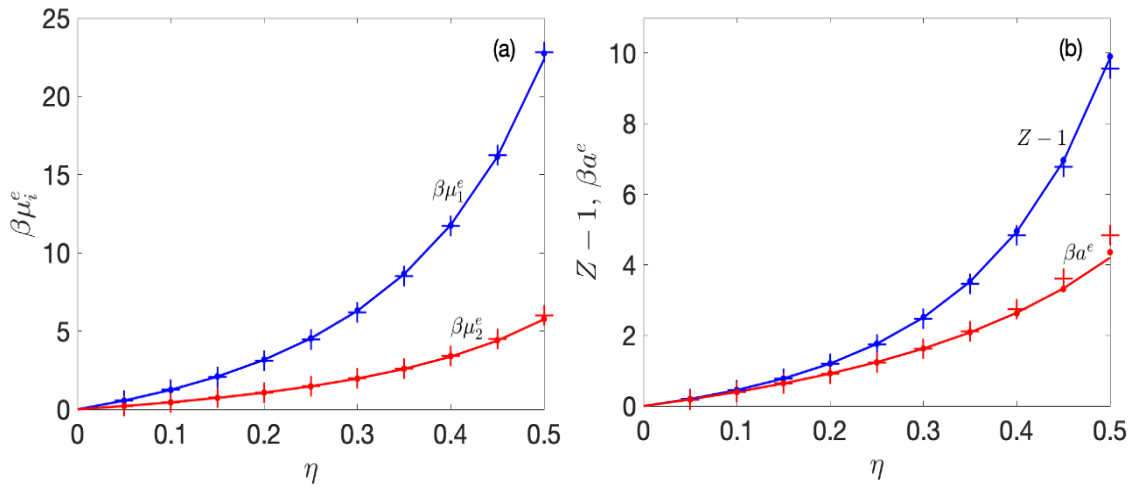
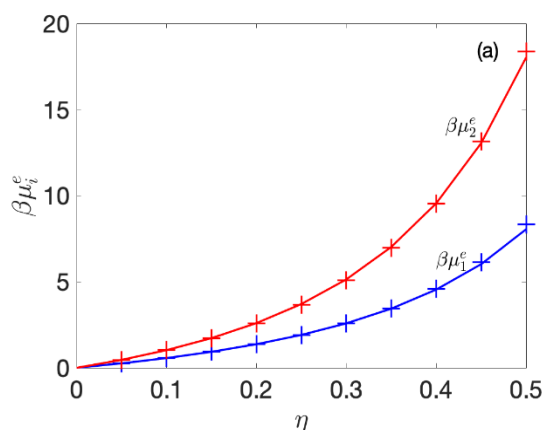


Figure 3. The same plots as shown in Figure 1, but for as a function of the packing fraction η at $x_1 = 0.5$ and $\sigma_2/\sigma_1 = 0.5$. Points show the MD [12] simulations.

In Figure 4, we exhibited similar results for $x_1 = 0.15$ and $\sigma_2/\sigma_1 = 1.5$ as



function of η . In this case $\beta\mu_2$ takes large values because of large σ_2 value.

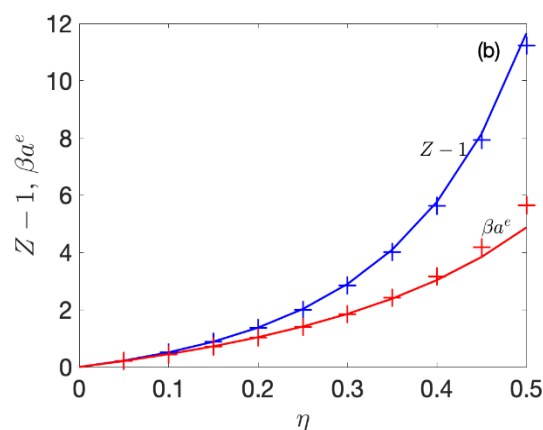


Figure 4. The same plots as shown in Figure 3, but for $x_1 = 0.15$ and $\sigma_2/\sigma_1 = 1.5$.

In Figures 5-6, we have shown the ARD% values for the $\beta\mu_1^e$ (blue), $\beta\mu_2^e$ (red), Z (green) and βa^e (black), which correspond to the plots shown in Figures 1-4 from the MS approximation. The ARD% values shown in Figure 5 and Figure 6a are obtained with respect to the MD data [12].

From plots in Figure 5, it has been observed that the ARD% values, which are the function of σ_2/σ_1 for $x_1 = 0.5$ and $\eta = 0.3$, are less than 2%, while those, which are the function of x_1 for $\sigma_2/\sigma_1 = 0.5$ and $\eta = 0.3$, are less than 3.5%.

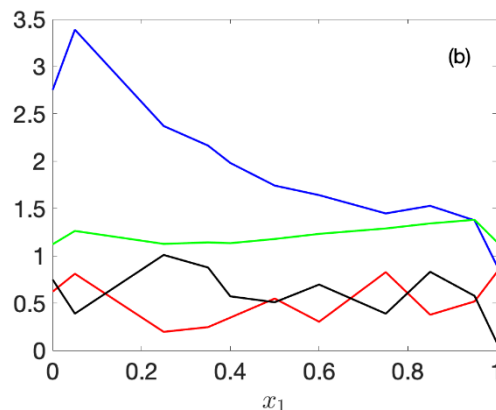
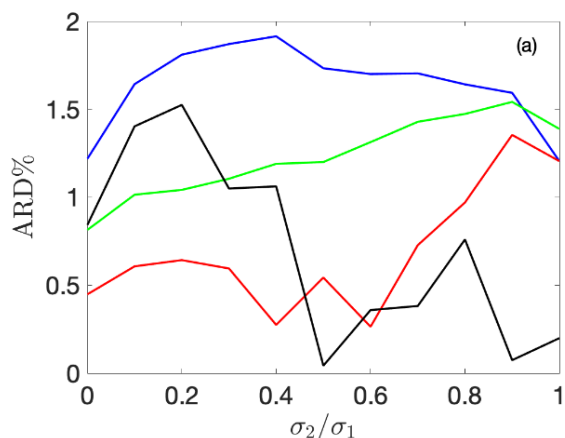


Figure 5. (a) Absolute relative deviation percent (ARD%) of $\beta\mu_1^e$ (blue), $\beta\mu_2^e$ (red), Z (green), and βa^e (black) vs σ_2/σ_1 at $x_1 = 0.5$ and $\eta = 0.3$; (b) same plots as shown in panel Figure 5a, but, vs x_1 at $\sigma_2/\sigma_1 = 0.5$ and $\eta = 0.3$.

For plots in Figure 6, the ARD% values of an excess chemical potential and pressure as a function of η are less than 5%, however, the ARD% value of an excess free energy becomes large when $\eta > 0.45$, and

reaches ~16% (black curve in panel Figure 6b) at $\eta = 0.5$. Note that the ARD% values for plots in Figure 6b are obtained with respect to the corresponding BMCSL values (curves in Figure 4).

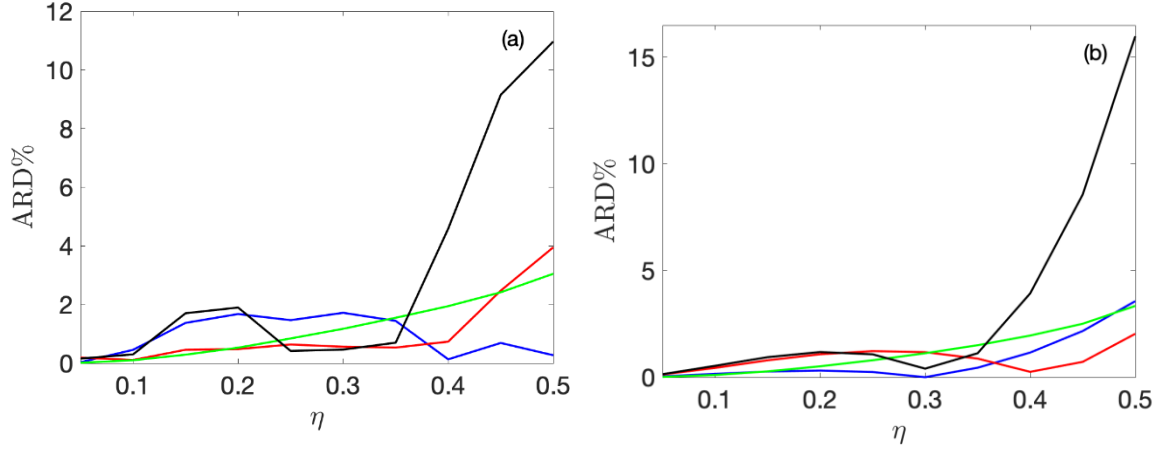


Figure 6. (a) Same plots as shown in Figure 5a, but vs η at $x_1 = \sigma_2/\sigma_1 = 0.5$; (b) same plots as shown in panel Figure 6a, but, vs η at $x_1 = 0.15$ and $\sigma_2/\sigma_1 = 0.5$.

Based on plots of the ARD% values of excess chemical potential in Figures 5 and 6, we note that an approximate expression (8) for evaluating an excess chemical potential can be reliably used for

the HS mixture in the MS approximation. Moreover, for the system, the virial pressure obtained in the MS approximation can be comparable against the accurate BMCSL value or the MD simulation.

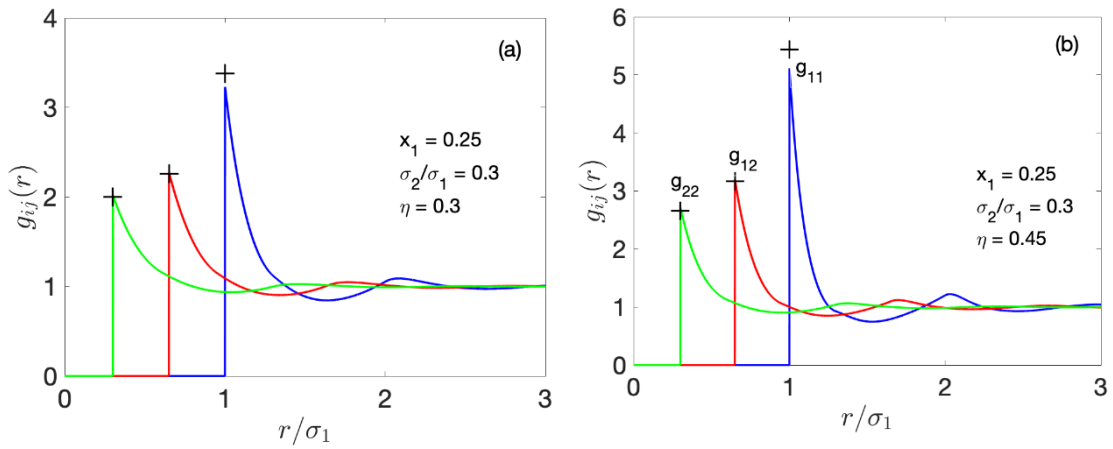


Figure 7. Radial distribution functions g_{ij} for the binary HS system for $x_1 = 0.25$, $\sigma_2/\sigma_1 = 0.3$ and $\eta = 0.35$ (a) and 0.45 (b). Cross denoting the contact value is taken from Ref. [10]

In Figure 7, we have shown the radial distribution function (RDF) for the binary HS mixture at $x_1 = 0.25$, $\sigma_2/\sigma_1 = 0.3$, $\eta = 0.35$ (a), and $x_1 = 0.25$, $\sigma_2/\sigma_1 = 0.3$, $\eta = 0.45$ (b). The contact values from the MC simulation are taken from Ref. [10], which are very close to the MS data, except for the g_{11} (blue) function. For plots in panel (a) of Figure 7, the contact values from the MC simulation are 3.38, 2.26 and

2.00 for g_{11} , g_{12} (red) and g_{22} (green), respectively. However, their values from the MS approximation are 3.23, 2.27, and 2.02. The difference between the contact values for the g_{11} from the MC and MS methods is 0.15, however, is the same as from the MC and PY methods, which is 0.38 [16]. For plots in panel (b) of Figure 7, the contact values from the MC simulation are 5.44, 3.17 and 2.66 for g_{11} , g_{12} and g_{22} ,

respectively, while they are 5.11, 3.19 and 2.72, respectively, from the MS approximation. Difference between the contact values of the g_{11}^{MC} and g_{11}^{MS} RDFs is 0.33, however, similar difference with the g_{11}^{PY} is 1.01 [16]. This difference clearly reveals that the RDF obtained from the MS approximation can be better than that from the PY approximation, which in turn, could give better values of thermodynamic quantities, such as, pressure and excess chemical potential. From Figure 7, it is visible that for high densities the contact values of the MS RDF functions are not as accurate as those of the MC simulation. Therefore, it causes less accurate calculation of thermodynamics property with relatively large ARD% value for high

CONCLUSIONS

In this work we have applied the Ornstein-Zernike integral equation for binary additive hard-sphere mixtures at equilibrium using the Martynov-Sarkisov approximation. We computed pressure using the virial route and the BMCSL formula. We obtained an excess chemical potential using an approximate expression based on correlation functions. The excess free energy has been computed using the Euler equation of thermodynamics. Moreover, excess chemical potential and free energy are evaluated using the BMCSL formulas. Our findings from the MS approximation have been compared with those obtained with the fairly accurate BMCSL formulas and the MD simulation. Furthermore, the absolute relative deviation percentage for thermodynamic quantities for the system has been computed as a function of diameter ratio of spheres, mole fraction of larger component and packing fraction, in which one of them is varied, while two others are kept constant. Large values of the ARD% come for the excess free energy for high density, and maximum of it is ~16% at $\eta = 0.5$. Note that, to our knowledge, this is the first calculation for the thermodynamic properties for the mixture in the MS approximation.

densities, since thermodynamic property is obtained by means of the correlation functions. Finally, we note that whereas thermodynamic properties from the MS approximation are less accurate than the BMCSL values, the BMCSL formulas we used in this can work only for the hard-sphere systems. However, the formulas we used in the MS approximation can work for the systems, for which any types of interaction potential, including the hard sphere, is used. Therefore, we can say that employing and testing the MS bridge function in this work has shown that for various systems the MS approximation can enable thermodynamic properties against those of other accurate approaches.

Acknowledgements

Not applicable.

Ethical approval

Not applicable.

Author contribution

Ts. Ts. formulated a theoretical problem. B. Ts. and Ts. Ts. carried out numerical calculations. B. Ts. wrote the first draft of the manuscript and Ts. Ts. helped with the revision of the manuscript. All authors reviewed the results and approved the final version of the article.

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Conflict of interest

The authors declare that there is no conflict of interest.

APPENDIX

The most common technique to obtain the chemical potential μ_i^e (i.e., the Gibbs free energy per particle) for the component i in

the N_m mixtures is through the Kirkwood charging formula [23, 24]

$$\beta\mu_i = \beta\mu_i^{id} + \beta\mu_i^e = \beta\mu_i^{id} + \sum_{j=1}^{N_m} \rho_j \int_0^1 d\lambda \int d\mathbf{r} \frac{\partial \beta u_{ij}(r, \lambda)}{\partial \lambda} g_{ij}(r, \lambda). \quad (A-1)$$

where $\beta\mu_i^{id}$ and $\beta\mu_i^e$ are the ideal and excess chemical potentials for the component i . In this technique a coupling parameter λ scales interactions of one particle added into $N - 1$ particle system, that is, when $\lambda = 0$, the particle is removed

and when $\lambda = 1$, the particle is fully coupled to the system. To eliminate a derivative of $\partial u_{i,j}/\partial \lambda$ in the Kirkwood charging formula, we start with an exact expression

$$[1 + h_{ij}(r, \lambda)] = e^{-\beta u_{ij}(r, \lambda) + h_{ij}(r, \lambda) - c_{ij}(r, \lambda) + B_{ij}(r, \lambda)}. \quad (A-2)$$

Taking the derivatives of both sides, we arrive at the following:

$$[1 + h_{ij}(r, \lambda)] \frac{\partial \beta u_{ij}(r, \lambda)}{\partial \lambda} = \frac{\partial}{\partial \lambda} \left(\frac{1}{2} h_{ij}^2(r) - c_{ij}(r) + B_{ij}(r) \right) - h_{ij}(r, \lambda) \frac{\partial c_{ij}(r, \lambda)}{\partial \lambda} + h_{ij}(r) \frac{\partial B_{ij}(r, \lambda)}{\partial \lambda}. \quad (A-3)$$

Inserting an expression (A-3) into the Kirkwood charging formula for the excess chemical potential (A-1), we have

$$\beta\mu_i^e = \sum_{j=1}^{N_m} \rho_j \left[\int d\mathbf{r} \left(\frac{1}{2} h_{ij}^2(r) - c_{ij}(r) + B_{ij}(r) \right) - \int_0^1 d\lambda \int d\mathbf{r} h_{ij}(r, \lambda) \frac{\partial c_{ij}(r, \lambda)}{\partial \lambda} + \int_0^1 d\lambda \int d\mathbf{r} h_{ij}(r, \lambda) \frac{\partial B_{ij}(r, \lambda)}{\partial \lambda} \right] \quad (A-4)$$

If we assume that $h_{ij}(r, \lambda) \approx \lambda h_{ij}(r)$, $c_{ij}(r, \lambda) \approx \lambda c_{ij}(r)$, and $B_{ij}(r, \lambda) \approx B_{ij}(\gamma^2(r, \lambda))$, the second and

the third integrals of an expression (A-4) lead to

$$\int_0^1 d\lambda \int d\mathbf{r} h_{ij}(r, \lambda) \frac{\partial c_{ij}(r, \lambda)}{\partial \lambda} = \frac{1}{2} \int d\mathbf{r} h_{ij}(r) c_{ij}(r), \quad (A-5)$$

and

$$\int_0^1 d\lambda \int d\mathbf{r} h_{ij}(r, \lambda) \frac{\partial B_{ij}(r, \lambda)}{\partial \lambda} = \frac{2}{3} \int d\mathbf{r} h_{ij}(r) B_{ij}(r), \quad (A-6)$$

respectively.

Combining the expressions (A-4), (A-5) and (A-6), we have the following formula:

$$\beta\mu_i^e = \sum_{j=1}^{N_m} \rho_j \int dr \left[\left(\frac{1}{2} h_{ij}^2(r) - c_{ij}(r) + B_{ij}(r) \right) + \left(1 + \frac{2h_{ij}}{3} \right) B_{ij} \right] \quad (A-7)$$

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