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

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Abstract

We present an equilibrium thermodynamic properties of binary hard-sphere mixtures from integral equation approach combined with the Percus-Yevick (PY) and the Martynov-Sarkisov (MS) approximations. We use the virial, the compressibility and the Boublík-Mansoori-Carnahan-Starling-Leland (BMCSL) equations of state in the PY approximation, while the virial equation of state is only employed in the MS approximation. We employ a closed-form expression for evaluating the excess chemical potential. The excess Helmholtz free energy is obtained using the Euler relation of thermodynamics. For a number of binary sets of the mixtures we compare our findings for thermodynamic properties with previously obtained results in the literature. Generally, the findings from the MS approximation show better agreement with the results than those from the PY approximation.

I. INTRODUCTION

The hard-sphere (HS) model plays a major role in the 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]. Mixtures of the HSs of different 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 the multicomponent systems. Computer simulations for its thermodynamic and structural properties began in the mid-1960s. Adler [5] used the molecular dynamic (MD) simulation to solve the equation of state (EOS) for the binary mixture. Rotenberg [6] performed the Monte-Carlo (MS) EOS calculation for a mixture of HSs. An alternative approach to study a liquid is the integral equation (IE) method in which the IE combined with approximate closures is solved to predict the structure and to obtain thermodynamic properties. Mansoori *et al.* [7] investigated the EOS for the mixture of the HSs using the MC and MD simulations, and proposed an analytical expression for the EOS using the solution the PY integral equation [8]. Barošová *et al.* [9] 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 [10, 11] and MD simulation [12]. Moreover, Ballone *et al.* [13] tested the PY approximation for the HS mixtures. Schmidt [14] and Malijevský *et al.* [15] applied the Martynov-Sarkisov (MS) [16] closure for the binary mixtures as well.

In the present article our goal is to report on thermodynamic properties for binary HS mixtures at equilibrium using the IE approach combined with the PY and the MS approximations. We employ the virial and the compressibility routes, and the Boublík-Mansoori-Carnahan-Starling-Leland (BMCSL) [7, 17] approach to calculate pressure in the PY approximation. The virial EOS is used to obtain pressure in the MS approximation. In terms of the IE methodology, the excess chemical potential can be obtained with an analytical expression based on the correlation functions [18, 19]. Such a closed-form expression is employed for computing the excess chemical potential. The excess Helmholtz free energy is obtained from thermodynamic relation. Then we compare our numerical results for thermodynamic properties with those obtained with the MC [9] and the MD [11] simulations.

The organization of this paper is as follows. In Section II we discuss theoretical formulation of the IE method for multicomponent mixture and thermodynamic quantities which we will compute. In Section III we present our results and discussion, which is followed by conclusions.

II. INTEGRAL EQUATION THEORY

For multicomponent mixtures we consider the site-site Ornstein-Zernike (SSOZ) equation which establishes a relation between the total correlation function and the direct correlation function. For binary systems with the total number density ρ, the SSOZ equation has a form

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

where $h_{ij}(r)$ and $c_{ij}(r)$ 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 SSOZ equation (1) contains two unknown correlation functions, it cannot be solved directly. In order to solve for these functions, an another equation, called a *closure relation* must be introduced, which couples the total and direct correlation functions with the pair interaction potential. A general closure equation for the mixture may be written in the form

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

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

The total and direct correlation functions can be found by numerical solutions of equation (1) and equation (2) provided that $u_{ij}(r)$, T and $B_{ij}(r)$ are known.

For HS mixture, a form of an interaction potential in this work is given by

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

with $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$ and $\sigma_{ii} = \sigma_i$ is the hard sphere diameter for the component i.

Since there is not an exact known expression for the bridge function, an approximated functions can be used for it, such the PY and MS approximations. In the PY approximation [8] the bridge function is approximated by

$$B_{ij}(r) = \ln(1+\gamma_{ij}) - \gamma_{ij}, \tag{4}$$

and in the MS approximation [16] by

$$B_{ij}(r) = (1+2\gamma_{ij})^{1/2} - \gamma_{ij} - 1. \tag{5}$$

A. Thermodynamic quantities

1. *Pressure*

For binary HS mixture, we use a following virial (v) EOS

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

where $g_{ij}(\sigma_{ij})$ are the contact values of the radial distribution functions. In the PY approximation the pressure from the compressibility (c) route can be computed with an analytical expression [20]

$$\begin{aligned}\frac{\beta p_c^{\mathrm{PY}}}{\rho} = 1 &+ \frac{1}{2\rho}\sum_{i,j=1}^{2}\rho_i\rho_j \int d\mathbf{r} c_{ij}(g_{ij}-2) \\ &+ \frac{1}{8\pi^3}\frac{1}{\rho}\int d\mathbf{k}[\mathrm{Tr}(R\hat{C}) + \ln\det|I - R\hat{C}|],\end{aligned} \tag{7}$$

where R is a diagonal matrix based on density of each component and $\hat{C}$ is 2×2 matrix whose element is $\hat{c}_{ij}(k)$. Here $\hat{c}_{ij}(k)$ is the Fourier transform of the direct correlation function $c_{ij}(r)$ and I is an identity matrix. A det means the determinant of the matrix.

In the PY approximation one may also employ a rather accurate BMCSL EOS [7, 17] which is basically an interpolation between above two expressions:

$$\frac{\beta p^{\mathrm{BMCSL}}}{\rho} = \frac{1}{3}\frac{\beta p_v^{\mathrm{PY}}}{\rho} + \frac{2}{3}\frac{\beta p_c^{\mathrm{PY}}}{\rho}. \tag{8}$$

2. An excess chemical potential

For the excess chemical potential for the component i, we use a closed-form expression [18, 19]

$$\beta\mu_i^e \approx \beta\mu_i^{\mathrm{HNC}} + \sum_{j=1}^{2}\rho_j \int d\mathbf{r}\Big(B_{ij} + \frac{2h_{ij}}{3}B_{ij}\Big), \tag{9}$$

where $\beta\mu_i^{\mathrm{HNC}}$ is the hypernetted chain (HNC)-type expression for the excess chemical potential with appropriate bridge function B_{ij},

$$\beta\mu_i^{\mathrm{HNC}} = \sum_{j=1}^{2}\rho_j \int d\mathbf{r}\Big(\frac{1}{2}h_{ij}^2 - c_{ij} - \frac{1}{2}h_{ij}c_{ij}\Big). \tag{10}$$

Note that an analytical expression (9) for the excess chemical potential can be used for any bridge functions since it does not require the explicit forms of them.

3. An excess free energy

Once we have the values of the compressibility factor $Z \equiv \beta p/\rho$ and the excess chemical potential $\beta\mu_i^e$, we can compute the excess Helmholtz free energy per particle using a following Euler equation of thermodynamics

$$\beta a^e = \sum_{i=1}^{2} x_i \beta\mu_i^e - Z + 1. \tag{11}$$

III. RESULTS AND DISCUSSION

In our calculation we chose a component 1 with a diameter σ_1 as a reference particle, which is a larger component of binary HS mixture, that is, $(\sigma_1 > \sigma_2)$, and a packing fraction η is given as $\eta = (\pi/6)\rho(x_1\sigma_1^3 + x_2\sigma_2^3)$. A simple Picard iterative method for solving the SSOZ equation (1) was employed, and the numerical tolerance for the root-mean-squared residual of the indirect correlation functions during successive was set at $10^{-8}\sigma_1$. All calculations were performed with the same number of grid points, $N = 16384$, and a length parameter, $L = 32\sigma_1$. We note that since the IE approach is an implicit method of the statistical mechanics, we do not consider the number of particles involved in the system.

We first performed 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. In Table I shows numerical result for the

EOSs and their comparisons with an accurate MD values [11]. Looking at the PY values in columns 2 and 3 the virial EOS underestimates the MD values (last column), while the compressibility EOS overestimates them. However, the BMCSL interpolation technique presents very good values (column 4). Column 5 shows the virial EOS values from the MS approximation, which are quite comparable against the BMCSL EOS and MD values.

TABLE I. Values of virial, compressibility, and BMCSL EOSs from the PY and MS approximations at various values of a packing fraction η, and $x_1 = 0.5$, and $\sigma_2/\sigma_1 = 0.5$ and MD results [11].

η	$\beta p_v^{\rm PY}/\rho$	$\beta p_c^{\rm PY}/\rho$	$\beta p^{\rm BMCSL}/\rho$	$\beta p_v^{\rm MS}/\rho$	MD [11]
0.15	1.77	1.78	1.78	1.77	1.7773
0.25	2.70	2.80	2.77	2.74	2.7642
0.35	4.23	4.67	4.54	4.47	4.5362
0.45	7.09	8.43	7.99	7.77	7.9623

In Table II we have compared our numerical values of the excess chemical potential for two components with the MD values [11]. In both approximations our values were obtained with the analytical expression (9). The MS values (columns 3 and 6) are better than the PY ones (columns 2 and 5), and are close to the MD values (columns 4 and 7) with an increase of η.

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

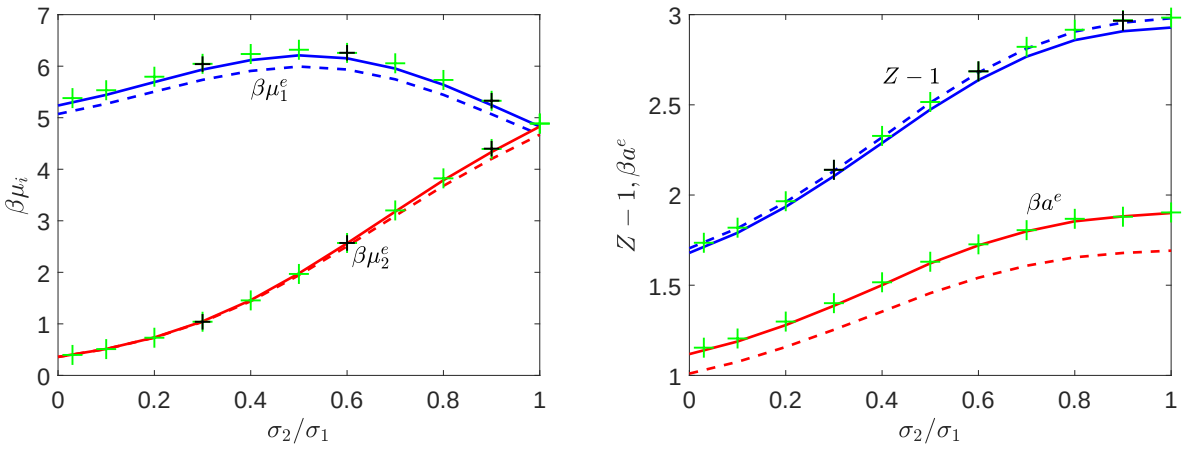
η	$\beta\mu_1^e$ (PY)	$\beta\mu_1^e$ (MS)	MD [11]	$\beta\mu_2^e$ (PY)	$\beta\mu_2^e$ (MS)	MD [11]
0.15	2.07	2.08	2.1070	0.73	0.74	0.7378
0.25	4.37	4.48	4.5322	1.46	1.48	1.4684
0.35	8.19	8.57	8.6696	2.55	2.62	2.5924
0.45	15.6	16.3	16.1404	4.37	4.54	4.4099

Table III demonstrates numerical values of the excess Helmholtz free energy calculated in the PY and MS approximations using the thermodynamic expression (11) against the MD values [11]. In evaluating βa^e in the PY approximation, we used values of $\beta p^{\rm BMCSL}/\rho$. Our results are in good agreement with the MD values up to $\eta = 0.35$. At $\eta = 0.45$ our PY value is lower than the MD value, while the MS one is slightly higher than it. Note that our all results shown in tables are independent on computational parameters N and L.

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

η	βa^e (PY)	βa^e (MS)	MD [11]
0.15	0.62	0.64	0.6451
0.25	1.15	1.24	1.2361
0.35	1.83	2.13	2.0939
0.45	3.00	3.67	3.3129

After above calculations, we continued our numerical experiments of thermodynamic quantities for a 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. Our findings as a function of σ_2/σ_1 at $\eta = 0.3$ and $x_1 = 0.5$ are presented in Figure 1, while those as functions of x_1 at $\eta = 0.3$ and $\sigma_2/\sigma_1 = 0.5$, and η at $\sigma_2/\sigma_1 = 0.5$ and $x_1 = 0.5$ have been exhibited in Figures 2 and 3 respectively. In all plots a dashed and solid curves are obtained from the PY and MS respectively. Black cross in the plots denotes the MC result [9], while green ones presents the MD data [11].

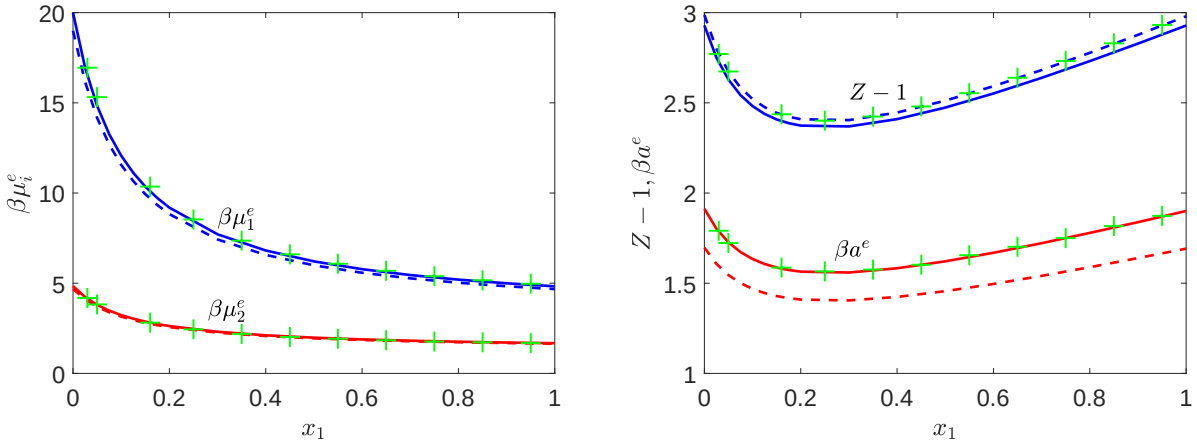


(a) (b)

FIG. 1. Results from the PY and MS approximations are shown with a solid and dashed 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 green crosses show the MC [9] and MD [11] simulations, respectively.

The plots of $\beta\mu_1^e$ for component 1 from the PY approximation shown as dashed curves

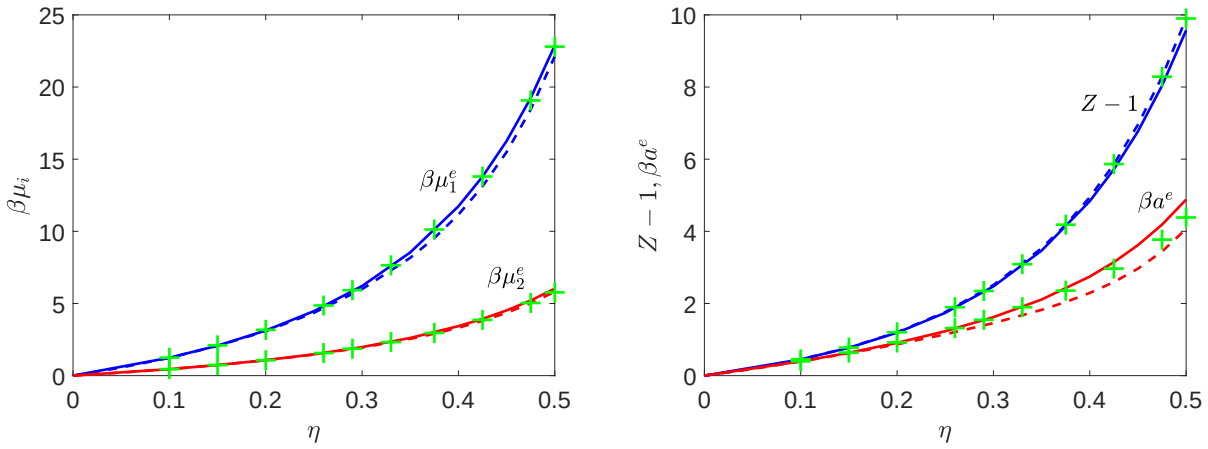
in all panels (1a-3a) show noticeable differences which look like an expected pattern shown in Table 2. However, the PY values of $\beta\mu_2^e$ follow the MD and MC simulations. The MS values for excess chemical potential for two components are almost indistinguishable from the MD and MC simulations. The compressibility factor $Z-1$ obtained from the PY and MS approximations closely follow the MD values (panels 1b-3b). Note that the plots of the excess Helmholtz free energy βa^e from the PY approximation show very visible differences which are related mostly to the underestimated values of $\beta\mu_1^e$. However the MS values for βa^e are generally in good agreement with the MD data, except for the case of a larger η (panel 3b).



(a) (b)

FIG. 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 $\sigma_2/\sigma_1 = 0.5$. Green crosses show the MD [11] simulations.

We say that a reason why the MS values for the excess chemical potential and compressibility factor are in good agreement with those from the MD data can be connected to a fact that the correlation functions obtained in this approximation might be as good as those from simulation data [21]. We here note that a similar discussion had also been given by Malijevsky *et al.* [15] in which they stated that when compared the pair distribution functions from the MS, PY and HNC closures with the MC simulation data, the the MS closure is the best among them.



(a) (b)

FIG. 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 $\sigma_2/\sigma_1 = 0.5$. Green crosses show the MD [11] simulations.

IV. CONCLUSIONS

In this work we have solved the SSOZ integral equation for various binary sets of the HS mixtures using the PY and the MS approximations. We have calculated the EOS with a virial and compressibility ways and the BMCSL technique in the PY approximation. Obviously, the BMCSL EOS has worked better than the virial and compressibility EOSs in this approximation. We computed the virial EOS when the MS bridge function is used. The excess chemical potential has been evaluated with an analytical expression while the excess Helmholtz free energy for the system is computed with a thermodynamic expression. We have compared our findings for thermodynamic quantities with the accurate MC and MD values. From these comparisons, it has been shown that results from the MS approximation are in better agreement with the MD values than those from the PY approximation. Finally, we note that the IE theory has worked successfully not only at moderate and high densities but also for asymmetric hard-sphere mixtures.

V. ACKNOWLEDGMENS

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