

Simple analytic equations of state for hard-core single and double Yukawa fluids and mixtures based on second-order Barker-Henderson perturbation theory

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A simple analytic expression with high precision for the radial distribution function of hard spheres is proposed. The form of the expression has been carefully selected to combine the well-known Camahan-Starling equation of state in it and satisfy the limit condition at low density, its simplicity and precision is superior to the well-known Percus-Yevick expression. The coefficients contained in the expression have been determined by fitting the Monte Carlo data for the first coordination shell, and by fitting both the Monte Carlo data and the numerical results of the Percus-Yevick expression for the second coordination shell. The expression has been applied to develop simple analytic equations of state for the hard-core single, double Yukawa fluids, and the hard-core Yukawa mixtures. The comparisons show that the agreement of our model with the computer simulation data is slightly better than the mean spherical approximation and other analytic models.

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I. INTRODUCTION

The theory of simple fluids with spherical potentials is rather well developed and little remains to be done as far as improving the agreement with known experiments (real life and computer simulations). However, most of these theoretical models involve extensive numerical computations and are often not practical for obtaining quick and accurate results for real fluids. In recent years, there has been growing interest in developing analytical expressions that not only are simpler to handle, but also give physical insights that could provide a basis for applications and extensions to more complicated fluid systems. The hard-core Yukawa (HCY) and hard-core double Yukawa (HCDY) fluids are fairly important since they have been widely used to research the normal fluids [1], the electrolyte solutions [2], the micromulsion [3,4], the colloid-polymer mixtures [5], the C_{60} system [6–8], and even real charged protein molecules (as colloid particles) [9,10]. Although people have obtained an analytical solution of the mean spherical approximation (MSA) for the HCY and HCDY fluid [11], the solution is given in terms of a set of simultaneous complex nonlinear equations. The concrete numerical calculations also is rather formidable.

The perturbation theories such as the Barker-Henderson (BH) [12] and the Weeks-Chandler-Anderson [13] are most frequently used in the research of thermodynamic properties for fluids. The perturbation theories require knowledge of the equation of state (EOS) and the radial distribution function (RDF) of a reference hard-sphere fluid. For this fluid, the Camahan-Starling (CS) EOS [14] combines simplicity and accuracy. As for the RDF, there are available analytical expressions from the solution of the Percus-Yevick (PY) integral equation [15,16]. However, the Laplace transformation of PY RDF is simple enough, its derivatives and the expression in coordinate space are too complicated to be convenient for practical applications. This results in the perturbation schemes having manifestly failed to provide a generally analytic and applicable EOS even for the simplest square-well or Sutherland fluids. Although for the HCY and HCDY

fluids [1,17], people have developed analytical EOSs based on the perturbation theory and the PY RDF of hard spheres, the EOSs are fairly complicated for the complication of the derivative of Laplace transformation of PY RDF. For the HCY fluid, Mansoori and Kioussis also developed their analytic model [18], since the model takes further approximations within the MSA framework, its precision is slightly worse than the analytic solution of the MSA model, and also is less accurate than the nonanalytic perturbation theory.

Nowadays, modern computers are fast and some people may think that the direct use of PY RDF may not have many difficulties. But one who has made many numerical calculations may find that in some cases the complicated calculations may encounter severe difficulties. For example, in phase equilibria calculations, we may encounter numerical integration-differentiation mixing calculations, or must solve equations containing such mixing calculations. These calculations most probably are nonlinear. It is well known that nonlinear calculations for some parameter ranges may enter a chaotic state. The chaotic state is interesting for some subjects, but for equilibrium thermodynamics and statistic mechanics, it may result in nonphysical solutions and should be avoided. Since Wertheim proposed thermodynamic perturbation theories (TPT1 and TPT2) for complicated fluids [19,20], many EOSs of simple fluids have been extended to complicated fluids [3,21]. If an EOS for simple fluid is nonanalytic, the extended EOSs may become more complicated. And the nonlinear and chaotic problems may become more severe in phase equilibria calculations or other applications. Thus the analytic EOS is very meaningful and important for practical applications.

The primary goal of the paper has been to develop a simple analytic expression for the RDF of hard spheres in coordinate space, which can combine the simplicity, accuracy, and analyticity in it. Such an expression is believed to be very useful for many practical applications. By using the expression, most present perturbation theories may become simple analytic ones, and the expression has been applied to develop simple analytic EOS for the HCY and HCDY fluids

combining the BH perturbation theory [12]. The results herein have been generalized to the HCY mixture with equal diameters, without introducing any further computational difficulty.

In Sec. II, the analytic expression is proposed. In Sec. III, the analytic EOS for the HCY fluids are developed. In Sec. IV, the results are extended to the HCDY fluids and HCY mixtures. Finally, the numerical results are given and remarked in Sec. V.

II. DEVELOPMENT OF ANALYTIC RDF

The expression of the RDF we proposed is as follows:

$$g(x) = \begin{cases} 0, & x < 1 \\ 1 + \sum_{m=1}^3 \frac{\eta^m}{(1-\eta)^m} g_m(x), & 1 \leq x < 3, \\ 1, & x \geq 3 \end{cases} \quad (1)$$

where $\eta = \pi\rho d^3/6$ is the packing fraction corresponding to the number density ρ for spheres of diameter d , and x is the radial coordination reduced to the hard sphere diameter d . The expression in Eq. (1) has some theoretical foundations. First, it satisfies the limit at low density, $g(x)$ tends one as η tends zero and second, is in terms of the expression of $g(1)$ from the CS EOS [14], the obtained $g(1)$ can be reformulated as the following form:

$$g(1) = \frac{1-0.5\eta}{(1-\eta)^3} = 1 + \frac{2.5\eta}{(1-\eta)} + \frac{2\eta^2}{(1-\eta)^2} + \frac{0.5\eta^3}{(1-\eta)^3}. \quad (2)$$

It is obvious that the form of Eq. (1) is in accordance with Eq. (2).

It should be pointed out that the CS EOS is quite accurate at low and intermediate densities but at higher densities it starts to slightly deviate from computer simulation data. In the last decade the Kolafa and other equations have been shown having higher precision for a hard sphere system at higher densities [22]. However, Mulero *et al.* [23] have pointed out that such complicated EOSs only give out a good description for some properties of a hard sphere system but for other properties, they give out worse results. The most important reason for the research of a hard sphere system is it has been taken as the reference system for most of thermodynamic perturbation theories, but Mulero *et al.* [23] also show that more complicated EOSs for hard spheres do not always give better results for the perturbation system. The simple CS EOS may give better results than most of the more complicated EOSs. Although the CS EOS slightly deviates from computer simulation data at higher densities, Ree [24] and Ross [25] have shown that a perturbation theory being applicable for fluids at high densities or all fluid densities will most probably be a variational theory. For such variational theory the packing fraction η may always take finite values which make the CS EOS more appropriate. Thus we have selected the CS EOS as a foundation in this work.

TABLE I. Determined coefficients C_{mn} and D_{mn} contained in the analytic expression of radial distribution function of hard spheres.

m	n					
	0	1	2	3	4	
C_{mn}	1	2.5	-0.1603	-1.5986	0.7212	-0.094
	2	2	-4.5491	-0.8231	1.8163	-0.346
	3	0.5	-5.8642	9.5502	-4.4809	0.633
D_{mn}	1	-0.34	-0.3419	1.0545	-0.5302	0.074
	2	1	3.5266	-5.8048	2.3145	-0.254
	3	-0.29	-2.8558	2.7126	-0.3177	-0.106

In previous works [26–29], people tend to directly expand the relevant functions of coordination $g_m(x)$ as polynomials of x . Such expansions are slowly convergent. In order to reach an acceptable fitting precision, Largo and Solana have to retain 128 terms in their expansion [26], and the expansion of Zhang only retaining several terms results in fairly poor fitting precision [27–29]. Instead of expanding $g_m(x)$ as polynomials of x , we proposed expanding $g_m(x)$ as polynomial of nonlinear base functions

$$g_m(x) = \begin{cases} \sum_{n=0}^4 C_{mn}(s-s^{-4})^n, & 1 \leq x < 2 \\ \sum_{n=0}^4 D_{mn}(s-s^{-7})^n, & 2 \leq x < 3, \end{cases} \quad (3)$$

here

$$s = \begin{cases} \exp(x-1), & 1 \leq x < 2 \\ \exp(x-2), & 2 \leq x < 3. \end{cases} \quad (4)$$

Such expansions are rapidly convergent, and we find that retaining five terms can give out best fitting results.

In order to determine six coefficients C_{m0} and D_{m0} , we need the expressions for $g(1)$ and $g(2)$. The expression for $g(1)$ is given in Eq. (2), and the expression for $g(2)$ is determined by fitting the MC data [30] at $x=2$ and is given by

$$g(2) = 1 - \frac{0.34\eta}{(1-\eta)} + \frac{\eta^2}{(1-\eta)^2} - \frac{0.29\eta^3}{(1-\eta)^3}. \quad (5)$$

Comparing Eq. (3) with Eqs. (2) and (5), C_{m0} and D_{m0} can be easily determined, other coefficients with $n \neq 0$ are determined by fitting the MC data [29] for C_{mn} and by fitting both the MC [30] and the PY data [31] for D_{mn} . The fitting procedure containing two steps is simple and straightforward. In the first step, we keep x invariable and fitted $g_m(x)$ at every x values. In the second step, we fitted $g_m(x)$ by using Eqs. (3) and (4). The fitted coefficients are listed in Table I. The totally average errors of the expression and the PY expression for 344 MC data points in the interval $1 \leq x < 2$ are 0.77 and 1.32%, respectively. The totally average error of the expression for 144 MC and 112 PY data points in the interval

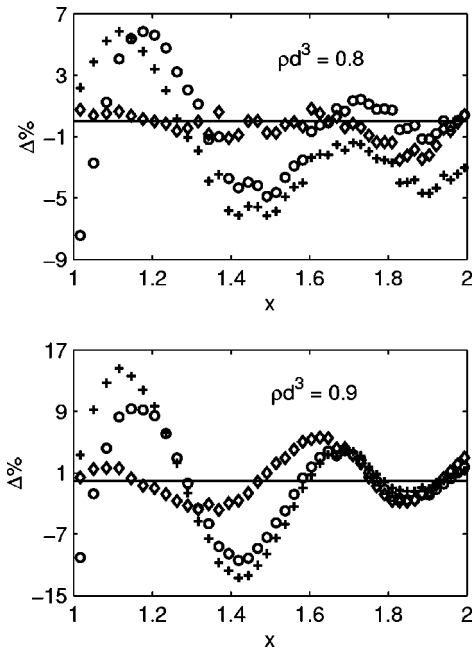


FIG. 1. Error comparison for the RDF of hard spheres at $\rho d^3 = 0.8$ and 0.9 . Open circles: Percus-Yevick expression; diamonds: analytic expression given in Eqs. (1) and (3); and crosses: Zhang's expression from Refs. [24–26].

$2 \leq x < 3$ is 0.62% . The error comparison of our expression with PY expression in the most important range ($1 \leq x < 2$) contrast to the MC data is shown in Fig. 1. The figure shows that our expression gives fairly well and improved results as compared with the PY expression, especially near the contact.

The MC data used to determine the coefficients is from Barker and Henderson [30]. Although the data is slightly old, it is cited in many of the latest works [32,33]. We think this is true for several reasons. The most important is that such data is scarce because people would not like doing repeated work after Barker and Henderson [30]. The second is that the errors in a perturbation theory from RDF of reference hard spheres mainly comes from neighborhoods of the contact, once the CS EOS is used to determine the RDF at contact, the data from BH is acceptable. The third is the good agreement of the improved expression of Tang and Lu [33] with the MC data shows the MC data must have reasonably good precision.

It should be pointed out that in the development of analytical RDF, we cannot make Eq. (1) and its first-order derivative satisfy the continuous conditions at two discontinuous points $x=2$ and 3 , and also cannot make it satisfy the thermodynamic consistent condition. There are two reasons for this. First, most potentials for real fluids are rapidly decreased as the radial coordination x increased. The most important range for perturbation theories is the first coordination shell $1 \leq x < 2$. Second, the coefficients contained in Eq. (1) has been determined mainly by fitting the MC data, and the MC data must satisfy the consistent condition and other conditions. Although some approximations have been introduced in the development of Eq. (1), this is not important for the application of perturbation theories. Some of these facts

are well known and can be further confirmed in the following sections. For the HCY, HCDY fluids, and the HCY mixtures it can be shown that even supposing the RDF equals one for all other coordination shells except the first shell, the influence for the numerical results is very little.

Since the problem being disposed here is similar to Zhang's works [27–29], it is worthwhile to compare the expression of RDF developed in this paper with Zhang's. We think our expression has three advantages over Zhang's. First of all, although Zhang also considered the CS EOS, the decomposition of the expression of $g(1)$ from the CS EOS is as follows:

$$g(1) = \frac{1 - 0.5\eta}{(1 - \eta)^3} = \frac{1}{(1 - \eta)} + \frac{1.5\eta}{(1 - \eta)^2} + \frac{0.5\eta^2}{(1 - \eta)^3}. \quad (6)$$

This is obviously different from our Eq. (2). Because the expression only contains three terms, if one directly develops RDF from it, the precision may be largely limited. So Zhang has artificially added one term in Eq. (6) to make the RDF have following form:

$$\begin{aligned} g(x) &= \frac{1 - 0.5\eta}{(1 - \eta)^3} \\ &= \frac{1}{(1 - \eta)} + g_1(x) \frac{\eta}{(1 - \eta)^2} + g_2(x) \frac{\eta^2}{(1 - \eta)^3} \\ &\quad + g_3(x) \frac{\eta^3}{(1 - \eta)^4}, \end{aligned} \quad (7)$$

and the third coefficient $g_3(x)$ should satisfy the condition, $g_3(1) = 0$. However, in order to develop RDF from our decomposition in Eq. (2), we do not need to add any term artificially, and the RDF developed in Eq. (1) can be seen as the direct extension of Eq. (2), which comes from CS EOS. So the decomposition in Eq. (2) is more reasonable than Eq. (6). In fact, one can add more terms both in Eqs. (1) and (7), such as $g_4(x)\eta^4(1 - \eta)^{-4}$ with $g_4(1) = 0$, etc. But it is not necessary.

Second, the expressions for $g_m(x)$ given in Eq. (3) and Zhang's works [27–29] have different form. Zhang's expressions only are polynomials of reduced coordination x , but our Eq. (3) is polynomials of nonlinear base functions. Although Zhang's expressions are simpler than Eq. (3), it cannot reach high precision. In order to obtain enough high precision in the work of Largo and Solana [26], which is similar to Zhang's works, polynomials of x have been retained up to the 16th order. Since Zhang has only kept several low-order terms in the expressions of $g_m(x)$, the corresponding RDF indeed has very low precision. We have stated previously that the totally average errors of the present expression and the PY expression for 344 MC data points in the interval $1 \leq x < 2$ are 0.77 and 1.32% . We have made comparative calculations by using Zhang's RDF, and found the average error is 2.35% ; this is about two times the PY expression, and at least three times the present one. In Fig. 1, the error of Zhang's RDF is also compared with the two other expressions. The figure shows that the error of Zhang's RDF is

much larger than the other two expressions. Although the error at contact is negligible for it has considered the CS EOS, the error is enlightened dramatically once the radial coordination is slightly deviated from the contact, and the error mainly comes from the neighborhood of contact. Such a case is a serious disadvantage for the application of perturbation theories. This may result in the EOS based on Zhang's expression being less accurate.

At last, by using Zhang's expression, one only can derive analytical EOS for the minus power potentials because of the polynomial form of $g_m(x)$, for example, the Lennard-Jones and generalized Lennard-Jones potentials. But for exponential potentials or exponent-minus potentials, for example, Morse potential, Yukawa-type and Buckingham (exp-6) potentials, etc., it cannot provide analytic EOS any more. However, by using the present expression, one can derive analytic EOS for all above-mentioned potentials, and even other composed or modified potentials. In subsequent sections, we will develop analytical EOS for the hard-core single, double Yukawa fluids, and the mixtures based on the second-order BH perturbation theory. The same procedure can be easily applied to other potentials to develop corresponding analytic EOSs. Otherwise, in addition to the BH theory, by using the present expression, one also can develop analytical EOS based on the Ross perturbation theory [25]. The Ross perturbation theory is a variational theory. It has been shown to have the highest precision as compared with other perturbation theories for fluids at high temperature and density. Even for fluids at normal conditions, it can provide better results than many other perturbation theories. It has been widely used in the research on shock-compressed properties of materials [34,35]. Its main disadvantage lies in the variational procedure being too time-consuming and very inconvenient. In order to overcome these shortcomings, Tang *et al.* have alternatively developed a mean spherical approximation (MSA) theory [36–38]. However, the MSA theory also has some disadvantages that are more severe than the Ross theory. The most important is that the MSA theory is inapplicable to fluids at high temperature and density, and at other conditions, the theory only gives results comparable with the Ross theory or even poorer. If the Ross theory can provide an analytical EOS, it may have advantages as compared to other perturbation theories. The relevant works are forthcoming, and will be published elsewhere.

III. APPLICATION TO THE HCY FLUIDS

The HCY potential is as follows:

$$u(r) = \begin{cases} \infty, & r < d \\ -\varepsilon \left(\frac{d}{r}\right) \exp\left[\lambda\left(1 - \frac{r}{d}\right)\right], & r \geq d, \end{cases} \quad (8)$$

where ε measures the strength of the interaction, d is the diameter of the hard core of the molecules, and λ is a positive parameter that characterize the range of the interaction.

In the second-order Barker-Henderson perturbation theory [12,39], the excess free energy can be expressed in the following form:

$$\frac{F}{NkT} = \frac{F_0}{NkT} + \frac{F_1}{NkT} \frac{1}{T_r} + \frac{F_2}{NkT} \frac{1}{T_r^2}, \quad (9)$$

with $T_r = kT/\varepsilon$, where ε is the energy parameter of the potential. The subscript 0 refers to the hard-sphere reference fluid,

$$\begin{aligned} \frac{F_1}{NkT} &= -12\eta \int_1^\infty \exp[\lambda(1-x)]g(x)x dx \\ &= -12\eta \sum_{m=0}^3 \frac{\eta^m}{(1-\eta)^m} L_m(\lambda), \end{aligned} \quad (10)$$

$$\begin{aligned} \frac{F_2}{NkT} &= -6\eta Q \int_1^\infty \exp[2\lambda(1-x)]g(x)dx \\ &= -6\eta Q \sum_{m=0}^3 \frac{\eta^m}{(1-\eta)^m} M_m(2\lambda), \end{aligned} \quad (11)$$

where

$$Q = kT \left(\frac{\partial p}{\partial P} \right)_0 = \frac{(1-\eta)^4}{(1+2\eta)^2 - (4-\eta)\eta^3} \quad (12)$$

is the macrocompressibility factor [12,39], $L_m(\lambda)$ and $M_m(\lambda)$ are nondimensional auxiliary coefficients introduced here, which are independent on the temperature and density, and only dependent on the potential parameter λ , constants C_{mn} and D_{mn} .

$$L_0(\lambda) = \int_1^\infty \exp[\lambda(1-x)]x dx = \frac{1}{\lambda} + \frac{1}{\lambda^2}, \quad (13)$$

$$M_0(\lambda) = \int_1^\infty \exp[\lambda(1-x)]dx = \frac{1}{\lambda}, \quad (14)$$

$$\begin{aligned} L_m(\lambda) &= \int_1^3 \exp[\lambda(1-x)]g_m(x)x dx \\ &= \sum_{n=0}^4 \int_1^2 C_{mn} \exp[\lambda(1-x)](s-s^{-4})^n x dx \\ &\quad + \sum_{n=0}^4 \int_2^3 D_{mn} \exp[\lambda(1-x)](s-s^{-7})^n x dx. \end{aligned} \quad (15)$$

The integration can be easily evaluated, and we obtained

$$L_m(\lambda) = \sum_{n=0}^4 \sum_{l=0}^n \frac{n!}{l!(n-l)!} (-)^l A_{mnl}(\lambda), \quad (16)$$

where

$$\begin{aligned} A_{mnl}(\lambda) &= C_{mn} \int_1^2 \exp[(n-5l-\lambda)(x-1)] x dx \\ &+ D_{mn} e^{-\lambda} \int_2^3 \exp[(n-8l-\lambda)(x-2)] x dx \\ &= C_{mn} W_1(n-5l-\lambda) + D_{mn} e^{-\lambda} W_2(n-8l-\lambda), \end{aligned} \quad (17)$$

and

$$\begin{aligned} W_1(\alpha) &= \left(\frac{2}{\alpha} - \frac{1}{\alpha^2} \right) (e^\alpha - 1) + \frac{1}{\alpha} \\ W_2(\alpha) &= \left(\frac{3}{\alpha} - \frac{1}{\alpha^2} \right) (e^\alpha - 1) + \frac{1}{\alpha}, \end{aligned} \quad (18)$$

$$\lim_{\alpha \rightarrow 0} W_1(\alpha) = \frac{3}{2}, \quad \lim_{\alpha \rightarrow 0} W_2(\alpha) = \frac{5}{2}. \quad (19)$$

By the same way, we have

$$\begin{aligned} M_m(\lambda) &= \int_1^3 \exp[\lambda(1-x)] g_m(x) dx \\ &= \sum_{n=0}^4 \int_1^2 C_{mn} \exp[\lambda(1-x)] (s-s^{-4})^n dx \\ &+ \sum_{n=0}^4 \int_2^3 D_{mn} \exp[\lambda(1-x)] (s-s^{-7})^n dx, \end{aligned} \quad (20)$$

or

$$M_m(\lambda) = \sum_{n=0}^4 \sum_{l=0}^n \frac{n!}{l!(n-l)!} (-)^l B_{mnl}(\lambda) \quad (21)$$

$$\begin{aligned} B_{mnl}(\lambda) &= C_{mn} \int_1^2 \exp[(n-5l-\lambda)(x-1)] dx \\ &+ D_{mn} e^{-\lambda} \int_2^3 \exp[(n-8l-\lambda)(x-2)] dx \\ &= \frac{C_{mn}}{(n-5l-\lambda)} [\exp(n-5l-\lambda) - 1] \\ &+ \frac{D_{mn} e^{-\lambda}}{(n-8l-\lambda)} [\exp(n-8l-\lambda) - 1]. \end{aligned} \quad (22)$$

The compressibility factor can be obtained from Eq. (11) in the form

$$\frac{PV}{NkT} = \eta \frac{\partial}{\partial \eta} \left(\frac{F}{NkT} \right) = \frac{P_0 V}{NkT} + \frac{P_1 V}{NkT} \frac{1}{T_r} + \frac{P_2 V}{NkT} \frac{1}{T_r^2}, \quad (23)$$

where

$$\frac{P_1 V}{NkT} = -12 \eta \sum_{m=0}^3 L_m(\lambda) \left(1 + \frac{m}{1-\eta} \right) \frac{\eta^m}{(1-\eta)^m}, \quad (24)$$

$$\frac{P_2 V}{NkT} = -6 \eta Q \sum_{m=0}^3 M_m(2\lambda) \left[1 + \frac{m}{1-\eta} + \frac{\eta}{Q} \frac{\partial Q}{\partial \eta} \right] \frac{\eta^m}{(1-\eta)^m}, \quad (25)$$

and

$$\frac{\eta}{Q} \frac{\partial Q}{\partial \eta} = - \frac{\eta(8+20\eta-4\eta^2)}{(1-\eta)[(1+2\eta)^2 - (4-\eta)\eta^3]}. \quad (26)$$

The excess internal energy is

$$\frac{U}{NkT} = -T \frac{\partial}{\partial T} \left(\frac{F}{NkT} \right) = \frac{F_1}{NkT} \frac{1}{T_r} + \frac{F_2}{NkT} \frac{2}{T_r^2}. \quad (27)$$

IV. EXTENSION TO THE HCDY FLUIDS AND THE HCY MIXTURES

Now we extend these formulas to the HCDY fluids and the HCY mixtures. The HCDY potential is as follows [11,17]:

$$u(r) = \begin{cases} \infty, & r < d \\ -\varepsilon \left(\frac{d}{r} \right) \left\{ \exp \left[\lambda_1 \left(1 - \frac{r}{d} \right) \right] - \exp \left[\lambda_2 \left(1 - \frac{r}{d} \right) \right] \right\}, & r \geq d. \end{cases} \quad (28)$$

λ_1 and λ_2 are positive parameters that characterize the range of the attractive and repulsive parts of the potential. By substituting the HCDY potential into the BH perturbation theory, we found most of the previous equations are applicable, only the equations for F_i/NkT and P_iV/NkT should be changed to the following form:

$$\begin{aligned} \frac{F_1}{NkT} &= -12\eta \int_1^\infty \{\exp[\lambda_1(1-x)] \\ &\quad - \exp[\lambda_2(1-x)]\} g(x) x dx \\ &= -12\eta \sum_{m=0}^3 \frac{\eta^m}{(1-\eta)^m} [L_m(\lambda_1) - L_m(\lambda_2)], \quad (29) \end{aligned}$$

$$\begin{aligned} \frac{F_2}{NkT} &= -6\eta Q \int_1^\infty \{\exp[\lambda_1(1-x)] \\ &\quad - \exp[\lambda_2(1-x)]\}^2 g(x) dx \\ &= -6\eta Q \sum_{m=0}^3 \frac{\eta^m}{(1-\eta)^m} \\ &\quad \times [M_m(2\lambda_1) - 2M_m(\lambda_1 + \lambda_2) + M_m(2\lambda_2)], \quad (30) \end{aligned}$$

and

$$\frac{P_1V}{NkT} = -12\eta \sum_{m=0}^3 \left(1 + \frac{m}{1-\eta}\right) \frac{\eta^m}{(1-\eta)^m} [L_m(\lambda_1) - L_m(\lambda_2)], \quad (31)$$

$$\begin{aligned} \frac{P_2V}{NkT} &= -6\eta Q \sum_{m=0}^3 \left[1 + \frac{m}{1-\eta} + \frac{\eta}{Q} \frac{\partial Q}{\partial \eta}\right] \frac{\eta^m}{(1-\eta)^m} \\ &\quad \times [M_m(2\lambda_1) - 2M_m(\lambda_1 + \lambda_2) + M_m(2\lambda_2)]. \quad (32) \end{aligned}$$

For the HCY mixtures with equal diameters [40]

$$u_{ij}(r) = \begin{cases} \infty, & r < d \\ -\varepsilon_{ij} \left(\frac{d}{r}\right) \exp\left[\lambda_{ij} \left(1 - \frac{r}{d}\right)\right], & r \geq d, \end{cases} \quad (33)$$

if defining the reduced temperature in Eq. (9) is $T_r = kT/\varepsilon_{11}$, we also found only the equations for F_i/NkT and P_iV/NkT should be changed to the following form [39]:

$$\begin{aligned} \frac{F_1}{NkT} &= 2\pi\rho \sum_i \sum_j y_i y_j \int_d^\infty [u_{ij}(r)/\varepsilon_{11}] g(r) r^2 dr \\ &= -12\eta \sum_i \sum_j y_i y_j (\varepsilon_{ij}/\varepsilon_{11}) \\ &\quad \times \int_1^\infty \exp[\lambda_{ij}(1-x)] g(x) x dx \\ &= -12\eta \sum_{m=0}^3 \frac{\eta^m}{(1-\eta)^m} \left[\sum_i \sum_j y_i y_j (\varepsilon_{ij}/\varepsilon_{11}) L_m(\lambda_{ij}) \right], \quad (34) \end{aligned}$$

$$\begin{aligned} \frac{F_2}{NkT} &= -\pi\rho Q \beta^2 \sum_i \sum_j y_i y_j \int_d^\infty [u_{ij}(r)/\varepsilon_{11}]^2 g(r) r^2 dr \\ &= -6\eta Q \sum_i \sum_j y_i y_j (\varepsilon_{ij}/\varepsilon_{11}) \\ &\quad \times \int_1^\infty \exp[2\lambda_{ij}(1-x)] g(x) dx \\ &= -6\eta Q \sum_{m=0}^3 \frac{\eta^m}{(1-\eta)^m} \\ &\quad \times \left[\sum_i \sum_j y_i y_j (\varepsilon_{ij}/\varepsilon_{11})^2 M_m(2\lambda_{ij}) \right]. \quad (35) \end{aligned}$$

and

$$\begin{aligned} \frac{P_1V}{NkT} &= -12\eta \sum_{m=0}^3 \left(1 + \frac{m}{1-\eta}\right) \frac{\eta^m}{(1-\eta)^m} \\ &\quad \times \left[\sum_i \sum_j y_i y_j (\varepsilon_{ij}/\varepsilon_{11}) L_m(\lambda_{ij}) \right], \quad (36) \end{aligned}$$

$$\begin{aligned} \frac{P_2V}{NkT} &= -6\eta Q \sum_{m=0}^3 \left[1 + \frac{m}{1-\eta} + \frac{\eta}{Q} \frac{\partial Q}{\partial \eta}\right] \frac{\eta^m}{(1-\eta)^m} \\ &\quad \times \left[\sum_i \sum_j y_i y_j (\varepsilon_{ij}/\varepsilon_{11})^2 M_m(2\lambda_{ij}) \right]. \quad (37) \end{aligned}$$

V. NUMERICAL RESULTS AND CONCLUSIVE REMARKS

In this section, we present the numerical results for thermodynamic properties of the HCY, HCDY fluids, and the HCY mixtures based on the equations derived in the previous sections (S1 and S2). In all of our calculations, we have considered two cases. The first case is to use the integrated expression of RDF of hard spheres in Eqs. (1) and (3), and consider the contribution of D_{mn} terms (S1). The second case is to use the simplified expression of RDF in Eqs. (1) and (3) eliminating D_{mn} terms, and to not consider the contribution of D_{mn} terms (S2). All of our calculated results listed in the following tables have shown that the difference between the two cases with and without D_{mn} terms is negligible. The fact further confirmed the statement in Sec. II, where we have pointed out it is not important in the applications of the per-

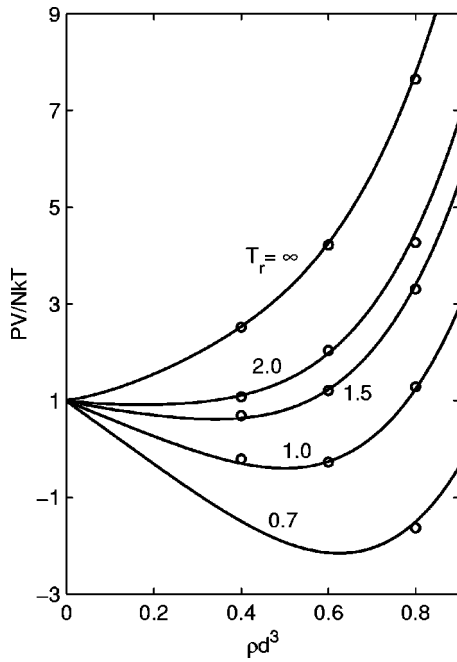


FIG. 2. Values of PV/NkT calculated in this work as a function of the reduced density ρd^3 for the HCY fluid with $\lambda = 1.8$. The curves are isotherms as labeled with T_r , the reduced temperature. The difference between the curves with and without D_{mn} terms are invisible. The open circles are Monte Carlo values.

turbation theories that the expression of RDF of hard spheres in Eq. (1) and its first-order derivative do not satisfy the continuous conditions at two discontinuous points $x=2$ and 3 , and do not satisfy the thermodynamic consistent condition.

The numerical results for HCY fluids have been compared with the MC, the MSA from energy equation (MSAE), the exponential approximation (EXP), the nonanalytical perturbation theory (NPT), and the Mansoori-Kioussis (MK) model [18]. The numerical results for HCDY have been

TABLE III. As for Table II, but for $-U/N\epsilon$, where U is the excess internal energy. This is the same for all the following tables and figures.

ρd^3	kT/ϵ	MC	MSA	EXP	NPT	MK	S1	S2
0.4	∞	2.495	2.513	2.495	2.495	2.513	2.514	2.511
	2.0	2.583	2.568	2.592	2.552	2.554	2.608	2.605
	1.5	2.622	2.594	2.638	2.572	2.567	2.639	2.637
	1.0	2.832	2.665	2.766	2.610	2.590	2.702	2.699
0.6	∞	3.975	3.995	3.975	3.975	3.995	3.999	3.986
	2.0	4.030	4.017	4.037	4.006	4.014	4.071	4.058
	1.5	4.051	4.026	4.063	4.017	4.020	4.095	4.082
	1.0	4.073	4.050	4.125	4.039	4.032	4.144	4.130
0.8	∞	5.573	5.602	5.573	5.573	5.602	5.592	5.570
	2.0	5.622	5.608	5.611	5.589	5.607	5.638	5.616
	1.5	5.630	5.611	5.625	5.594	5.609	5.654	5.632
	1.0	5.635	5.616	5.655	5.605	5.613	5.685	5.663
	0.7	5.658	5.624	5.699	5.699	5.618	5.725	5.703

compared with the MC, the MSAE. The numerical results for HCY mixtures have been compared with the molecular dynamic simulation data (MD) and the MSAE. All calculations have been obtained with $\lambda = 1.8$ for HCY fluid, with $\lambda_1 = 1.8$ and $\lambda_2 = 2$ for HCDY fluid [11]. For the equimolar HCY mixtures, the parameters are taken as $\lambda_{11} = \lambda_{12} = \lambda_{22} = 2.45$ with $\epsilon_{22} = 2\epsilon_{11}$ and different values of ratio $\epsilon_{12}/\epsilon_{11}$.

The calculated values of compressibility factor are plotted versus density in Fig. 2 for five different isotherms, and are compared with the MC and other models in Table II. The uncertainty in the MC values of PV/NkT is approximately 0.05. The agreement of the present calculations with both MC and other models is excellent and slightly better than the MK model. The numerical results for the values of the excess internal energy $-U/N\epsilon$ are listed in Table III, which are also in very good agreement with the corresponding MC and

TABLE II. Values of PV/NkT for the HCY fluid with $\lambda = 1.8$. MC: Monte Carlo simulation data; MSAE: calculated by the MSA from the energy route; EXP: exponential approximation; NPT: nonanalytical perturbation theory; MK: Mansoori and Kioussis' model; S: analytical perturbation theory in this work; S1: considering D_{mn} terms; and S2: neglecting D_{mn} terms.

ρd^3	kT/ϵ	MC	MSAE	EXP	NPT	MK	S1	S2
0.4	∞	2.52	2.518	2.518	2.518	2.518	2.518	2.515
	2.0	1.08	1.122	1.114	1.123	1.101	1.106	1.113
	1.5	0.69	0.666	0.657	0.664	0.627	0.639	0.647
	1.0	-0.21	-0.229	-0.228	-0.246	-0.322	-0.291	-0.278
0.6	∞	4.22	4.283	4.283	4.283	4.283	4.283	4.279
	2.0	2.04	1.978	1.978	1.985	1.966	1.987	2.008
	1.5	1.21	1.219	1.222	1.226	1.196	1.230	1.258
	1.0	-0.27	-0.283	-0.259	-0.281	-0.343	-0.270	-0.229
0.8	∞	7.65	7.750	7.750	7.750	7.750	7.749	7.743
	2.0	4.27	4.433	4.446	4.459	4.428	4.480	4.465
	1.5	3.31	3.332	3.355	3.368	3.323	3.401	3.381
	1.0	1.29	1.137	1.190	1.195	1.114	1.259	1.229
	0.7	-1.63	-1.668	-1.544	-1.582	-1.721	-1.463	-1.506

TABLE IV. As for Table II, but for F/NkT , where F is the excess Helmholtz free energy, and this is the same for all the following tables and figures.

ρd^3	kT/ε	MSA	EXP	NPT	MK	S1	S2
0.4	∞	1.130	1.130	1.130	1.130	1.130	1.130
	2.0	-0.139	-0.151	-0.132	-0.127	-0.151	-0.149
	1.5	-0.569	-0.590	-0.559	-0.546	-0.588	-0.586
0.6	∞	2.042	2.042	2.042	2.042	2.042	2.042
	2.0	0.039	0.025	0.048	0.045	0.025	0.031
	1.5	-0.631	-0.654	-0.620	-0.621	-0.656	-0.647
0.8	∞	3.403	3.403	3.402	3.403	3.402	3.397
	2.0	0.600	0.588	0.613	0.602	0.595	0.606
	1.5	-0.334	-0.355	-0.318	-0.332	-0.346	-0.331
	1.0	-2.206	-2.247	-2.183	-2.199	-2.236	-2.214
	0.7	-4.164	-4.695	-4.586	-4.599	-4.681	-4.649

other models. The uncertainty in the MC values of $-U/N\varepsilon$ is approximately 0.005. Our numerical results for the excess Helmholtz free energy are listed in Table IV and are plotted in Fig. 3 versus density for four isotherms. There are no MC values of the Helmholtz free energy for comparison. However, it can be shown that the agreement of our results with the NPT are excellent and also in good agreement with other models.

In Table V, we listed the numerical results of $-U/N\varepsilon$ and

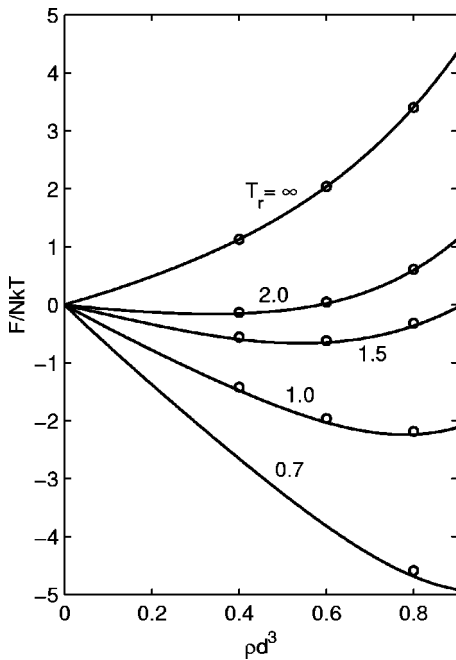


FIG. 3. Values of F/NkT calculated in this work as a function of the reduced density ρd^3 for four isotherms labeled with the appropriate value of T_r , where F is the excess Helmholtz free energy. The difference between the curves with and without D_{mn} terms are invisible. The open circles are the nonanalytic perturbation theory results of Henderson *et al.*

TABLE V. Values of PV/NkT and $-U/N\varepsilon$ for the HCDY fluid with $\lambda_1=1.8$ and $\lambda_2=2$.

kT/ε	ρd^3	$-U/N\varepsilon$			PV/NkT				
		MC	S1	S2	MC	MSAE	S1	S2	
0.3	0.3	0.221	0.223	0.222	1.23	1.23	1.23	1.23	
	0.4	0.295	0.296	0.296	1.55	1.54	1.54	1.55	
	0.5	0.367	0.369	0.367	2.07	2.06	2.07	2.08	
	0.6	0.439	0.438	0.437	2.88	2.86	2.90	2.92	
	0.7	0.509	0.507	0.504	4.13	4.09	4.16	4.18	
	0.8	0.577	0.572	0.569	6.01	5.95	6.03	6.00	
	0.9	0.644	0.636	0.637	8.85	8.79	8.72	8.52	
	0.7	0.3	0.220	0.221	0.221	1.65	1.65	1.65	1.65
		0.4	0.294	0.295	0.294	2.11	2.10	2.10	2.10
0.5		0.367	0.367	0.366	2.77	2.74	2.75	2.75	
0.6		0.439	0.438	0.436	3.72	3.67	3.69	3.70	
0.7		0.509	0.506	0.503	5.06	5.02	5.05	5.05	
0.8		0.577	0.571	0.568	7.00	7.00	7.01	7.00	
0.9		0.644	0.636	0.637	9.94	9.91	9.89	9.79	
1.5		0.3	0.220	0.220	0.220	1.82	1.82	1.82	1.82
		0.4	0.294	0.294	0.294	2.32	2.32	2.32	2.32
	0.5	0.367	0.367	0.366	3.03	3.02	3.02	3.03	
	0.6	0.439	0.438	0.436	4.04	4.00	4.01	4.01	
	0.7	0.509	0.506	0.503	5.43	5.39	5.40	5.40	
	0.8	0.577	0.571	0.568	7.41	7.39	7.41	7.40	
	0.9	0.644	0.636	0.637	10.37	10.35	10.34	10.30	

TABLE VI. Compressibility factors PV/NkT for the equimolar Lorentz-Berthelot HCY mixture with equal diameters at $\rho d^3 = 0.75$ and several values of the reduced temperature. MD: molecular dynamics.

T_r	MD	MSAE	S1	S2
0.77	-1.77	-2.20	-2.239	-2.205
1.0	-0.21	-0.27	-0.246	-0.219
1.25	1.09	1.08	1.105	1.126
2.5	3.88	3.83	3.845	3.855
5.0	5.29	5.23	5.234	5.239
10.0	5.97	5.93	5.933	5.939

TABLE VII. As for Table VI, but for $-U/NkT$.

T_r	MD	MSAE	S1	S2
0.77	7.817	7.403	7.542	7.517
1.0	5.746	5.634	5.749	5.730
1.25	4.540	4.486	4.568	4.553
2.5	2.241	2.228	2.253	2.245
5.0	1.116	1.111	1.118	1.115
10.0	0.557	0.555	0.557	0.555

TABLE VIII. Values of PV/NkT for the equimolar HCY mixture with equal diameters, at $kT/\varepsilon_{11}=1$ and $\rho d^3=0.75$, for several values of the ratio $\varepsilon_{12}/\varepsilon_{11}$.

$\varepsilon_{12}/\varepsilon_{11}$	MD	MSAE	S1	S2
2.0	-1.43	-1.65	-1.590	-1.558
1.7	-0.80	-0.94	-0.905	-0.876
1.41	-0.21	-0.27	-0.246	-0.219
1.35	0.00	-0.12	-0.097	-0.071
1.27	0.16	0.06	0.089	0.114
1.20	0.29	0.22	0.252	0.276

PV/NkT for the HCDY fluid. We also listed the MC data both for $-U/N\varepsilon$ and PV/NkT , because there are no MSA results for $-U/N\varepsilon$, so we only listed the MSA results for PV/NkT . The table shows that the agreement of our results with the MC data and the MSA results are excellent.

Tables VI–IX list the numerical results of PV/NkT and $-U/NkT$ for an equimolar HCY mixture. For Tables VI and VII, the calculations were performed for several reduced temperatures $T_r=kT/\varepsilon_{11}$ and a fixed reduced density $\rho d^3=0.75$ with $\varepsilon_{12}/\varepsilon_{11}=\sqrt{2}$ (the value corresponds to a Lorentz-Berthelot mixture). For Tables VIII and IX, the calculations were performed at $T_r=1$ and $\rho d^3=0.75$ for several values of the ratio $\varepsilon_{12}/\varepsilon_{11}$, the other interaction parameters being the same as for Tables VI and VII. The MD and MSAE data also have been listed in the tables for comparison. The uncertainty in the MD data is about 0.05 for PV/NkT and about 0.001 for $-U/NkT$. These tables show that both the MSAE and our results are in good agreement with the MD data, and our results even are slightly better than the MSAE results.

TABLE IX. As for Table VIII, but for $-U/NkT$.

$\varepsilon_{12}/\varepsilon_{11}$	MD	MSAE	S1	S2
2.0	7.042	6.812	6.952	6.929
1.7	6.330	6.190	6.332	6.311
1.41	5.746	5.634	5.749	5.730
1.35	5.646	5.516	5.619	5.600
1.27	5.531	5.375	5.457	5.439
1.20	5.457	5.258	5.316	5.299

In summary, we have shown that it is possible to obtain simple analytical expression for the RDF of hard spheres with high precision by carefully selecting the fitting functions. The precision of the analytic expressions at the most important first shell is higher than the well-known PY expression. By using the expression, most of present perturbation theories can become simple analytical ones, and this has been implemented for the important HCY, HCDY fluids, and HCY mixtures. The above comparisons and results indicate that present models for the HCY, HCDY fluids, and HCY mixtures yield very good results for the thermodynamic properties. The extension to other potentials is straightforward and is to be done. Alternatively, thermodynamic properties of fluids with continuous potentials could be obtained from those of an equivalent HCDY fluid with its potential parameters suitably determined.

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