

# Monte Carlo and theoretical calculations of the first four perturbation coefficients in the high temperature series expansion of the free energy for discrete and core-softened potential models

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The first four perturbation coefficients in the expansion of the Helmholtz free energy in power series of the inverse of the reduced temperature for a number of potential models with hard-sphere cores plus core-softened and discontinuous tails are obtained from Monte Carlo simulations. The potential models considered include square-well, double square-well, and square-shoulder plus square-well, with different potential parameters. These simulation data are used to evaluate the performance of a traditional macroscopic compressibility approximation (MCA) for the second order coefficient and a recent coupling parameter series expansion (CPSE) for the first four coefficients. Comprehensive comparison indicates the incapability of the MCA for the second order coefficient in most non-stringent situations, and significance of the CPSE in accurately calculating these four coefficients.

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## I. INTRODUCTION

High temperature series expansion (hereafter abbreviated as HTSE) of free energy is on the basis of a class of perturbation theories constituting a successful approach to obtain the equilibrium properties of fluids and solids.<sup>1</sup> In many situations, truncation of the HTSE after the first-order term, giving rise to a first-order perturbation theory, provides satisfactory enough results. In other situations, particularly at low temperatures and especially for short-ranged potentials, higher-order terms need to be included.<sup>2</sup> The second-order Barker-Henderson (BH) perturbation theory based on a macroscopic compressibility approximation (MCA)<sup>3</sup> was one of the first attempts to go beyond first-order and since then has been frequently used. However, values of the second-order coefficient predicted by the MCA are unsatisfactory for some potential models.<sup>4,5</sup> On the other hand, convergence of the HTSE is not guaranteed at low enough temperatures, for which systems with very short-ranged potentials may remain in the fluid phase. This highlights a need for a better knowledge of the higher-order coefficients in the HTSE or, alternatively, to resort to a different kind of theory.

The first of these possibilities can be faced, to some extent, by means of Monte Carlo (MC) simulation, in the form that we will summarize in Sec. II. Concerning the second choice, perturbation theories, other than the HTSE, are still an appealing choice, as they are based on some reference system whose thermodynamic and structural properties are known accurately and often analytically. Within this context, one of us<sup>6</sup> derived quite recently an accurate perturbation formulation based on a coupling parameter series expansion (CPSE) that, in certain particular situations, can provide the perturbation coefficients of the HTSE. The availability of accu-

rate simulation data for these higher-order coefficients in the HTSE can help to test the performance of the CPSE in predicting these coefficients, which is vital to higher-order implementation of the HTSE.

Simulation data for the first- and second-order perturbation coefficients in the HTSE have been reported by several authors<sup>7-13</sup> for different potential models. In a recent work,<sup>14</sup> there have been obtained from Monte Carlo simulations the third- and fourth-order perturbation coefficients for square-well (SW) fluids with variable range. In this work we wish to gain insight into the efficacy of the Zhou CPSE<sup>6</sup> in predicting these coefficients and to this end we first determine from Monte Carlo simulations the first- to fourth-order perturbation coefficients for fluids interacting through square well potential and two core-softened (CS) potentials, respectively, and then both the Monte Carlo results and CPSE predictions are compared with each other. The main reason, that we investigate additionally two CS potentials, can be explained as follows. The CS potential is one kind of very important model potentials. It has been demonstrated that the CS potential system, i.e., the system with softening of the repulsive part of interparticle interaction, can effectively approximate real substances<sup>15</sup> by demonstrating some unusual phase transitions—transition between two crystal phases of the same symmetry, which ends in a critical point similar to the gas–liquid one and liquid–liquid phase transition (LLPT), and many features of common network-forming liquids such as water and silica, including polymorphism and thermodynamic anomalies. However, the reported studies examine the CS systems and relevant anomalies mainly by computer simulation,<sup>16</sup> and few theoretical investigations indicate how easily these artificial potentials can be tackled by traditional theories.<sup>17</sup> Consequently, the CS potentials may be better suited than other traditional potential models in demonstrating the potential of an approximate theory.

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Structure of the present paper is organized as follows: in Sec. II the potential models considered and simulation details are described, and the procedure used to calculate the coefficients of the HTSE in the framework of the CPSE is detailed; the results are collected and analyzed in Sec. III; and our conclusions are summarized in Sec. IV.

## II. MODELS AND METHODS

The model potentials considered are described as follows:

Square-well (SW) potential,

$$u(r) = \begin{cases} \infty, & r < \sigma \\ -\varepsilon, & \sigma \leq r \leq \lambda\sigma, \\ 0, & r > \lambda\sigma \end{cases} \quad (1)$$

where  $\varepsilon$  is an energy parameter of the potentials considered and  $\lambda$  is the potential width in units of the diameter  $\sigma$  of the hard sphere (HS).

Double square-well (DSW) potential,

$$u(r) = \begin{cases} \infty, & r < \sigma \\ -\delta\varepsilon, & \sigma \leq r \leq \lambda_1\sigma \\ -\varepsilon, & \lambda_1\sigma \leq r \leq \lambda_2\sigma \\ 0, & r > \lambda_2\sigma \end{cases} \quad (2)$$

Square-shoulder plus square-well (SSSW) potential,

$$u(r) = \begin{cases} \infty, & r < \sigma \\ \delta\varepsilon, & \sigma \leq r \leq \lambda_1\sigma \\ -\varepsilon, & \lambda_1\sigma \leq r \leq \lambda_2\sigma \\ 0, & r > \lambda_2\sigma \end{cases} \quad (3)$$

In Eqs. (2) and (3),  $\delta$  is a positive number, and is used to adjust the softness of the CS potentials considered;  $\lambda_1$  and  $\lambda_2$ , both in units of the HS diameter  $\sigma$ , serve to adjust the widths of different potential ranges.

The first of these potential models is perhaps the most widely used to test performance of approximate statistical mechanics theories and model real materials with success. The latter two are particularly interesting as they have been proposed to give account of the liquid-liquid transition in water, which in turn might explain the anomalous properties of water at low temperatures.<sup>18</sup>

In the HTSE an excess Helmholtz free energy per particle  $f_{ex}$  of a fluid with an intermolecular potential  $u(r)$  can be expressed as an expansion in power series of an inverse of reduced temperature  $T^* = k_B T / \varepsilon$ , where  $k_B$  is Boltzmann constant and  $T$  is the absolute temperature, in a form

$$\beta f_{ex} = \beta f_{ex-ref} + \sum_{n=1}^{\infty} \frac{a_n(\rho)}{T^{*n}}. \quad (4)$$

In this expansion,  $f_{ex-ref}$  is a Helmholtz free energy of a reference fluid, for the potential models considered presently, the HS fluid is a natural choice as the reference fluid, and corresponding  $f_{ex-ref}$  is obtained by integrating the well-known Carnahan-Starling equation of state.<sup>19</sup>  $a_n$  is the coefficient of

the  $n$ th perturbation term, and the first several can be obtained by means of simulations from the fluctuations of the perturbation energy as calculated in the reference system. The first four terms are given by<sup>7,20</sup>

$$a_1 = \frac{1}{N} \sum_i \langle N_i \rangle_0 u_1^*(r_i), \quad (5)$$

$$a_2 = -\frac{1}{2} \frac{1}{N} \sum_{i,j} [\langle N_i N_j \rangle_0 - \langle N_i \rangle_0 \langle N_j \rangle_0] u_1^*(r_i) u_1^*(r_j), \quad (6)$$

$$a_3 = \frac{1}{6} \frac{1}{N} \sum_{i,j,k} [\langle N_i N_j N_k \rangle_0 - 3 \langle N_i N_j \rangle_0 \langle N_k \rangle_0 + 2 \langle N_i \rangle_0 \langle N_j \rangle_0 \langle N_k \rangle_0] \times u_1^*(r_i) u_1^*(r_j) u_1^*(r_k), \quad (7)$$

$$a_4 = -\frac{1}{24} \frac{1}{N} \sum_{i,j,k,l} [\langle N_i N_j N_k N_l \rangle_0 - 4 \langle N_i N_j N_k \rangle_0 \langle N_l \rangle_0 - 3 \langle N_i N_j \rangle_0 \langle N_k N_l \rangle_0 + 12 \langle N_i N_j \rangle_0 \langle N_k \rangle_0 \langle N_l \rangle_0 - 6 \langle N_i \rangle_0 \langle N_j \rangle_0 \langle N_k \rangle_0 \langle N_l \rangle_0] u_1^*(r_i) u_1^*(r_j) u_1^*(r_k) u_1^*(r_l), \quad (8)$$

where  $N_i$  is the number of molecular distances in the interval  $(r_i, r_{i+1})$ , with  $\Delta r = r_{i+1} - r_i \ll \sigma$ ,  $i = 0, 1, \dots$ , angular brackets indicate averages, subscript 0 means that the averages are performed in the reference system, and  $a_3$ , where  $u_1(r)$  is the perturbation part of the potential considered, and is equal to  $u(r)$  subtracted by the HS potential.

For the particular case of a system with the SW potential,  $u_1^*(r) = -1$  within the potential well  $1 \leq x \leq \lambda$ , where  $x = r/\sigma$ , and the expressions of these perturbation terms take the simple form<sup>8</sup>

$$a_1 = -\frac{\langle M \rangle_0}{N}, \quad (9)$$

$$a_2 = -\frac{1}{2} \frac{1}{N} \langle (M - \langle M \rangle_0)^2 \rangle_0, \quad (10)$$

$$a_3 = -\frac{1}{6} \frac{1}{N} \langle (M - \langle M \rangle_0)^3 \rangle_0, \quad (11)$$

$$a_4 = -\frac{1}{24} \frac{1}{N} [\langle (M - \langle M \rangle_0)^4 \rangle_0 - 3 \langle (M - \langle M \rangle_0)^2 \rangle_0^2], \quad (12)$$

where  $M$  is the number of pairs separated by a distance  $x \leq \lambda$ . The expressions (5)–(12) can be evaluated from simulation in the HS reference system, as said before. Thus, using expressions (9)–(12), the terms up to  $n = 4$  for the SW fluid were obtained long time ago<sup>8</sup> for  $\lambda = 1.5$  and more recently<sup>14</sup> for  $1.1 \leq \lambda \leq 3.0$  with step 0.1. Expressions (5)–(8) are required for potential models with continuous tails as well as for potentials with a combination of several subwells or shoulders and wells, like DSW and SSSW potentials considered here. However, the calculations of the perturbation terms from simulations for  $n > 2$  for potentials with continuous tails is computationally very demanding and so, in general, only the first- and second-order perturbation coefficients have been reported

TABLE I. Simulation results of  $a_1$  to  $a_4$  for the SW fluids with different well widths. The numbers between parenthesis are the statistical uncertainties in the last decimal place.

$\rho^*$	$a_1$	$a_2$	$a_3$	$a_4$
$\lambda = 1.2$				
0.10	-0.1697	-0.0741(1)	-0.0201(2)	-0.0042(8)
0.20	-0.3792	-0.1413(1)	-0.0302(5)	-0.005(4)
0.30	-0.6365(1)	-0.1968(1)	-0.0313(6)	-0.008(5)
0.40	-0.9507	-0.2366(2)	-0.0283(6)	-0.003(8)
0.50	-1.3307	-0.2574(1)	-0.024(2)	-0.003(6)
0.60	-1.7852	-0.2596(2)	-0.017(2)	-0.00(1)
0.70	-2.3204	-0.2475(3)	-0.012(1)	-0.008(8)
0.80	-2.9372(1)	-0.2290(1)	-0.009(2)	-0.003(7)
0.90	-3.6276(1)	-0.2128(2)	-0.005(2)	-0.000(8)
$\lambda = 1.5$				
0.10	-0.5333	-0.1941(1)	-0.0550(7)	-0.025(6)
0.20	-1.1399	-0.2915(1)	-0.075(2)	-0.04(1)
0.30	-1.8156	-0.3209(2)	-0.074(2)	-0.03(2)
0.40	-2.5494	-0.3168(2)	-0.055(1)	-0.03(1)
0.50	-3.3227	-0.3086(2)	-0.029(2)	0.00(1)
0.60	-4.1086	-0.3077(4)	-0.011(1)	0.00(2)
0.70	-4.8724(1)	-0.3059(5)	-0.002(2)	0.00(1)
0.80	-5.5744(1)	-0.2854(7)	0.005(4)	0.00(1)
0.90	-6.1725(1)	-0.2390(5)	0.013(2)	0.01(2)
$\lambda = 2.0$				
0.10	-1.5053	-0.4467(3)	-0.235(2)	-0.22(3)
0.20	-3.0715	-0.5505(2)	-0.283(5)	-0.33(3)
0.30	-4.6622	-0.5458(2)	-0.181(2)	-0.22(3)
0.40	-6.2448	-0.5359(3)	-0.088(3)	-0.11(4)
0.50	-7.8001	-0.5505(6)	-0.053(4)	-0.01(3)
0.60	-9.3322	-0.5964(5)	-0.057(5)	-0.04(3)
0.70	-10.8790(1)	-0.6728(8)	-0.06(1)	-0.0(1)
0.80	-12.5170(1)	-0.756(2)	-0.05(2)	0.1(1)
0.90	-14.3477(3)	-0.800(2)	-0.00(2)	0.2(2)
$\lambda = 3.0$				
0.10	-5.4780(1)	-1.422(2)	-2.68(2)	-9.7(3)
0.20	-11.0207(1)	-1.594(1)	-3.17(2)	-15.0(7)
0.30	-16.6041(1)	-1.489(1)	-2.10(2)	-9.9(5)
0.40	-22.2073(1)	-1.398(2)	-1.06(3)	-4.4(3)
0.50	-27.8038(1)	-1.392(2)	-0.46(3)	-1.3(2)
0.60	-33.3744(1)	-1.479(2)	-0.21(4)	-0.5(4)
0.70	-38.9459(1)	-1.648(2)	-0.17(2)	-0.1(7)
0.80	-44.6359(4)	-1.855(5)	-0.1(1)	0(1)
0.90	-50.6304(4)	-2.04(1)	0.0(1)	0(2)

for a number of these potential models. An exception is a recent paper from us,<sup>21</sup> in which also the term for  $n = 3$  was reported for several potential models with continuous tails.

In this work, we have carried out simulations in the  $NVT$  ensemble of the reference HS fluid to obtain the values of  $a_1$  to  $a_4$  from expressions (5)–(8) for the potential models described above with different potential parameters. To be specific, for the SW fluids, the considered values of the potential parameter  $\lambda$  are 1.2, 1.5, 2.0, and 3.0, respectively; for the DSW fluids, three sets of parameter combinations are considered, they are set 1:  $\lambda_1 = 1.1$ ,  $\lambda_2 = 1.2$ , and  $\delta = 0.5$ ; set 2:  $\lambda_1 = 1.2$ ,  $\lambda_2 = 1.5$ , and  $\delta = 0.5$ ; and set 3:  $\lambda_1 = 1.4$ ,  $\lambda_2 = 2.0$ , and  $\delta = 0.5$ , respectively; for the SSSW fluids, the considered parameter combinations are set 1:  $\lambda_1 = 2.0$ ,  $\lambda_2 = 2.2$ , and  $\delta$

TABLE II. As in Table I, but for the DSW fluids with different well width combinations

$\rho^*$	$a_1$	$a_2$	$a_3$	$a_4$
$\lambda_1 = 1.1$ $\lambda_2 = 1.2$ $\delta = 0.5$				
0.10	-0.1306	-0.0494	-0.0129(1)	-0.0027(4)
0.20	-0.2904	-0.0959(1)	-0.0210(3)	-0.003(2)
0.30	-0.4845	-0.1376(1)	-0.0251(3)	-0.005(2)
0.40	-0.7178	-0.1734(1)	-0.0268(5)	-0.003(3)
0.50	-0.9948	-0.2030	-0.027(1)	-0.003(5)
0.60	-1.3176	-0.2282(1)	-0.027(1)	0.000(7)
0.70	-1.6846	-0.2526(2)	-0.027(1)	-0.01(1)
0.80	-2.0873	-0.2785(3)	-0.030(1)	0.00(1)
0.90	-2.5067(1)	-0.3035(3)	-0.034(4)	-0.01(1)
$\lambda_1 = 1.2$ $\lambda_2 = 1.5$ $\delta = 0.5$				
0.10	-0.4484	-0.1549(1)	-0.0413(3)	-0.014(3)
0.20	-0.9504	-0.2493(1)	-0.056(1)	-0.019(9)
0.30	-1.4973	-0.3080(2)	-0.054(1)	-0.01(2)
0.40	-2.0740	-0.3550(1)	-0.042(1)	-0.01(1)
0.50	-2.6573	-0.4029(3)	-0.031(3)	0.02(2)
0.60	-3.2160	-0.4450(5)	-0.026(3)	0.01(4)
0.70	-3.7123(1)	-0.4602(7)	-0.017(4)	0.01(4)
0.80	-4.1058(1)	-0.429(1)	0.000(7)	0.01(4)
0.90	-4.3587(2)	-0.3570(7)	0.018(5)	0.03(3)
$\lambda_1 = 1.4$ $\lambda_2 = 2.0$ $\delta = 0.5$				
0.10	-1.3072	-0.3871(2)	-0.150(2)	-0.11(2)
0.20	-2.6421	-0.5327(2)	-0.148(4)	-0.13(3)
0.30	-3.9673	-0.5983(3)	-0.069(3)	-0.06(3)
0.40	-5.2510	-0.6419(3)	-0.019(4)	-0.03(5)
0.50	-6.4781	-0.6822(7)	-0.012(5)	0.03(6)
0.60	-7.6605	-0.7405(8)	-0.039(8)	-0.04(7)
0.70	-8.8484(1)	-0.826(1)	-0.05(1)	0.0(1)
0.80	-10.1352(2)	-0.904(2)	-0.05(2)	0.1(3)
0.90	-11.6431(4)	-0.909(3)	-0.02(3)	0.2(3)

$= 0.5$ ; set 2:  $\lambda_1 = 1.5$ ,  $\lambda_2 = 2.2$ , and  $\delta = 2.0$ ; and set 3:  $\lambda_1 = 1.6$ ,  $\lambda_2 = 2.3$ , and  $\delta = 2.0$ , respectively. We considered systems with  $N = 500$  particles, initially placed in a FCC configuration,  $\Delta r = 0.1\sigma$ ,  $5 \times 10^4$  cycles for equilibration and  $10^6$  cycles for production, each cycle consisting of  $N$  attempted particle moves. The results are reported in Tables I–III for the potential models cited with different sets of parameters as mentioned above and reduced densities  $\rho^* = \rho\sigma^3$  ranging from 0.1 to 0.9, where  $\rho = N/V$  throughout the text is the number density. The data quoted in these tables are averages performed over as many as  $10^2$  independent runs. Partial averages performed every 10 independent runs have been used to estimate the statistical uncertainty as the standard deviation.

Two theoretical approaches are available for estimating the perturbation coefficient(s). One is the well-known MCA,<sup>3</sup> which calculates  $a_2$  in the way,

$$a_2 = \pi\rho \int dr r^2 (\beta u_1(r))^2 g_{HS}(r, \rho) \frac{1}{\beta} \left( \frac{\partial \rho}{\partial P} \right)_{HS}, \quad (13)$$

where  $\beta = 1/k_B T$ ,  $g_{HS}(r, \rho)$  is radial distribution function (rdf) of the reference HS fluid, obtained from the Verlet-Weis correction<sup>22</sup> of the Percus-Yevick solution,<sup>23</sup>  $\frac{1}{\beta} \left( \frac{\partial \rho}{\partial P} \right)_{HS}$  is inverse of a reduced compressibility of the HS fluid

TABLE III. As in Table I but for the SSSW fluids with different potential parameters.

$\rho^*$	$a_1$	$a_2$	$a_3$	$a_4$
$\lambda_1 = 2.0$	$\lambda_2 = 2.2$	$\delta = 0.5$		
0.10	0.2000	-0.4167(2)	-0.075(2)	-0.02(2)
0.20	0.4345	-0.7609(4)	-0.153(4)	-0.02(6)
0.30	0.6798	-1.0676(4)	-0.223(6)	0.0(2)
0.40	0.9010	-1.3683(4)	-0.28(2)	-0.1(2)
0.50	1.0573(1)	-1.671(1)	-0.33(2)	0.2(4)
0.60	1.1164	-1.977(2)	-0.31(4)	0.1(7)
0.70	1.0793(1)	-2.310(3)	-0.28(5)	0.3(8)
0.80	1.0181(2)	-2.675(5)	-0.25(8)	0(2)
0.90	1.1025(6)	-2.966(8)	-0.4(1)	0(4)
$\lambda_1 = 1.5$	$\lambda_2 = 2.2$	$\delta = 2.0$		
0.10	-0.4581	-1.5795(5)	0.30(1)	0.1(4)
0.20	-0.7530	-2.710(1)	0.46(4)	0.4(6)
0.30	-0.8667(1)	-3.331(2)	0.68(5)	1(1)
0.40	-0.8181	-3.588(2)	0.73(7)	0(2)
0.50	-0.6747(1)	-3.743(2)	0.54(9)	0(1)
0.60	-0.5562(1)	-3.903(6)	0.4(1)	1(3)
0.70	-0.6219(3)	-3.902(5)	0.3(2)	0(3)
0.80	-1.0342(4)	-3.524(8)	0.1(2)	-1(3)
0.90	-1.9014(4)	-2.874(7)	-0.2(1)	0(3)
$\lambda_1 = 1.6$	$\lambda_2 = 2.3$	$\delta = 2.0$		
0.1	-0.3126	-1.8500(6)	0.34(2)	0.1(7)
0.2	-0.4538(1)	-3.048(2)	0.50(5)	0(1)
0.3	-0.4340(1)	-3.658(1)	0.66(5)	0(1)
0.4	-0.3084(1)	-3.958(2)	0.59(7)	1(2)
0.5	-0.1796(1)	-4.172(3)	0.4(1)	0(2)
0.6	-0.1862(1)	-4.265(6)	0.32(9)	0(2)
0.7	-0.4723(2)	-4.081(8)	0.2(2)	1(5)
0.8	-1.1372(4)	-3.716(8)	0.2(1)	0(6)
0.9	-2.1875(5)	-3.59(1)	0.6(2)	0(3)

( $P$  denoting pressure), calculated by integrating the Carnahan-Starling equation of state.<sup>19</sup>

In contrast with the MCA, which in practice only provides  $a_2$ , the CPSE works for all perturbation coefficients of the HTSE in principle. The CPSE features its expression as

$$\beta f_{ex-Zhou} = \beta f_{ex-ref} + \sum_{n=1}^{\infty} \beta f_{per-n}, \quad (14)$$

where

$$\beta f_{per-n} = (1/n!)2\pi\rho \int dr r^2 \beta u_1(r) \times \left. \frac{\partial^{(n-1)} g_{imag}(r, \zeta, \rho, T)}{\partial \zeta^{(n-1)}} \right|_{\zeta=0}, \quad (15)$$

and  $g_{imag}(r, \zeta, \rho, T)$  is rdf of an imaginary bulk fluid with a pair potential  $u(r; \zeta) = u_{HS}(r) + \zeta u_1(r)$ ,  $\partial^{(n-1)} g_{imag}/\partial \zeta^{(n-1)}|_{\zeta=0}$  is  $(n-1)$ -order derivative of  $g_{imag}$  with respect to  $\zeta$  evaluated at  $\zeta = 0$ , and  $\partial^0 g_{imag}(r, \zeta, \rho, T)/\partial \zeta^0|_{\zeta=0} = g_{imag}(r, 0, \rho, T)$  is actually the rdf of the HS reference fluid. Given that both the HTSE and CPSE use the HS fluid as the reference fluid, both perturbation schemes have the same first-order term as clearly seen in their expressions. For the numerical details on the calculation of  $\partial^{(n-1)} g_{imag}/\partial \zeta^{(n-1)}|_{\zeta=0}$ , the interested readers can have a

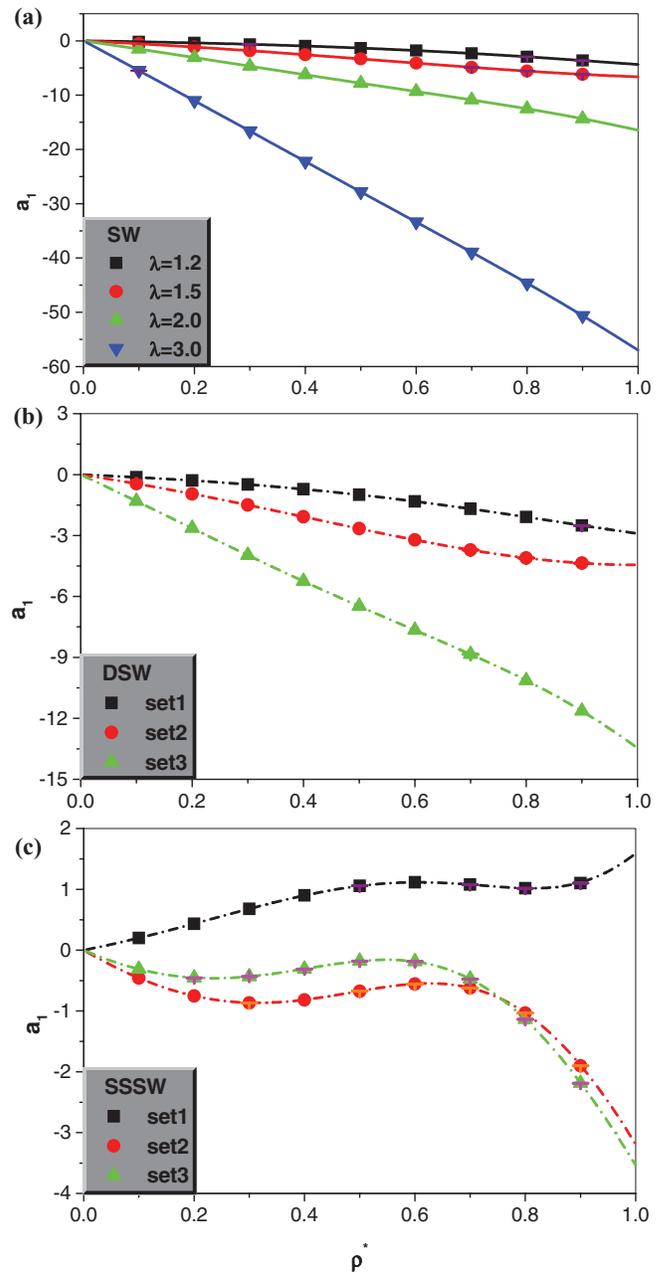


FIG. 1. HTSE coefficient  $a_1$  for fluids with the SW, DSW, and SSSW potentials, respectively. Points are the simulation data of this work and the short-dashed curves are the theoretical results from the CPSE.

reference to original papers<sup>6</sup> and one review paper<sup>24</sup> relevant to the CPSE, and not repeated here.

Although they are two different perturbation frameworks, the relationship between the CPSE and HTSE is established by a mathematical equation proved recently by Zhou,<sup>24</sup> i.e.,

$$a_n = \beta f_{per-n} \Big|_{T^*=1}, \quad n \geq 1. \quad (16)$$

Equation (16) is also the basis of using the CPSE to calculate  $a_n$ , the most essential input information in implementing the HTSE.

### III. RESULTS AND DISCUSSIONS

The results of  $a_1$  to  $a_4$  for SW fluids in general are in excellent agreement with the data reported in Ref. 14, with

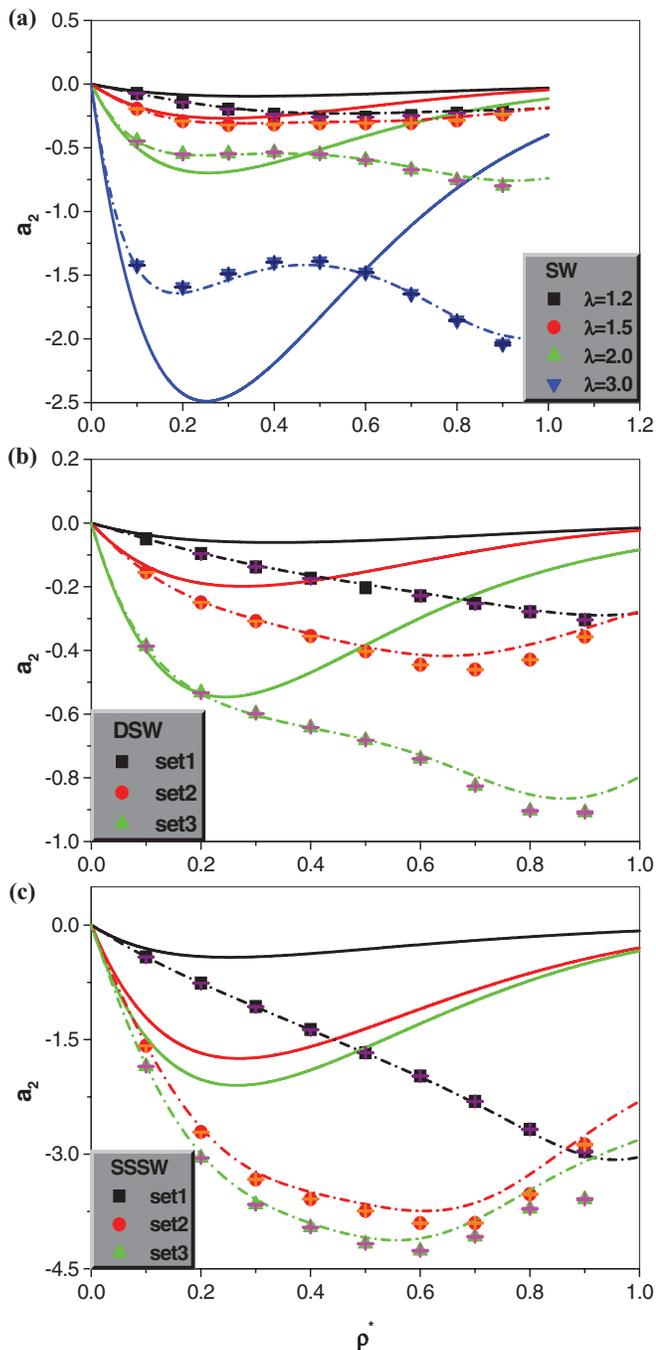


FIG. 2. As in Fig. 1, but for the HTSE coefficient  $a_2$  and the continuous curves are the results of the BH MCA.

the exception of  $a_2$  to  $a_4$  for  $\lambda = 3.0$ , for which the absolute values of the present data are greater for  $\rho^* \leq 0.5$ . These differences are believed to be due to the fact that we have used a greater number of particles in the simulations as well as a very big number of independent runs. The statistical error becomes considerably high for  $a_3$  and  $a_4$ , especially for values of these quantities close to zero. Performing simulations with different numbers of particles, from  $N = 256$  to  $N = 1372$ , we have found that the error increases with the number of particles used in the simulation, a fact that was also noted in Ref. 14. The relative error is more notable for  $\lambda \leq 1.5$ , because the values of  $a_3$  and  $a_4$  are very small. This may have a considerable

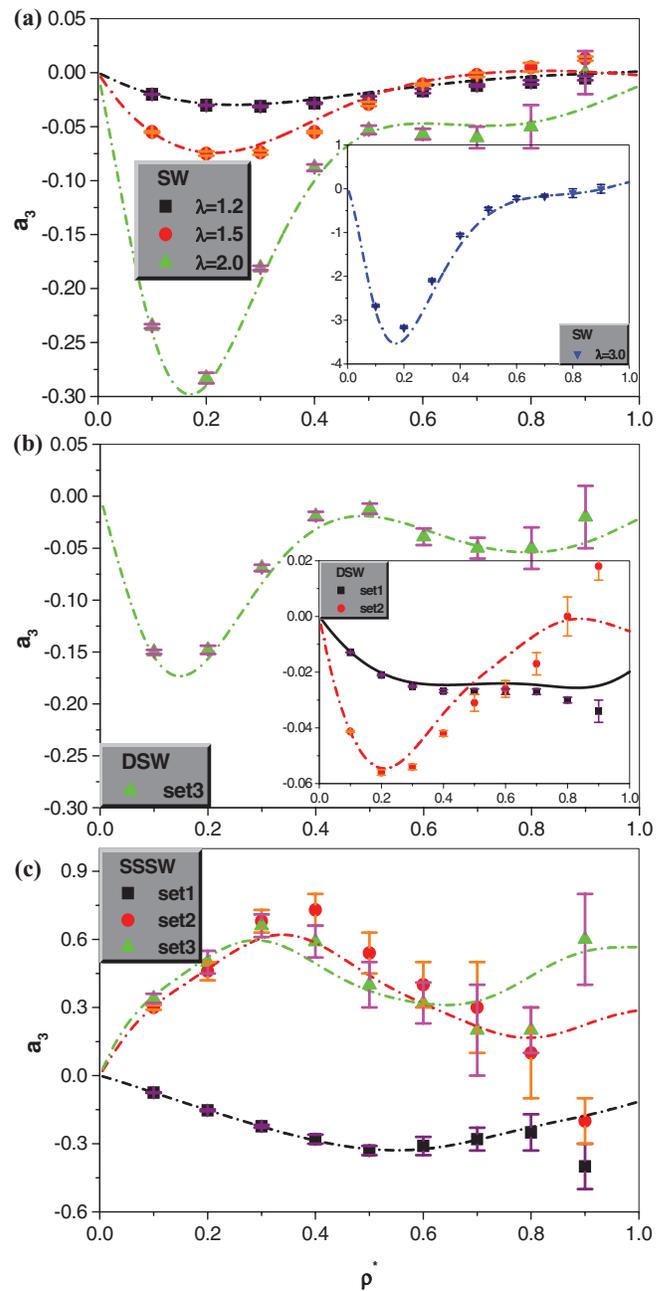


FIG. 3. As in Fig. 1, but for the HTSE coefficient  $a_3$ .

importance for  $\lambda = 1.2$ , as in this case the fluid phase extends to reduced temperatures well below  $T^* = 1$  and so the perturbation terms with  $n > 2$ , even if they are small, may have a considerable contribution to the free energy. The absolute values of  $a_3$  and  $a_4$  increase with  $\lambda$  and become even greater than  $a_2$  at low densities for  $\lambda = 3.0$ , but their relative importance will be small, because in this case the reduced temperatures in the fluid phase are well above  $T^* = 1$ . The results for the square shoulder (SS) potential are equal to those for the SW potential, except for the change in the signs of  $a_1$  and  $a_3$ .

Concerning the DSW potential model, one can see in Table II that the statistical errors in  $a_1$  and  $a_2$  are negligible and, for the sets of parameters considered in this work, the magnitude of  $a_3$  is very small and that of  $a_4$  negligible for reduced densities  $\rho^* \geq 0.4$ , on accounting for the fact that, for

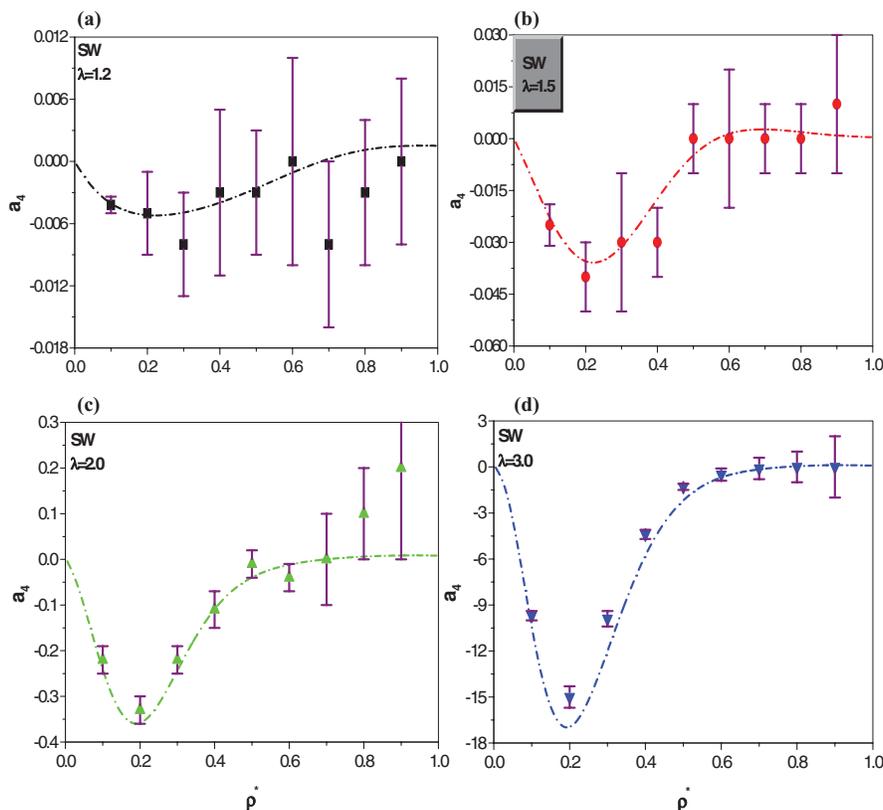


FIG. 4. As in Fig. 1, but for the SW fluids HTSE coefficient  $a_4$ .

the latter, the statistical error is even greater than the magnitude of  $a_4$  itself at moderate to high densities. Similar considerations as for the DSW apply to the values of  $a_1$  and  $a_2$  for the SSSW potential listed in Table III. The magnitude of  $a_3$  in this case is considerable at all densities while that of  $a_4$ , although it may be of the order of that of  $a_3$  or even greater for some sets of potential parameters, apparently cannot be reliably obtained from simulation, as the statistical errors become greater than the values of  $a_4$  themselves at all densities.

Comparison between the CPSE, MCA, and simulation data can be graphically discussed. To avoid an excessive number of the figures, it is advisable to group the figures for each  $a_i$ ,  $i = 1, \dots, 3$ , including as subfigures the results for all the potential models considered, and one figure for  $a_4$  for each potential model. Thus, there are six figures altogether, Figs. 1–3 for  $a_1$ ,  $a_2$ , and  $a_3$ , respectively, and Figs. 4–6 for  $a_4$  with SW, DSW, and SSSW potential, respectively.

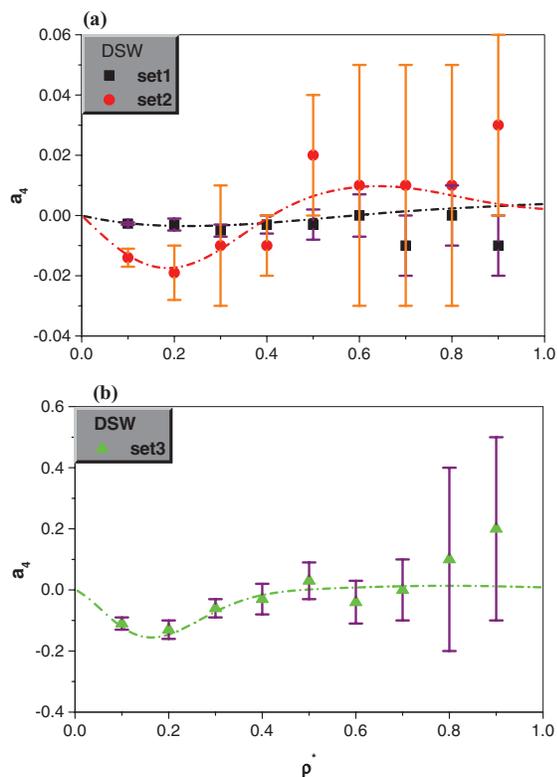
Figure 1 compares the results of  $a_1$  obtained from the CPSE described in Sec. II with the simulation data listed in Tables I–III. The agreement is excellent in all the cases studied, as one might have expected, as the first-order term in the CPSE at  $T^* = 1$  is equal to the first-order perturbation coefficient in the HTSE and the latter is known to be accurately predicted from theory provided that we use an accurate expression for the rdf of the reference hard-sphere fluid. The theoretical second-order coefficient  $a_2$  is compared in Fig. 2 with the simulation data listed in Tables I–III. Again the CPSE predictions agree very satisfactorily with simulations for all the potential models and parameter values considered. In con-

trast, the Barker-Henderson MCA, which is also included for comparison, strongly deviates from simulation data at both, low and high densities, especially for large potential widths.

Similar accuracy is provided by the CPSE for the third-order coefficient  $a_3$ , as Fig. 3 shows, even for the extreme case of the SW potential with  $\lambda = 3.0$ , for which the values of  $a_3$  are considerably great.

Figures 4–6 display the results for the fourth-order perturbation coefficient  $a_4$ . In this case, the simulation data are affected by a considerable uncertainty, as said before, which prevents a detailed analysis of the theoretical predictions, but even so the CPSE seems to work quite well and this is particularly clear for SW fluids with large well widths, as Fig. 4 shows. As a matter of fact, for this coefficient the CPSE seems to be more reliable than the simulation itself, as the statistical uncertainty of the latter seems to be impossible to reduce at present and, therefore, accurate simulation data cannot be obtained from the procedure described in Sec. II.

It should be pointed out that if the sign of  $u_1(r)$ , the perturbation part of the potential considered, is changed,  $a_i$ ,  $i =$  positive odd integer, will change the sign, but  $a_i$ ,  $i =$  positive even integer, remains unchanged, and this conclusion can be clearly and easily confirmed with the help of the procedure used in the CPSE to calculate the  $a_i$  by numerical derivative based on the finite difference method. Thus, with a simple transform the simulation data reported here actually also apply for a square shoulder potential, double square shoulder potential, and square well plus square shoulder potential, and

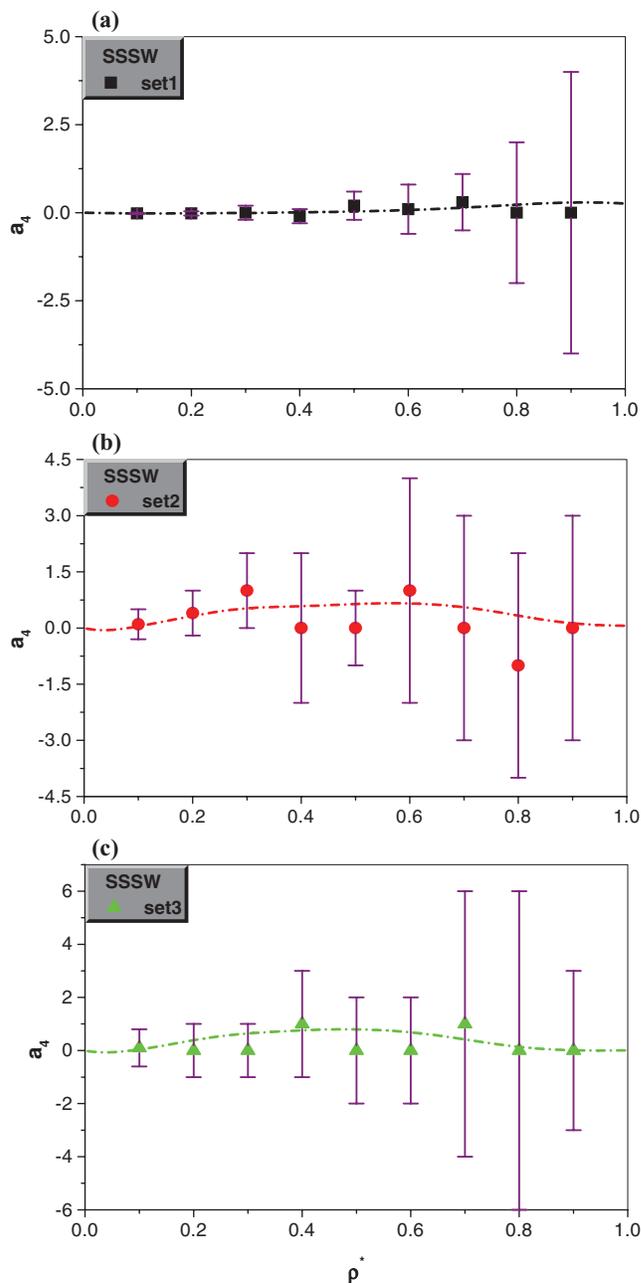
FIG. 5. As in Fig. 1, but for the DSW fluids HTSE coefficient  $a_4$ .

the above analysis may also prove useful at least in these potential models.

#### IV. CONCLUSIONS

To conclude, the present paper provides comprehensive simulation data sources for the first four coefficients of the HTSE for fluid state characterized by several model potentials, and besides that, the theoretical calculations for these coefficients are performed in the framework of the CPSE for a particular unit reduced temperature wherein each expansion term in the CPSE is proved<sup>24</sup> to be exactly equal to the relevant order expansion coefficient of the HTSE. A traditional MCA is also used for calculations of the second order coefficient only. Detailed comparison based on these coefficients from the two different routes leads to several natural conclusions:

- (i) The CPSE shows excellent performance in achieving accurate calculations of higher order coefficients of the HTSE. Specifically, the CPSE perfectly coincides with the simulation data for the case of the second order coefficient wherein the simulation errors are negligibly small. For the higher-order coefficients wherein simulation errors are very large, and exact and clear comparisons are not possible; however, for these uncertain cases, the CPSE curves not only reproduce the density dependence of the simulation data but also pass through nearby the simulated data points, which are distributed in both sides of the curve. This clearly indicates the potential of the CPSE in providing accurate sources for

FIG. 6. As in Fig. 1, but for the SSSW fluids HTSE coefficient  $a_4$ .

these higher-order coefficients although the accuracies remain to be tested in the future. In the present conditions, these higher-order coefficients are unobtainable accurately even by simulation approach, and the excellent properties of the CPSE as mentioned above provide the chance for acquiring fitting expressions for these higher-order coefficients.

- (ii) The MCA for the second order coefficient is only quantitatively reliable at very low densities, and its deviation from the “exact” simulation results tends to become more evident as density increases, and eventually the MCA becomes qualitatively incorrect. This finding clearly indicates that the MCA is a crude approximation, and one is uncertain whether including the second

order perturbation term from the MCA will certainly improve the HTSE.

- (iii) Upon acquirement of the higher-order coefficients of the HTSE, one can construct a higher-order HTSE thermodynamic perturbation theory. Simulation approach has two shortcomings in getting these coefficients: (1) Simulation results for third order or higher order coefficients are inevitably with very large statistical errors as shown in Figs. 3–6, and this makes it difficult and even impossible to fit these discrete points to a continuous curve as a function of density; (2) Moreover, even for the second-order coefficient, which is readily estimated accurately by simulation calculations, the simulations take longer time, and the coefficients with different potential parameters need to be simulated individually. Consequently, using simulation data to obtain fitting expressions for these higher-order coefficients beyond first one is unworkable at least in present conditions. Encouragingly, ability of the CPSE to help one in quickly and accurately acquiring these coefficients beyond first order enables it to play a significant role in constructing a higher-order HTSE thermodynamic perturbation theory and evaluating the convergence of the latter, and relevant studies will be reported in subsequent papers.
- (iv) The present CPSE is not accompanied by renormalization method, and is only a mean field theory; so, the CPSE is not expected to be very accurate near the critical point, although we cannot go further in the discussion of this point as simulation data for the critical parameters are not available for the fluids considered, apart from the square-well fluid. For the latter, it was shown in two previous papers<sup>25,26</sup> from one of the present authors that the third-order CPSE provides quite satisfactory predictions for the liquid-vapor coexistence, even near the critical point, and the critical parameters for several well widths; the third-order CPSE, combined with a non-hard sphere perturbation technique, can be applied even for states hardly or not accessible by simulation, such as fluids at extremely low temperatures and near glass states, as demonstrated in a previous paper.<sup>2</sup> In any case, the limited accuracy near the critical point is a common feature of most of the existing mean field theories of fluids. Sometimes, simple perturbation approaches in combination with renormalization techniques have been developed, as demonstrated in a pioneering work by White and co-workers,<sup>27</sup> but in general their accuracy relies on the use of a number of adjustable parameters, and particularly, an excellent mean field theory is a necessary premise for formulating a global theory valid over entire phase

space. The present CPSE obviously meets this requirement, and its combination with renormalization techniques will be reported in separate papers.

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