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Theory and computer simulation for the equation of state of additive hard-disk fluid mixtures

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A procedure previously developed by the authors to obtain the equation of state for a mixture of additive hard spheres on the basis of a pure fluid equation of state is applied here to a binary mixture of additive hard disks in two dimensions. The equation of state depends on two parameters which are determined from the second and third virial coefficients for the mixture, which are known exactly. Results are compared with Monte Carlo calculations which are also reported. The agreement between theory and simulation is very good. For the fourth and fifth virial coefficients of the mixture, the equation of state gives results which are also in close agreement with exact numerical values reported in the literature.

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I. INTRODUCTION

Since the derivation by Lebowitz [1] and Lebowitz *et al.* [2] of the solutions of the Percus-Yevick (PY) theory and the scaled particle theory (SPT), respectively, for additive hard-sphere fluid mixtures, there has been a sustained interest in this kind of mixture. Currently, there is available a good equation of state for these mixtures, the so-called BMCSL (Boublík, Mansoori, Carnahan, Starling, and Leland) equation of state, derived independently by Boublík [3] and by Mansoori *et al.* [4], on a semiempirical basis, as well as a considerable amount of simulation data. In spite of this, the search for an improved equation of state continues [5–7]. Moreover, in the last few years, a new subject of intensive research in this field has raised up, namely the phase behavior of this system [8–12].

One reason for this interest is that the hard-sphere fluid mixture is an adequate reference system in perturbation theories for more realistic mixtures. Moreover, the equation of state and the contact values of the pair correlation function of the hard-sphere fluid are used in the context of some theories for models of polyatomic pure fluids and mixtures, as is the case for the bonded hard-sphere (BHS) theory [13–15]. Another interesting aspect is the close relation between binary hard-sphere mixtures with high values of the diameter ratio and real colloidal suspensions.

In principle, we could think that two-dimensional hard-disk pure fluids and mixtures are lacking of interest because they are systems more distant from real systems. However, this is not exactly true. On the one hand, two-dimensional fluids can be considered a first approximation to the study of adsorption of molecules by a solid surface. On the other hand, two-dimensional fluids are often used as a coherency test for theories initially developed for three-dimensional fluids.

In spite of this, the amount of research, both from theory as well as from computer simulation, devoted to two-dimensional hard-disk fluids is much more scarce than for the three-dimensional case. This is particularly true for mixtures. This is partially due to the fact that some integral equation theories frequently used to obtain the pair correlation function and the equation of state of a three-dimensional hard-sphere fluid are not applicable for even dimensionality.

In a recent paper [7] we have developed a procedure that allows us to obtain the equation of state for a three-dimensional binary mixture of hard spheres from any equation of state for the pure fluid and the second and third virial coefficients for the mixture, which are known analytically. In the present paper, we apply the same procedure to obtain the equation of state of a two-dimensional binary mixture of hard disks. Results are compared with those from other equations of state and with canonical ensemble (NVT) Monte Carlo calculations which are also reported for several diameter ratios and mole fractions.

II. EQUATION OF STATE FOR A BINARY MIXTURE OF HARD DISKS

A. Monte Carlo simulations

NVT Monte Carlo simulations have been performed for systems consisting of $N=256$ particles in a square box with periodic boundary conditions. Each system consists of $N_1=x_1N$ disks of diameter σ_1 and $N_2=x_2N$ disks of diameter σ_2, with $\sigma_1>\sigma_2$, where x_1 and x_2 are the corresponding mole fractions. Diameter ratios $\sigma_2/\sigma_1=2/3$, 1/2, and 1/3, and mole fractions $x_1=0.25$, 0.5, and 0.75, have been considered. Particles were initially placed in a regular array with diameters chosen randomly to be σ_1 or σ_2 with the constraints of fixed x_1 and packing fraction $\eta_{mix}=(\pi/4)\rho\Sigma_i x_i\sigma_i^2$ for the mixture, where ρ is the total number density. Systems were allowed to equilibrate for 500 to 5000 cycles, each of them consisting of an attempt move per particle, depending on density. For the higher densities, overlaps between particles in the initial configuration, which were present in some cases, were removed before starting equilibration. The equation of state was determined from measurements of the partial pair correlation functions $g_{ij}(r)$ performed over 10^4 to 1.2×10^5 additional cycles, extrapolating to contact, and using the virial equation. In some cases several independent runs were performed to increase accuracy. Results are shown in Table I together with the estimated errors determined as the standard deviation.

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TABLE I. Monte Carlo simulation data for the compressibility factor of binary hard-disk fluid mixtures. The numbers enclosed in parentheses indicate the estimated error in the last significant figure.

		Z_{mix}^{MC}		
σ_2/σ_1	η_{mix}	$x_1=0.25$	$x_1=0.50$	$x_1=0.75$
2/3	0.20	1.559(6)	1.561(5)	1.565(4)
	0.30	2.036(8)	2.043(8)	2.051(8)
	0.40	2.79(1)	2.79(1)	2.80(1)
	0.45	3.31(1)	3.31(2)	3.33(1)
	0.50	4.02(2)	4.02(1)	4.04(2)
	0.55	4.98(2)	4.98(2)	5.03(2)
	0.60	6.31(2)	6.30(1)	6.36(3)
1/2	0.20	1.534(6)	1.540(6)	1.556(7)
	0.30	1.998(7)	2.008(7)	2.039(8)
	0.40	2.72(1)	2.71(1)	2.77(1)
	0.45	3.20(2)	3.22(2)	3.29(2)
	0.50	3.88(1)	3.90(2)	3.98(2)
	0.55	4.79(2)	4.81(2)	4.93(2)
	0.60	6.03(3)	6.04(2)	6.22(3)
1/3	0.20	1.491(6)	1.510(8)	1.538(9)
	0.30	1.907(8)	1.940(8)	2.004(9)
	0.40	2.55(1)	2.59(1)	2.71(1)
	0.45	2.99(2)	3.07(1)	3.20(2)
	0.50	3.60(2)	3.69(2)	3.89(2)
	0.55	4.39(3)	4.52(2)	4.79(2)
	0.60		5.66(3)	6.06(1)

B. Theory

Our starting point is the virial theorem for a multicomponent two-dimensional fluid consisting of particles with circular shapes, which is expressed in the form

$$\begin{aligned} Z_{mix}&=\frac{pV}{NkT}\\ &=1-\frac{\pi}{2}\frac{\rho}{kT}\sum_i\sum_j x_ix_j\int r^2\frac{\partial u_{ij}}{\partial r}g_{ij}(r;\rho,T,x_i,x_j)dr, \end{aligned} \tag{1}$$

where $\rho=N/V$ is the number density for the mixture, u_{ij} is the intermolecular potential between particles *i* and *j*, and g_{ij} is the pair correlation function (PCF) for these particles. The latter depends on the mole fractions x_i and x_j for species *i* and *j*, in addition to density and temperature.

When the pure fluids that form the mixture have the same form of the intermolecular potential and the PCF, it is reasonable to approximate the pair correlation functions g_{ij} in the mixture by that corresponding to a pure fluid with distances, density, and temperature scaled in a suitable way. This is done in some theories such as the mean density approximation [16] and the van der Waals one-fluid theory (vdW1). In the former, for a two-dimensional fluid

$$g_{ij}(r/\sigma_{ij},\rho,T,x_i,x_j)=g_0(r/\sigma_0,\rho\sigma_0^2,kT/\varepsilon_{ij}), \tag{2}$$

whereas in the vdW1 theory

$$g_{ij}(r/\sigma_{ij},\rho,T,x_i,x_j)=g_0(r/\sigma_0,\rho\sigma_0^2,kT/\varepsilon_0), \tag{3}$$

where

$$\sigma_0^2=\sum_i\sum_j x_ix_j\sigma_{ij}^2 \tag{4}$$

and

$$\varepsilon_0\sigma_0^2=\sum_i\sum_j x_ix_j\varepsilon_{ij}\sigma_{ij}^2. \tag{5}$$

In particular, if the particles interact by means of a hard-disk potential, both approximations lead to

$$g_{ij}(r/\sigma_{ij},\rho,x_i,x_j)=g_0(r/\sigma_0,\rho\sigma_0^2), \tag{6}$$

where g_0 is the PCF g^{HD} for a pure fluid consisting of hard disks with diameter σ_0 defined by Eq. (4) with

$$\sigma_{ij}=\frac{1}{2}(\sigma_i+\sigma_j). \tag{7}$$

In this case the virial theorem for a pure fluid leads to

$$Z_{mix}^{HD}=1+\frac{1}{2}\pi\rho\sigma_0^2g^{HD}(\eta_0)=1+2\eta_0g^{HD}(\eta_0), \tag{8}$$

where $\eta_0=\rho\pi\sigma_0^2/4$ is the fictitious packing fraction of the reference pure fluid and g^{HD} the contact value of its PCF. From expression (8) it is clear that the reference fluid gives the right second virial coefficient of the mixture

$$B_{mix}^{HD}=\frac{\pi}{2}\sum_i\sum_j x_ix_j\sigma_{ij}^2, \tag{9}$$

where σ_{ij} is given by expression (7), provided that in the low-density limit, the PCF of the reference fluid fulfills the condition $g^{HD}(0)=1$, as it ought to be.

However, for our purposes it is more convenient to define the reference fluid as one not only having the same second virial coefficient but also the same packing fraction as the mixture. Therefore, we will modify expression (8) in the form

$$\begin{aligned} Z_{mix}^{HD}&=1+\frac{1}{2}\pi\rho\sigma_0^2g^{HD}(\eta_{mix})\\ &=1+2\eta_{mix}\left(\sum_i\sum_j x_ix_js_{ij}/s_{mix}\right)g^{HD}(\eta_{mix})\\ &=1+s[Z^{HD}(\eta_{mix})-1], \end{aligned} \tag{10}$$

where

$$s=\frac{1}{s_{mix}}\sum_i\sum_j x_ix_js_{ij}, \tag{11}$$

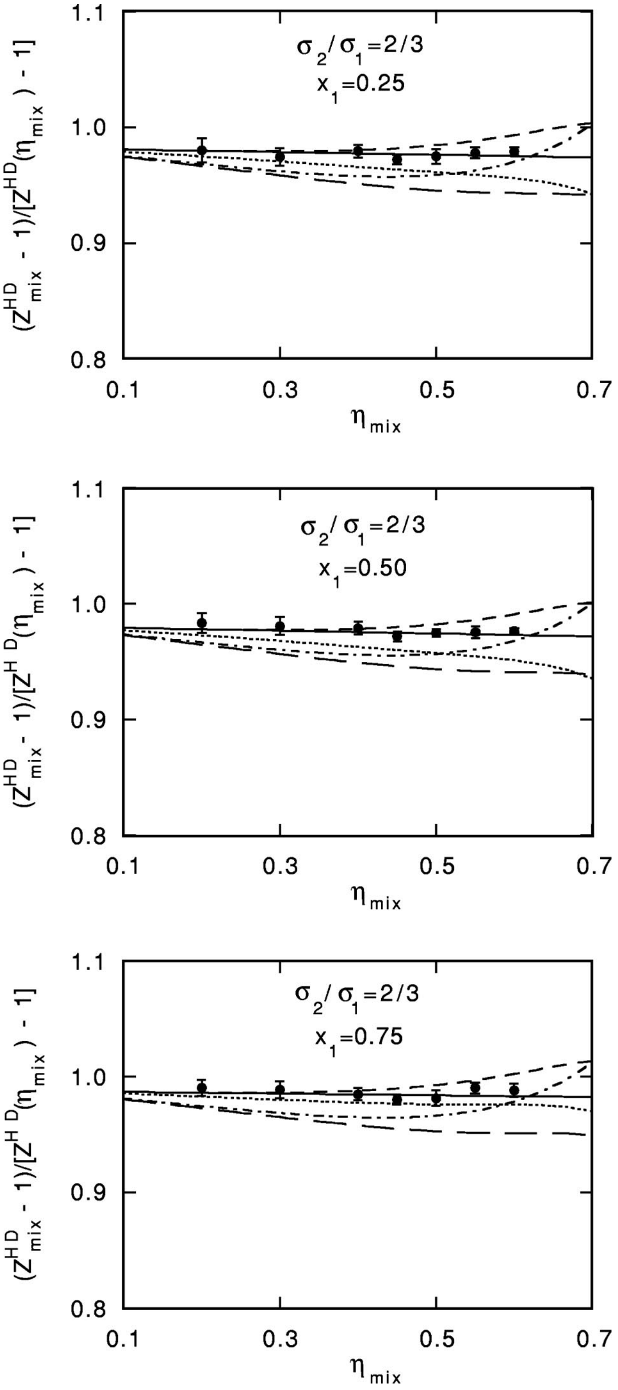

FIG. 1. Ratio of the excess compressibility factor Z^{HD}_{mix} for hard-disk fluid mixtures with respect to that for the pure fluid, as given by Eq. (15), as a function of the packing fraction η_{mix} for the diameter ratio $\sigma_2/\sigma_1 = 2/3$ and different mole fractions. Circles: Monte Carlo simulations. Continuous line: Eq. (17). Long-dashed line: Eq. (24). Dashed line: Eq. (26). Dotted line: Eq. (27). Dash-dotted line: Eq. (28).

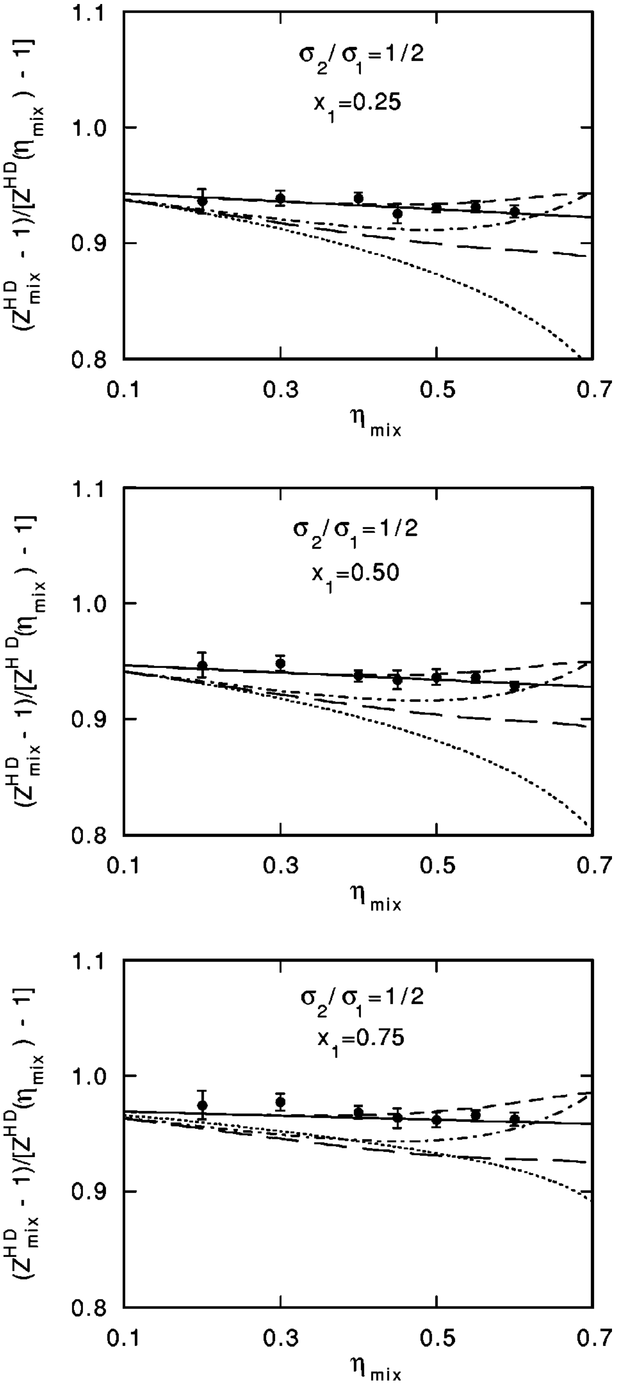

FIG. 2. As in Fig. 1 for the diameter ratio $\sigma_2/\sigma_1 = 1/2$.

$$s_{mix} = \frac{\pi}{4} \sum_i x_i \sigma_i^2 \tag{12}$$

is the average surface of a disk, and

$$s_{ij} = \frac{\pi}{4} \sigma_{ij}^2 \tag{13}$$

with σ_{ij} given by Eq. (7).

In expression (10) we can use for Z^{HD} any equation of state suitable for the pure fluid. However, in order to reproduce the right second virial coefficient (9), the equation of state chosen must, in turn, predict correctly the second virial coefficient for the pure fluid. There have been proposed for the latter several equations of state fulfilling this condition.

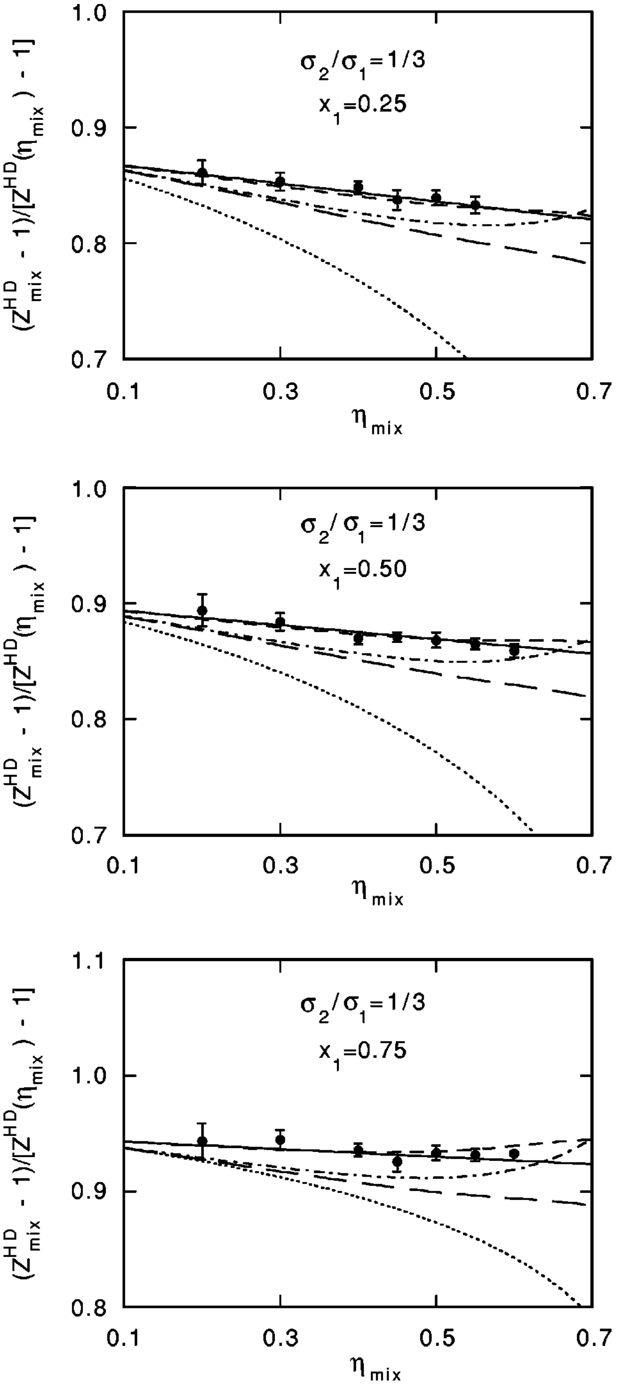

FIG. 3. As in Fig. 1 for the diameter ratio $\sigma_2/\sigma_1=1/3$.

Among them, we have the equation of state proposed by Henderson [17]

$$Z^{HD}=\frac{1+\eta^2/8}{(1-\eta)^2}, \tag{14}$$

which is simple and reasonably accurate. In this equation, $\eta=(\pi/4)\rho\sigma^2$ is the packing fraction of a pure fluid of hard disks of diameter σ and number density ρ. A bit more complicated, but also more accurate, is the equation of state from Woodcock [18]

$$Z^{HD}=1+\frac{4x}{1-x}+\sum_{i=2}^{n}(B_i-4)x^{i-1}, \tag{15}$$

where $x=V_0/V$, $V_0=N(\sqrt{3}/2)\sigma^2$ being the two-dimensional regular close-packing ''volume,'' V is the volume (surface) of the system, and B_i is the virial coefficient of order i in the expansion of the compressibility factor Z^{HD} in the power series of x. Another suitable equation of state has been recently proposed by Santos *et al.* [19] in the form

$$Z^{HD}=\left[1-2\eta+\frac{2\eta_{cp}-1}{\eta_{cp}^2}\eta^2\right]^{-1}, \tag{16}$$

where η has the same meaning as in Eq. (14) and $\eta_{cp}=(\sqrt{3}/6)\pi$ is the close-packing fraction.

Taking $\eta=\eta_{mix}$, any of these equations of state, together with the simulation data listed in Table I, can be used to calculate the ratio $(Z^{HD}_{mix}-1)/[Z^{HD}(\eta_{mix})-1]$ that, according to Eq. (10), should be constant with density. Results for this ratio are shown in Figs. 1–3, where we can see that, rather than constant, the ratio is approximately a linear function of the packing fraction of the mixture. This is more clearly seen for high values of the diameter ratio. To account for this fact, we will modify Eq. (10) in the form

$$Z^{HD}_{mix}=1+s(a+b\eta_{mix})[Z^{HD}(\eta_{mix})-1]. \tag{17}$$

In order to obtain parameters a and b, we can impose the condition that the equation of state must reproduce exactly the second and third virial coefficients of the mixture, which are known exactly. The second virial coefficient is given by Eq. (9), whereas the expression for the third is [20]

$$C^{HD}_{mix}=\frac{\pi}{3}(a_{11}x_1^3\sigma_1^4+a_{12}x_1^2x_2\sigma_{12}^4+a_{21}x_1x_2^2\sigma_{12}^4+a_{22}x_2^3\sigma_2^4), \tag{18}$$

where σ_{ij} is given by expression (7) and coefficients a_{ij} are given by

$$a_{11}=a_{22}=\pi-3^{3/2}/4, \tag{19}$$

$$\begin{aligned}a_{12}=3[&\pi+2(\xi_1^{-2}-1)\cos^{-1}(1/2\xi_1)\\&-(1/2\xi_1^2)(1+1/2\xi_1^2)(4\xi_1^2-1)^{1/2}],\end{aligned} \tag{20}$$

and a_{21} is given by the last expression by changing ξ_1 to ξ_2, where $\xi_1=\sigma_{12}/\sigma_1$ and $\xi_2=\sigma_{12}/\sigma_2$.

Then, the condition that Eq. (17) must reproduce exactly the second and third virial coefficients gives

$$a=1 \tag{21}$$

and

$$b=\frac{1}{s_{mix}}\frac{C^{HD}_{mix}}{B^{HD}_{mix}}-\frac{C^{HD}}{2}, \tag{22}$$

where

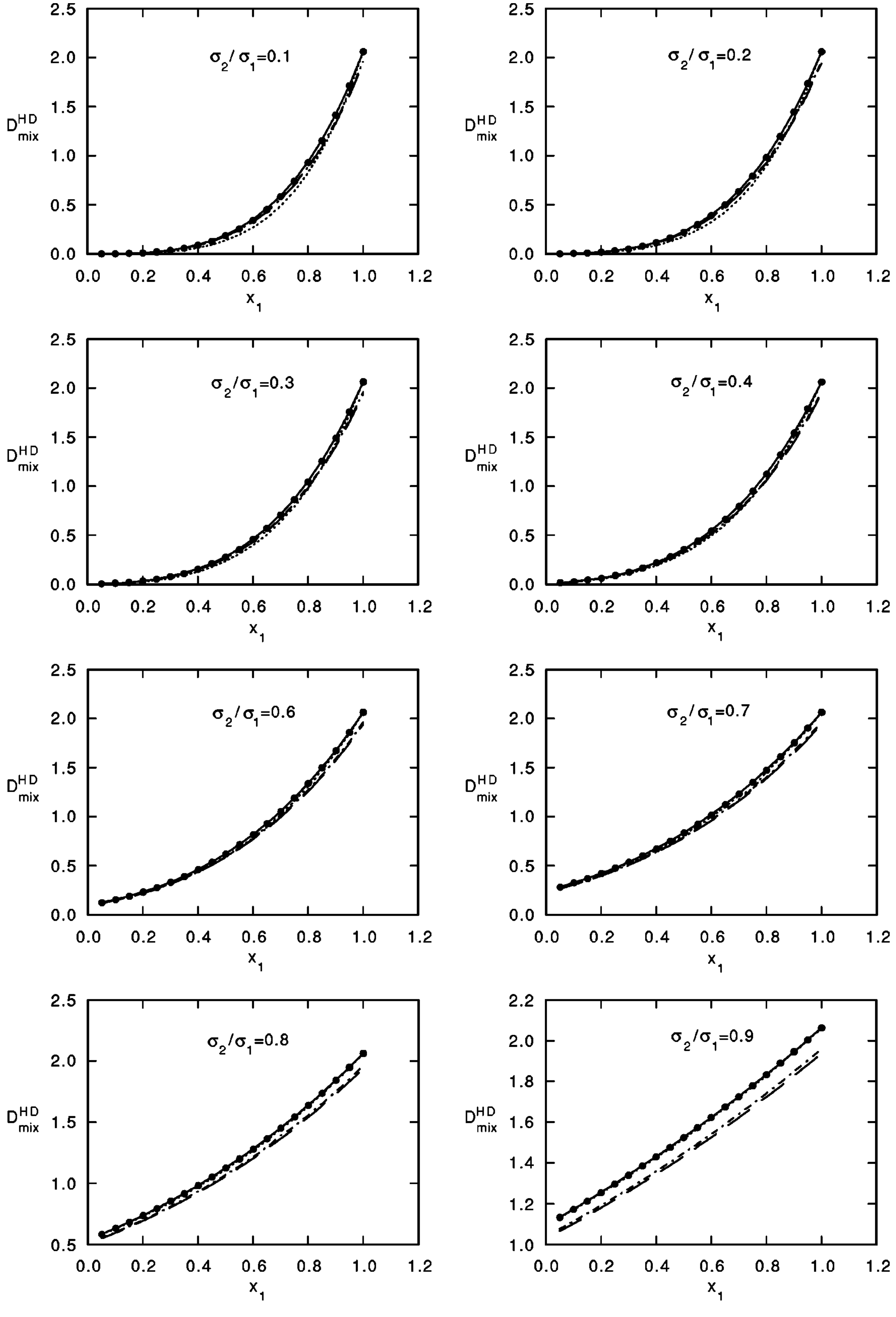

FIG. 4. Fourth virial coefficient D_{mix}^{HD} of two-dimensional mixtures of additive hard disks, in units of σ_1^6, for several values of the diameter ratio as a function of the mole fraction. Circles: exact values from Ref. [22]. Lines have the same meaning as in Fig. 1.

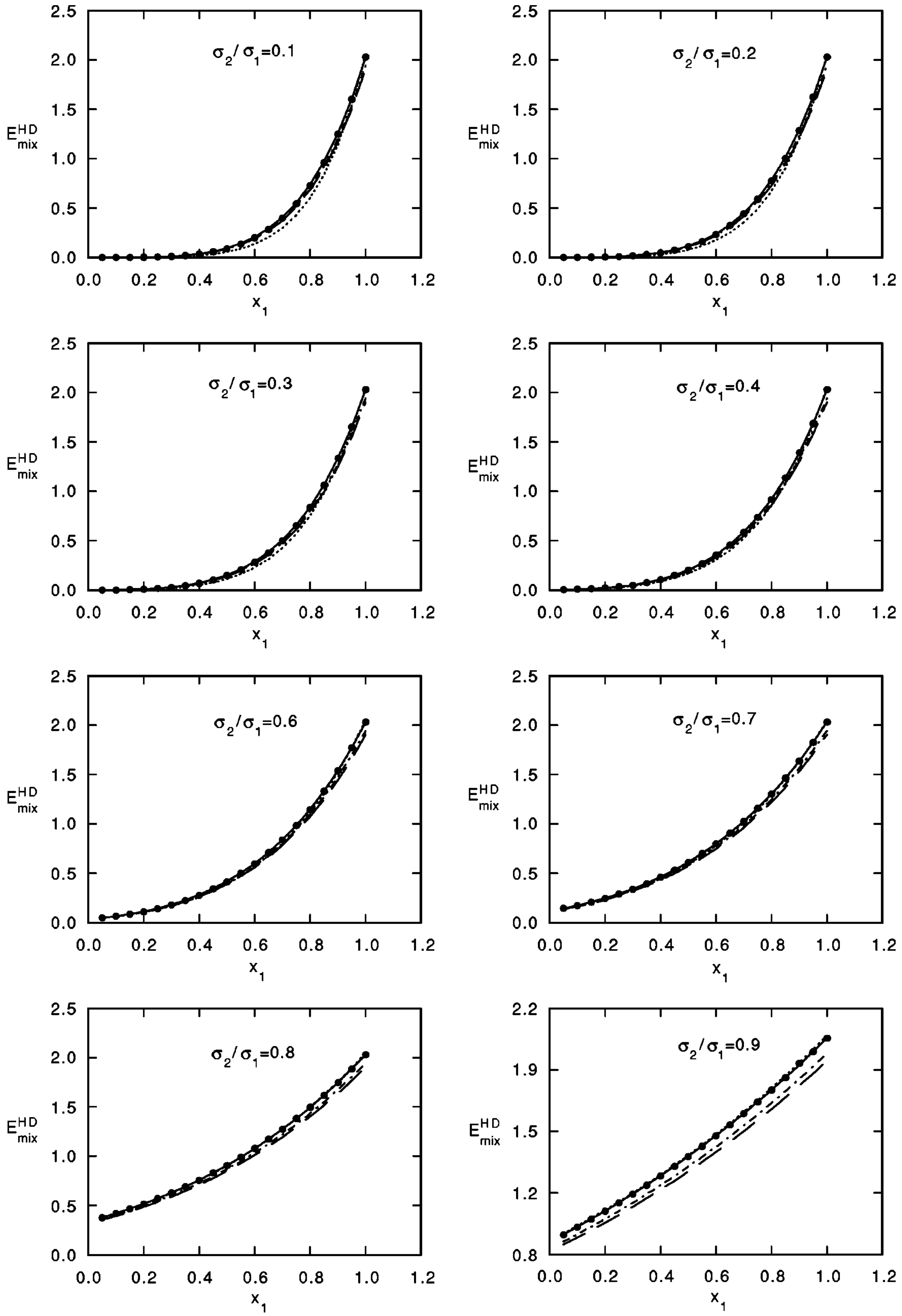

FIG. 5. As in Fig. 4 for the fifth virial coefficient in units of σ_1^8. Circles: exact values from Refs. [23] and [24]. Lines have the same meaning as in Fig. 1.

$$C^{HD}=4\left(\frac{4}{3}-\frac{\sqrt{3}}{\pi}\right) \tag{23}$$

is the third virial coefficient for a pure hard-disk fluid. Equation (17), together with parameters (21) and (22) is the two-dimensional equivalent of the equation of state previously derived [7] for three-dimensional hard-sphere fluid mixtures [21].

III. RESULTS AND DISCUSSION

Results from the equation of state (17), taking Eq. (15) for Z^{HD}, are compared in Figs. 1–3 with the simulation data listed in Table I. Also included, for comparison, are the results from other equations of state. One of them is the equation of state which results [20] from the scaled particle theory

$$Z_{mix}^{SPT}=\frac{1-(1-\xi)\,\eta_{mix}}{(1-\eta_{mix})^2}, \tag{24}$$

where

$$\xi=\left(\sum_i x_i\sigma_i\right)^2 \bigg/ \sum_i x_i\sigma_i^2 . \tag{25}$$

Another is the equation of state derived from the rescaled virial expansion (RVE) [20]

$$Z_{mix}^{RVE}=\frac{1+c_1\eta_{mix}+c_2\eta_{mix}^2}{(1-\eta_{mix})^2}, \tag{26}$$

where c_1 and c_2 are determined from the condition that the equation of state must exactly reproduce the second and third virial coefficients of the mixture.

Also are shown in Figs. 1–3 the results from the equation of state obtained [20] from the application of the conformal solution theory to the equation of state (14), derived by Henderson [17] for the pure fluid. Introducing the fictitious packing fraction $\eta_0=\rho\pi\sigma_0^2/4$ for the reference pure fluid into Eq. (14), the resulting equation of state for the mixture is

$$Z_{mix}^{H}=\frac{1+\eta_0^2/8}{(1-\eta_0)^2}. \tag{27}$$

Finally, we have considered an equation of state recently proposed [6] in the form

$$Z_{mix}^{SBL}=1+[Z^{HD}(\eta_{mix})-1]\xi+\frac{\eta_{\rm mix}(1-\xi)}{1-\eta_{mix}}, \tag{28}$$

where ξ is given by Eq. (25) and, for $Z^{HD}(\eta_{mix})$, we have taken Eq. (16).

As we can see in Figs. 1–3, Eqs. (24), (26), and (28) appreciably deviate from simulation data at all densities, although it is to be noted that a plot like that of these figures enhances the deviations. Equation (27) gives good agreement for low to moderate densities, but overestimates the simulation data at high densities. The results from Eq. (17) are, as a whole, in closer agreement with simulation data than those obtained from the other equations considered.

On the other hand, in Figs. 4 and 5 we compare the values of the fourth and fifth virial coefficients predicted by Eqs. (17) and (26) with existing numerical data [22–24]. In this case, Eq. (26) provides the best agreement, although this is hardly appreciated at the scale of these figures. However, it is to be noted that the accuracy of Eq. (17) depends on the accuracy of the equation of state $Z^{HD}(\eta_{mix})$ used for the pure fluid. In this sense, the equation of state (15) used is the most accurate among all the equations considered. However, we cannot discard that, using an equation of state still more accurate for the pure fluid, the predictions for the fourth and fifth virial coefficients of the mixture would improve.

On the other hand, it is rather surprising that Eq. (27) gives the poorest agreement with simulation data, as shown in Figs. 1–3, in spite of the fact that it reproduces exactly the second virial coefficient and apparently, in Figs. 4 and 5, with reasonable accuracy the fourth and fifth virial coefficients. However, it is to be noted that a plot like that of Figs. 1–3 enhances the deviations, whereas the contrary occurs in Figs. 4 and 5. Thus, although hardly appreciated in these figures, the values of the fourth and fifth virial coefficients predicted by Eq. (27) are too low by amounts of 8% and 10% on average, respectively, as compared with exact values, with the highest deviations occurring for the lowest values of the diameter ratio. Moreover, an accurate prediction of the first few virial coefficients does not guarantee an accurate equation of state. In fact, the exact virial expansion, truncated at the fifth term, gives trivially the exact values of the first five virial coefficients, but it is easy to see that it strongly underestimates the values of the compressibility factor.

In summary, the procedure previously developed [7] for obtaining the equation of state for a multicomponent hard-sphere fluid mixture on the basis of any equation of state for the pure fluid, is found in this paper to be satisfactory also for a two-dimensional hard-disk fluid mixture. The agreement of the derived equation of state with the reported simulation data is, on the whole, better than for other equations of state proposed in the literature. The new equation also reproduces very accurately the numerical data available for the fourth and fifth virial coefficients of the mixture.

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