Comment on “Theory and computer simulation for the equation of state of additive hard-disk fluid mixtures”

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A flaw in the comparison between two different theoretical equations of state for a binary mixture of additive hard disks and Monte Carlo results, as recently reported in C. Barrio and J. R. Solana, Phys. Rev. E 63, 011201 (2001), is pointed out. It is found that both proposals, which require the equation of state of the single component system as input, lead to comparable accuracy but the one advocated by us [A. Santos, S. B. Yuste, and M. López de Haro, Mol. Phys. 96, 1 (1999)] is simpler and complies with the exact limit in which the small disks are point particles.

In a recent paper, Barrio and Solana [1] proposed an equation of state (EOS) for a binary mixture of additive hard disks. Such an equation reproduces the (known) exact second and third virial coefficients of the mixture and may be expressed in terms of the EOS of a single component system. They also performed Monte Carlo simulations and found that their recipe was very accurate provided an accurate EOS for the single component system (in their case it was the EOS proposed by Woodcock [2]) was taken as input. The comparison with other EOS for the mixture available in the literature indicated that their proposal does the best job with respect to the Monte Carlo data. Among these other EOS for the binary mixture, only the one introduced by us a few years ago [3] also shares with Barrio and Solana’s EOS the fact that it may be expressed in terms of the EOS for a single component system. What we want to point out here is that the comparison made in Ref. [1] is flawed by the fact that it was not performed by taking the same EOS for the single component system in both proposals.

Let us consider a binary mixture of additive hard disks of diameters \( \sigma_1 \) and \( \sigma_2 \). The total number density is \( \rho \), the mole fractions are \( x_1 \) and \( x_2 = 1 - x_1 \), and the packing fraction is \( \eta = \frac{\pi}{2} \rho \sigma^2 \), where \( \langle \sigma^n \rangle \equiv \sum_{i=1}^{2} x_i \sigma_i^n \). Let \( Z = p/\rho k_B T \) denote the compressibility factor, \( p \) being the pressure, \( T \) the absolute temperature, and \( k_B \) the Boltzmann constant. Then, Barrio and Solana’s EOS for a binary mixture of hard disks, \( Z_{\text{BS}}(\eta) \), may be written in terms of a given EOS for a single component system, \( Z_s(\eta) \), as

\[
Z_{\text{BS}}(\eta) = 1 + \frac{1}{2} (1 + \beta \eta) (1 + \xi) [Z_s(\eta) - 1], \tag{1}
\]

where \( \xi \equiv \langle \sigma^2 \rangle / \langle \sigma^2 \rangle \) and \( \beta \) is adjusted as to reproduce the exact third virial coefficient for the mixture \( B_3 \), namely

\[
\beta = \frac{B_3}{(\pi/4)^2 \langle \sigma^2 \rangle^2 (1 + \xi)} - \frac{b_3}{2}. \tag{2}
\]

Here, \( b_3 = 4(4/3 - \sqrt{3}/\pi) \) is the reduced third virial coefficient for the single component system while \( B_3 \) is given by

\[
B_3 = \frac{\pi}{3} \left( a_{11} x_1^3 \sigma_1^4 + 3 a_{12} x_1^2 x_2 \sigma_1^2 \sigma_2^2 + 3 a_{21} x_1 x_2^2 \sigma_1^2 \sigma_2^2 + a_{22} x_2^3 \sigma_2^4 \right), \tag{3}
\]

where

\[
a_{ij} = \pi + 2 (\sigma_i^2 / \sigma_j^2 - 1) \cos^{-1}(\sigma_i / 2 \sigma_j) - \sqrt{4 \sigma_i^2 / \sigma_j^2 - 1} (1 + \sigma_i^2 / 2 \sigma_j^2) \sigma_j^2 / 2 \sigma_i^2 \tag{4}
\]

and \( \sigma_{ij} = (\sigma_i + \sigma_j) / 2 \).

The EOS for the mixture, consistent with a given EOS for a single component system that we introduced recently reads [3]
\[ Z_m^{\text{SYH}}(\eta) = (1 - \xi) \frac{1}{1 - \eta} + \xi Z_s(\eta). \]  

(5)

We stress the fact that Eq. (5) is simpler than Eq. (1) [which must be complemented with Eqs. (2)–(4)]. In addition, the structure of Eq. (5) is valid for any number of components, while the third virial coefficient is known exactly only for binary mixtures.

In Table I, we show the results of Eqs. (1) and (5) when Woodcock’s EOS is used for the single component system [cf. Eq. (15) in Ref. [1]] is used as input in both, as well as the available MC data. Although not shown, we have also performed the comparison using other EOS for the single component system, namely the one by Henderson, ours, and the very accurate Levin(6) approximant of Erpenbeck and Luban. In all instances, it is fair to say that both recipes are of comparable accuracy with respect to the Monte Carlo results, their difference being generally smaller than the error bars of the simulation data. Nevertheless, in the particular case of using Woodcock’s EOS for \( Z_s(\eta) \), as seen in Table I, \( Z_m^{\text{BS}}(\eta) \) performs slightly better than \( Z_m^{\text{SYH}}(\eta) \). This may be fortuitous since it is known that the Levin(6) approximant gives the most accurate approximation to \( Z_s(\eta) \) [6,7] and when using it in Eqs. (1) and (5), the apparent (slight) superiority of \( Z_m^{\text{BS}}(\eta) \) is no longer there. For instance, the theoretical values of Table I corresponding to the packing fraction \( \eta = 0.6 \) are increased by about 0.03 when the Levin(6) approximant rather than Woodcock’s EOS is used as input, so that in this case the accuracy of \( Z_m^{\text{SYH}}(\eta) \) is slightly better than that of \( Z_m^{\text{BS}}(\eta) \).

**TABLE I.** Compressibility factor for different binary mixtures of hard disks as obtained from Monte Carlo simulations, from Eq. (1), and from Eq. (5). In the two latter, Woodcock’s equation of state for the single component system is used.

| \( \sigma_2/\sigma_1 \) | \( \eta \) | \( x_1 = 0.25 \) | \( x_1 = 0.50 \) | \( x_1 = 0.75 \) |
|-----------------|---|-----------------|-----------------|-----------------|
|                 | MC | Eq. (1) | Eq. (5) | MC | Eq. (1) | Eq. (5) | MC | Eq. (1) | Eq. (5) |
| 2/3             | 0.20 | 1.559(6) | 1.559 | 1.559 | 1.561(5) | 1.558 | 1.558 | 1.565(4) | 1.563 | 1.563 |
|                 | 0.30 | 2.036(8) | 2.040 | 2.040 | 2.043(8) | 2.039 | 2.039 | 2.051(8) | 2.048 | 2.048 |
|                 | 0.40 | 2.79(1)  | 2.79  | 2.79  | 2.79(1)  | 2.78  | 2.78  | 2.80(1)  | 2.80  | 2.80  |
|                 | 0.45 | 3.31(1)  | 3.32  | 3.32  | 3.31(2)  | 3.32  | 3.32  | 3.33(1)  | 3.34  | 3.34  |
|                 | 0.50 | 4.02(2)  | 4.02  | 4.02  | 4.02(1)  | 4.02  | 4.02  | 4.04(2)  | 4.05  | 4.05  |
|                 | 0.55 | 4.98(2)  | 4.97  | 4.97  | 4.98(2)  | 4.96  | 4.96  | 5.03(2)  | 5.00  | 5.00  |
|                 | 0.60 | 6.31(2)  | 6.29  | 6.28  | 6.30(1)  | 6.28  | 6.27  | 6.36(3)  | 6.33  | 6.33  |
| 1/2             | 0.20 | 1.534(6) | 1.536 | 1.536 | 1.540(6) | 1.538 | 1.538 | 1.556(7) | 1.552 | 1.552 |
|                 | 0.30 | 1.998(7) | 1.995 | 1.995 | 2.008(7) | 2.000 | 2.000 | 2.039(8) | 2.027 | 2.026 |
|                 | 0.40 | 2.72(1)  | 2.70  | 2.70  | 2.71(1)  | 2.71  | 2.71  | 2.77(1)  | 2.76  | 2.76  |
|                 | 0.45 | 3.20(2)  | 3.21  | 3.21  | 3.22(2)  | 3.22  | 3.22  | 3.29(2)  | 3.29  | 3.29  |
|                 | 0.50 | 3.88(1)  | 3.88  | 3.87  | 3.90(2)  | 3.89  | 3.89  | 3.98(2)  | 3.98  | 3.98  |
|                 | 0.55 | 4.79(2)  | 4.77  | 4.76  | 4.81(2)  | 4.80  | 4.78  | 4.93(2)  | 4.91  | 4.90  |
|                 | 0.60 | 6.03(3)  | 6.02  | 6.00  | 6.04(2)  | 6.05  | 6.03  | 6.22(3)  | 6.21  | 6.20  |
| 1/3             | 0.20 | 1.491(6) | 1.490 | 1.490 | 1.510(8) | 1.506 | 1.506 | 1.538(9) | 1.536 | 1.536 |
|                 | 0.30 | 1.907(8) | 1.905 | 1.904 | 1.940(8) | 1.937 | 1.936 | 2.004(9) | 1.996 | 1.995 |
|                 | 0.40 | 2.55(1)  | 2.54  | 2.54  | 2.59(1)  | 2.60  | 2.60  | 2.71(1)  | 2.71  | 2.70  |
|                 | 0.45 | 2.99(2)  | 3.00  | 2.99  | 3.07(1)  | 3.07  | 3.06  | 3.20(2)  | 3.21  | 3.21  |
|                 | 0.50 | 3.60(2)  | 3.59  | 3.57  | 3.69(2)  | 3.69  | 3.68  | 3.89(2)  | 3.88  | 3.87  |
|                 | 0.55 | 4.39(3)  | 4.39  | 4.36  | 4.52(2)  | 4.52  | 4.50  | 4.79(2)  | 4.78  | 4.76  |
|                 | 0.60 | 5.49    | 5.44  | 5.44  | 5.66(6)  | 5.68  | 5.64  | 6.06(1)  | 6.03  | 6.00  |

*Ref. [2]*
Let us try to understand why both EOS give practically equivalent results. First, it may be shown that $Z_{m}^{SYH}(\eta)$, while not reproducing the exact third virial coefficient $B_3$, yields a very good estimate of it \cite{8}. If we replace that estimate into Eq. (2), we get

$$\beta \simeq \frac{1 - \xi}{1 + \xi} \left(1 - \frac{b_3}{2}\right).$$

(6)

By using this estimate in Barrio and Solana’s EOS, we have

$$Z_{m}^{BS}(\eta) - Z_{m}^{SYH}(\eta) \simeq (1 - \xi) \Delta(\eta),$$

(7)

where

$$\Delta(\eta) = \frac{1}{2} \left[1 + \left(1 - \frac{b_3}{2}\right) \eta \right] [Z_s(\eta) - 1] - \eta \frac{\eta}{1 - \eta}. \quad (8)$$

According to the approximation involved in Eq. (7), the difference $Z_{m}^{BS}(\eta) - Z_{m}^{SYH}(\eta)$ is small if the asymmetry of the mixture is small ($\xi \lesssim 1$) and/or $\Delta(\eta)$ is small. The function $\Delta(\eta)$ is plotted in Fig. 1 for the cases where $Z_{s}(\eta)$ is given by Henderson’s EOS, by Woodcock’s EOS, and by the Levin(6) approximant. In all instances it is practically zero up to $\eta \approx 0.2$ but then it grows rapidly. The most disparate mixture considered in Barrio and Solana’s simulations corresponds to $x_1 = 0.25$, $\alpha = \sigma_2/\sigma_1 = 1/3$, which yields $\xi = 0.75$. This explains the fact that $Z_{m}^{BS}(\eta) - Z_{m}^{SYH}(\eta) \lesssim 0.05$ in the simulated cases. It should be noted however that the right-hand side of Eq. (7) tends to overestimate the actual difference $Z_{m}^{BS}(\eta) - Z_{m}^{SYH}(\eta)$, so that its main purpose is to illustrate the fact that both EOS yield practically equivalent results for not very asymmetric mixtures. On the other hand, more important differences can be expected for disparate mixtures, especially in the case of large densities. At a given density and a given diameter ratio $\alpha \leq 1$ the smallest value of the parameter $\xi$ corresponds to a mole fraction $x_1 = \alpha/(1 + \alpha)$ for the large disks, namely $\xi = 4\alpha/(1 + \alpha)^2$. Thus, $\xi \ll 1$ if $\alpha \ll 1$ and, according to Eq. (7), $Z_{m}^{BS}(\eta) - Z_{m}^{SYH}(\eta) \simeq \Delta(\eta)$.

![FIG. 1. Plot of $\Delta(\eta)$ by assuming Henderson’s EOS (dotted line), Woodcock’s EOS (dashed line), and the Levin(6) approximant (solid line) for the pure fluid.](image)
Let us consider now the limit in which the small disks become point particles ($\alpha \to 0$) and occupy a negligible fraction of the total area. In that case, the compressibility factor of the mixture reduces to

$$Z_m(\eta) \to \frac{x_2}{1 - \eta} + x_1 Z_s(\eta).$$  \hspace{1cm} (9)

The first term represents the (ideal gas) partial pressure due to the point particles in the available area (i.e., the total area minus the area occupied by the large disks), while the second term represents the partial pressure associated with the large disks. In the limit $\alpha \to 0$ with $x_1$ finite (or, more generally, $x_1 \gg \alpha$), we have $\xi \to x_1$ and $\beta \to (1 - b_3/2)x_2/(1 + x_1)$ [note in that limit the approximation (6) is correct], so that

$$Z^\text{SYH}_m(\eta) \to \frac{x_2}{1 - \eta} + x_1 Z_s(\eta),$$

$$Z^\text{BS}_m(\eta) \to 1 + \frac{1}{2} \left[ 1 + x_1 + x_2 \left( 1 - \frac{b_3}{2} \right) \eta \right] \left[ Z_s(\eta) - 1 \right].$$

Therefore, while Eq. (6) is consistent with the exact property (5), Eq. (1) violates it. In fact, the right-hand side of (7), with $\xi = x_1$, gives the deviation of Barrio and Solana’s EOS from the exact compressibility factor in the special case $\alpha \to 0$.

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