The effective colloid interaction in the Asakura–Oosawa model. Assessment of non-pairwise terms from the virial expansion

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The relevance of neglecting three- and four-body interactions in the coarse-grained version of the Asakura–Oosawa model is examined. A mapping between the first few virial coefficients of the binary nonadditive hard-sphere mixture representative of this model and those arising from the (pairwise) depletion potential approximation allows for a quantitative evaluation of the effect of such interactions. This turns out to be especially important for large size ratios and large reservoir polymer packing fractions.

I. INTRODUCTION

The description of the thermodynamic properties of complex fluids is in general not an easy task. In it, one faces the presence of many degrees of freedom and maybe also different length and time scales. An approach that is usually followed is to recur to coarse-graining. In this approach, what one attempts is to integrate out the irrelevant degrees of freedom and hence to end up with a simpler (equivalent) system with an effective interaction that hopefully captures exactly the essential features of the real interaction. Achieving an exact coarse-graining is, however, also difficult. This is due to the fact that, even if the underlying original molecular interactions are pairwise, the resulting effective potential turns out to be in general a many-body one. For this reason, in the coarse-graining process it is usual to replace the full many-body potential by a simpler effective one in which only pair interactions are involved. The question then arises as to whether the thermodynamic properties derived with the effective potential provide a reliable account of the same properties for the original fluid.

In the early 20th century, Kamerlingh Onnes introduced the (then empirical) virial series to provide a mathematical representation of experimental pressure-density-temperature data of gases and liquids. In a broader context, one refers to a virial expansion of a given property when such a property is expressed as a power series in density. Thus, the virial expansion represents in principle a systematic way for calculating the properties of bulk matter, provided of course that the coefficients in the expansion (the so-called virial coefficients) are known accurately either through direct measurement or from theoretical developments. At least formally, one of the great achievements of statistical mechanics, and a major breakthrough in the theoretical approach to calculating virial coefficients involved in the equation of state of fluids, occurred when Mayer was able to obtain general expressions for the corresponding virial coefficients in terms of sums of cluster integrals over the interaction among groups of fluid particles. In particular, the second virial coefficient depends only on pair interactions, while the third virial coefficient depends on two- and three-body interactions, and so on. If the intermolecular potential is simple enough, some of such virial coefficients may be calculated analytically. For instance, in the case of the hard-sphere (HS) fluid, the first four virial coefficients are known analytically. The same applies to the celebrated Asakura–Oosawa (AO) model, which describes colloidal HSs in a solvent of ideal polymers that interpenetrate each other but interact with the colloids via a HS repulsion. In this case, considering that the system may be taken as a nonadditive hard-sphere (NAHS) binary mixture with high size asymmetry, analytical results for the first four virial coefficients have been very recently reported. In general, however, numerical evaluation is required and even for simple potentials such as the ones just mentioned there are various technical difficulties involved in computing the higher order virial coefficients. A noteworthy aspect of the usefulness of virial coefficients is that the comparison of these coefficients for the original system and the ones stemming out of the coarse-grained interaction potential will indicate to what extent and under which conditions the neglect of the many-body terms in the latter has an impact on whether the thermodynamic properties of both systems agree.

Ever since its introduction, the AO model has received a lot of attention in the literature, including some very recent contributions. It is well known that its coarse-
grained description involves an effective (depletion) pairwise interaction between the colloids that, among other things, leads to fluid-fluid demixing. Attempts to examine whether the thermodynamics obtained with the depletion potential agrees with the one of the full mixture have also been reported. In particular, it was found that, for a polymer/colloid size ratio $q$ smaller than the threshold value $q_0 = 2/\sqrt{3} - 1 \approx 0.1547$, the AO pair depletion potential turns out to be the only one contributing to the exact effective interaction among the solutes. Recently, Ashton and Wilding focused, via simulation, on the dominant many-body effect neglected in the pair potential description if $q > q_0$, namely the one associated with the interaction between three colloidal particles. To this end, they examined the difference between the third virial coefficient of the full system and that of the effective system.

Here we will follow a similar route but also profit from the availability of the first five virial coefficients of the full NAHS mixture corresponding to the AO model to derive, by the exact mapping that may be performed between both sets of coefficients, the second, third, and fourth virial coefficients that follow from the depletion pair potential which is obtained from the coarse-graining of the same mixture. The aim is to quantify the deviations from the exact results that one gets for both the third and fourth virial coefficients when computing them with the effective depletion potential. As we will see, the influence of non-pairwise interactions on the third and fourth virial coefficients is rather small for $q \lesssim 0.4$ but becomes increasingly important for larger values of the size ratio $q$.

The paper is organized as follows. In Sec. II, and in order to make the paper self-contained, we recall the results for the first five virial coefficients of the original AO binary mixture. This is followed in Sec. III by the introduction of the osmotic pressure of the colloidal system, which allows us to make the mapping between the virial coefficients of the mixture and those coming out of the effective one-component colloidal system. The analytical results that follow from the pair depletion potential approximation are presented in Sec. IV. Section V provides a comparison between the exact and the approximate results. The paper is closed in Sec. VI with further discussion and some concluding remarks.

II. VIRIAL COEFFICIENTS OF THE AO MODEL

Consider a binary fluid mixture of $N = N_c + N_p$ spheres (colloids+polymers) in a volume $V$. The colloid and polymer mole fractions are $x_c = N_c/N$ and $x_p = N_p/N = 1 - x_c$, respectively. Analogously, the partial and total number densities are $\rho_c = N_c/V$, $\rho_p = N_p/V$, and $\rho = \rho_c + \rho_p = N/V$. The interactions are assumed to be of HS type. The distance of closest approach between spheres of species $\alpha$ and $\gamma$, denoted by $\sigma_{\alpha\gamma}$, is such that $\sigma_{cc} = \sigma_c$, $\sigma_{pp} = 0$, and $\sigma_{cp} = \frac{1}{2} \sigma_c (1 + q)$, with the size ratio $q$ acting as the (positive) nonadditivity parameter. The colloid packing fraction is $\eta_c = \frac{\pi}{6} \rho_c \sigma_c^3$. For simplicity, from now on we choose $\sigma_c = 1$ as the unit of length. This NAHS mixture defines the well known AO model.

The usual virial expansion of the mixture reads

\begin{equation}
\beta \alpha(\rho_c, \rho_p) = \rho_c \ln (\rho_c A_c^3) + \rho_p \ln (\rho_p A_p^3) - \rho + \sum_{n=2}^{\infty} B_n(x_c, q) \rho^n, \tag{2.1}
\end{equation}

where $a$ is the free energy per unit volume, $p$ is the pressure, $\beta = 1/k_B T$ ($k_B$ being the Boltzmann constant and $T$ being the absolute temperature), $\Lambda_n$ is the thermal de Broglie wavelength of species $\alpha$, and the notation $B_n(x_c, q)$ makes it explicit that the virial coefficients depend only on the mole fraction $x_c$ of the colloids and on the size ratio $q$.

The second, third, fourth, and fifth virial coefficients of the AO model are given by

\begin{equation}
B_2(x_c, q) = x_c^2 B_{11} + 2x_c x_p B_{12}(q), \tag{2.3}
\end{equation}

\begin{equation}
B_3(x_c, q) = x_c^3 C_{111} + 3x_c^2 x_p C_{112}(q), \tag{2.4}
\end{equation}

\begin{equation}
B_4(x_c, q) = x_c^4 D_{1111} + 4x_c^3 x_p D_{1112}(q) + 6x_c^2 x_p^2 D_{1122}(q), \tag{2.5}
\end{equation}

\begin{equation}
B_5(x_c, q) = x_c^5 E_{1111} + 5x_c^4 x_p E_{1112}(q) + 10x_c^3 x_p^2 E_{1122}(q) + 10x_c^2 x_p^3 E_{11222}(q), \tag{2.6}
\end{equation}

where all the composition-independent coefficients, except $E_{11112}$ and $E_{11122}$, are exactly known as functions of $q$:

\begin{equation}
B_{11} = \frac{\pi}{6}, \quad B_{12} = \frac{\pi (1 + q)^3}{6}, \tag{2.7}
\end{equation}

\begin{equation}
C_{111} = \left(\frac{\pi}{6}\right)^2 10, \quad C_{112} = \left(\frac{\pi}{6}\right)^2 \frac{1 + 6q + 15q^2 + 8q^3}{3}, \tag{2.8}
\end{equation}

\begin{equation}
D_{1111} = \left(\frac{\pi}{6}\right)^3 \left(\frac{2707}{70} + \frac{219\sqrt{2}}{35\pi} - \frac{4131 \cos^{-1} \frac{1}{3}}{70\pi}\right), \tag{2.9}
\end{equation}

\begin{equation}
D_{1122} = -\left(\frac{\pi}{6}\right)^3 q^5 \left(\frac{27}{20} + \frac{12q}{5} + \frac{51q^2}{35} + \frac{51q^3}{140} + \frac{17q^4}{420}\right), \tag{2.10}
\end{equation}

\begin{equation}
D_{1112} = \begin{cases} D_{1112}^{(a)}, \quad q \leq q_0, \\ D_{1112}^{(a)} + D_{1112}^{(b)}, \quad q > q_0, \end{cases} \tag{2.11}
\end{equation}

with $q_0$ defined as

\begin{equation}
q_0 = 2/\sqrt{3} - 1 \approx 0.1547.
\end{equation}
In Eq. (2.2) it turns out to be convenient to consider the semi-grand-canonical ensemble \((\mu_p, N_c, V, T)\), where \(\mu_p\) is the chemical potential of the polymer component. In that ensemble, the pressure of the mixture can be written as\(^{13}\)

\[
\beta p(\rho_c, z_p) = z_p + \beta \Pi(\rho_c, z_p),
\]

(3.1)

where

\[
z_p = \frac{e^{\beta \mu_p}}{\Lambda_p^3}
\]

(3.2)

is the polymer fugacity and \(\Pi(\rho_c, z_p)\) is the osmotic pressure that takes into account the (formally) exact effective colloid-colloid interactions mediated by the polymers. Its virial expansion is

\[
\beta \Pi(\rho_c, z_p) = \rho_c + \sum_{n=2}^{\infty} B_n^{\text{eff}}(z_p, q) \rho_c^n,
\]

(3.3)

where \(B_n^{\text{eff}}(z_p, q)\) are the virial coefficients of the effective one-component colloidal fluid. The fugacity \(z_p\) of the polymer component can be equivalently represented by the reservoir polymer packing fraction \(\eta_{p,r} = \frac{z_p}{\Lambda_p^3 q^3}\).

Thus, henceforth we make the change \(B_n^{\text{eff}}(z_p, q) \to B_n^{\text{eff}}(\eta_{p,r}, q)\). The effective virial coefficients \(B_n^{\text{eff}}(\eta_{p,r}, q)\) can be further expressed as a series in powers of \(\eta_{p,r}\),

\[
B_n^{\text{eff}}(\eta_{p,r}, q) = \sum_{j=0}^{\infty} B_n^{(j)}(q) \eta_{p,r}^j.
\]

(3.4)

Our aim in this section is to obtain the exact relations between the effective coefficients \(B_n^{(j)}\) (with \(n+j \leq 5\)) and the binary-mixture virial coefficients in Eqs. (2.3)–(2.6). Making use of Eqs. (2.7)–(2.15) and the numerical values of Table I, one can then know the exact \(q\)-dependence of the coefficients \(B_n^{(j)}\).

The details of the mapping of the binary-mixture virial coefficients onto the effective one-component colloidal coefficients are given in Appendix A. The results for \(B_n^{(j)}\) with \(n+j \leq 5\) are

\[
B_2^{(0)} = B_{11}, \quad B_4^{(0)} = C_{111},
\]

(3.5a)

\[
B_4^{(0)} = D_{1111}, \quad B_5^{(0)} = E_{11111},
\]

(3.5b)

\[
B_2^{(1)} = \frac{6}{\pi q^3} \left(3\frac{C}{2} - 2B_{12}^2\right),
\]

(3.6)

\[
B_2^{(2)} = 2 \left(\frac{6}{\pi q^3}\right)^2 D_{1122}, \quad B_2^{(3)} = \frac{5}{2} \left(\frac{6}{\pi q^3}\right)^3 E_{11222},
\]

(3.7)

\[
B_3^{(1)} = \frac{6}{\pi q^3} \left(\frac{8}{3} D_{1112} - 6B_{12}C_{112} + \frac{8}{3} B_{12}^3\right).
\]

(3.8)
\begin{align}
B_{3}^{(2)} &= \left(\frac{6}{\pi q^{3}}\right)^{2}(5E_{1122} - 16B_{12}D_{1122}), \\
B_{4}^{(1)} &= \frac{6}{\pi q^{3}}\left(\frac{15}{4}E_{11112} - 8B_{12}D_{1112} - \frac{27}{8}C_{1122}^{12} + 9B_{12}C_{1122} - 2B_{12}^{4}\right),
\end{align}

Equations (3.5)–(3.10) provide the sought relationships between the effective and binary-mixture virial coefficients that account for all the three- and four-body interactions up to the fourth virial coefficients of the effective system.

IV. VIRIAL COEFFICIENTS ARISING FROM THE USE OF THE EFFECTIVE PAIR AO POTENTIAL

By integrating out the polymer degrees of freedom, it is possible to derive the formally exact effective many-body interaction potential of the colloids, \( \Phi_{\text{eff}}(r_{Nc}) \equiv \Phi_{\text{eff}}(r_1, r_2, \ldots, r_{Nc}) \), in the AO model. The result is\(^{13}\)

\[
\Phi_{\text{eff}}(r_{Nc}) = -z_p \int dr \prod_{i=1}^{Nc} \left[ 1 - \Theta\left(\frac{1 + q}{2} - |r - r_i|\right) \right] + \sum_{i=1}^{Nc-1} \sum_{j=i+1}^{Nc} \phi_{\text{HS}}(r_{ij}),
\]

where \( \Theta(x) \) is the Heaviside step function and \( \phi_{\text{HS}}(r) \) is the original colloid-colloid HS pair potential of diameter \( \sigma_c = 1 \). If \( q < q_0 \), a polymer particle cannot overlap with more than two nonoverlapping colloids, so that \( \Phi_{\text{eff}} \) is exactly given by\(^{13}\)

\[
\beta \Phi_{\text{eff}}(r_{Nc}) = -z_p V \left[ 1 - \eta_p(1 + q)^3 \right] + \sum_{i=1}^{Nc-1} \sum_{j=i+1}^{Nc} \beta \phi_{\text{dep}}(r_{ij}),
\]

where \( \phi_{\text{dep}}(r) \) is the effective pair AO depletion potential. It is given by

\[
\beta \phi_{\text{dep}}(r) = \begin{cases} 
\infty, & r < 1, \\
-\eta_p \omega(r), & 1 < r < 1 + q, \\
0, & r > 1 + q,
\end{cases}
\]

where

\[
\omega(r) = \frac{1}{2q^3}(1 + q - r)^2(2 + 2q + r).
\]

The corresponding Mayer function is

\[
f_{\text{dep}}(r) = f_{\text{HS}}(r) + \left[e^{\eta_p \omega(r)} - 1\right] \Theta(r - 1) \Theta(1 + q - r) = f_{\text{HS}}(r) + \sum_{j=1}^{\infty} f_{\text{dep}}^{(j)}(r) \eta_p \omega(r),
\]

with \( f_{\text{HS}}(r) = -\Theta(1 - r) \) and \( f_{\text{dep}}^{(j)}(r) = \Theta(r - 1) \Theta(1 + q - r) \).

On the other hand, if \( q_0 < q \leq 1 \), \( m \)-body terms with \( 3 \leq m \leq 11 \) gradually contribute to \( \Phi_{\text{eff}} \), the upper limit \( (m = 11) \) being due to the fact that a polymer can overlap simultaneously with 12 nonoverlapping colloids only if \( q > 1.25 \). Therefore, Eq. (4.2) becomes an approximation (henceforth referred to as the depletion approximation) if \( q > q_0 \). In the remainder of this section we explicitly evaluate the effective virial coefficients \( B_{3}^{(2)} \) with \( n+j \leq 5 \) for any \( 0 \leq q \leq 1 \) in this depletion approximation.

A. Second virial coefficient

As a consequence of (4.5), the second virial coefficient is

\[
B_{2}^{\text{eff}} = -2\pi \int_{0}^{\infty} dr r^2 f_{\text{dep}}(r) = \frac{2\pi}{3} - 2\pi \sum_{j=1}^{\infty} \frac{\eta_j^3}{j!} \int_{1}^{1+q} dr r^2 [\omega(r)]^j.
\]

From here one can easily obtain

\[
\frac{B_{2}^{(1)}}{B_{2}^{\text{HS}}} = -\frac{3}{2} \left(1 + \frac{5q}{4} + \frac{q^2}{2} + \frac{q^3}{12}\right),
\]

\[
\frac{B_{2}^{(2)}}{B_{2}^{\text{HS}}} = -\frac{27}{40q} \left[1 + \frac{16q}{9} + \frac{68q^2}{63} + \frac{17q^3}{63} + \frac{17q^4}{63}\right],
\]

\[
\frac{B_{2}^{(3)}}{B_{2}^{\text{HS}}} = \frac{27\pi}{112} \left[1 + \frac{19q}{8} + \frac{113q^2}{54} + \frac{451q^3}{540} + \frac{41q^4}{270} + \frac{41q^5}{3240}\right],
\]

where \( B_{2}^{\text{HS}} = \frac{2\pi}{3} \). Equations (4.7)–(4.9) agree with Eqs. (3.6) and (3.7). Of course, this is an expected result since the pair approximation is exact at the level of the second virial coefficient.

B. Third virial coefficient

We now turn to the third virial coefficient

\[
B_{3}^{\text{eff}} = -\frac{(2\pi)^{-3}}{3} \int dk \left[ \tilde{f}_{\text{dep}}(k) \right]^3,
\]

where

\[
\tilde{f}_{\text{dep}}(k) = \int dr e^{-ikr} f_{\text{dep}}(r) = \frac{4\pi}{k} \int_{0}^{\infty} dr r \sin(kr) f_{\text{dep}}(r)
\]
is the Fourier transform of \( f_{\text{dep}}(r) \). From Eq. (4.5) we have

\[
\tilde{f}_{\text{dep}}(k) = \tilde{f}_{\text{HS}}(k) + \sum_{j=1}^{\infty} \tilde{f}_{\text{dep}}^{(j)}(k) \eta_{j,p,r},
\]

(4.12)

where

\[
\tilde{f}_{\text{HS}}(k) = \frac{4\pi}{k^3} (k \cos k - \sin k),
\]

(4.13)

\[
\tilde{f}_{\text{dep}}^{(j)}(k) = \frac{4\pi}{j!} \int_{1}^{1+q} dr \ r \sin(kr) \ [\omega(r)]^j,
\]

(4.14)

According to Eqs. (4.10) and (4.12), the coefficients \( B_3^{(1)} \) and \( B_3^{(2)} \) are given by

\[
B_3^{(1)} = -(2\pi)^{-3} \int dk \ [\tilde{f}_{\text{HS}}(k)]^2 \tilde{f}_{\text{dep}}^{(1)}(k),
\]

(4.15)

\[
B_3^{(2)} = -(2\pi)^{-3} \int dk \tilde{f}_{\text{HS}}(k) \left\{ \tilde{f}_{\text{HS}}(k) \tilde{f}_{\text{dep}}^{(2)}(k) + \left[ \tilde{f}_{\text{dep}}^{(1)}(k) \right]^2 \right\}.
\]

(4.16)

The explicit expressions of \( \tilde{f}_{\text{dep}}^{(1)}(k) \) and \( \tilde{f}_{\text{dep}}^{(2)}(k) \) can be obtained from application of Eqs. (4.4) and (4.14) but, for conciseness, they will be omitted here. Insertion of those expressions into Eqs. (4.15) and (4.16) yields (for \( 0 \leq q \leq 1 \))

\[
B_3^{(1)} \over B_{3\text{HS}} = -3 \left( 1 + \frac{4q^2}{5} - \frac{4q^4}{25} + \frac{14q^3}{75} + \frac{2q^5}{175} + \frac{q^6}{35} + \frac{q^6}{315} \right),
\]

(4.17)

\[
B_3^{(2)} \over B_{3\text{HS}} = -\frac{27}{20q} \left( 1 - \frac{107q}{90} - \frac{1529q^2}{315} - \frac{9253q^3}{2520} - \frac{3889q^4}{5670} + \frac{4663q^5}{9450} + \frac{1049q^6}{113400} \right).
\]

(4.18)

As a byproduct, since Eq. (4.18) must be exact for \( q < q_0 \), Eq. (3.9) allows one to obtain the exact expression of \( E_{11122} \) for \( q < q_0 \):

\[
E_{11122} = -\frac{\pi^4 q^5}{800} \left( 3 + \frac{79q}{18} + \frac{281q^2}{63} + \frac{3529q^3}{504} + \frac{2519q^4}{378} + \frac{34583q^5}{11340} + \frac{3769q^6}{5670} + \frac{68040q^7}{68040} \right).
\]

(4.19)

The exact values of \( E_{11122} \) corresponding to \( q = 0.05, 0.10, \) and \( 0.15 \) are \(-1.22960 \times 10^{-7}, -4.25092 \times 10^{-6}, \) and \(-3.50057 \times 10^{-5} \), respectively. By comparison with the third column of Table I, we observe that the MC results agree with the exact values within the associated uncertainties.

C. Fourth virial coefficient

Finally, we consider the effective fourth virial coefficient in the pair depletion approximation. It is given by

\[
B_4^{(\text{eff})} = -\frac{1}{8} \left( 3 \begin{array}{c} \square \\ \square + \square \end{array} + 6 \begin{array}{c} \square \\ \square + \square \end{array} \right),
\]

(4.20)

where each thick bond represents a Mayer function (4.5). Expanding in powers of \( \eta_{p,r} \), one gets

\[
B_4^{(1)} = -\frac{3}{4} \left( 2 \begin{array}{c} \square \\ \square + \square \end{array} + 4 \begin{array}{c} \square \\ \square + \square \end{array} + \begin{array}{c} \square \\ \square + \square \end{array} \right).
\]

(4.21)

Now, a thin solid line between two circles represents the HS Mayer function \( f_{\text{HS}}(r) \), while a dotted line represents a term \( f_{\text{dep}}^{(1)}(r) \). Interestingly, Eq. (4.21) can be written as

\[
B_4^{(1)} = -6\pi \int_1^{1+q} dr \ r^2 \omega(r) y_{2\text{HS}}(r),
\]

(4.22)

where

\[
y_{2\text{HS}}(r) = \begin{array}{c} \square \\ \square + 2 \begin{array}{c} \square \\ \square + \square \end{array} \end{array} + \begin{array}{c} \square \\ \square + \square \end{array} \begin{array}{c} \square \\ \square + \square \end{array} + \begin{array}{c} \square \\ \square + \square \end{array}.
\]

(4.23)

is the HS cavity function to second order in density, which is exactly known.\(^{26,27}\)

After some lengthy algebra it is possible to find a fully analytical expression for \( B_4^{(1)} \) (see Appendix B). Again, since that expression of \( B_4^{(1)} \) is exact for \( q \leq q_0 \), use of Eq. (3.10) allows us to derive an exact analytical form of \( E_{1111112} \) for \( q \leq q_0 \) [see Eq. (B9)]. The values corresponding to \( q = 0.05, 0.10, \) and \( 0.15 \) are 0.0265884, 0.0435074, and 0.0663594, respectively. Comparison with the second column of Table I shows again an excellent agreement of the MC results with the exact values.

V. COMPARISON BETWEEN THE EXACT AND THE APPROXIMATE COEFFICIENTS \( B_{3\text{HS}}^{(1)} \), \( B_{3\text{HS}}^{(2)} \), AND \( B_{4\text{HS}}^{(1)} \)

As said before, the (depletion) pair-potential approximation (4.2) is only correct if \( q < q_0 \approx 0.1547 \). Beyond that value, the virial coefficients \( B_{n\text{eff}}^{(1)} \) (with \( n \geq 3 \)) obtained from the AO pair potential (4.3) differ from the exact ones. In particular, the exact coefficient \( B_{4\text{HS}}^{(1)} \) is influenced by three-body interactions,\(^{24}\) while the exact coefficient \( B_{4\text{eff}}^{(1)} \) is influenced by both three- and four-body interactions.

Here we restrict ourselves to \( B_3^{(1)} \), \( B_3^{(2)} \), and \( B_4^{(1)} \). In the depletion approximation, they are given by Eqs. (4.17), (4.18), and (B4)–(B8), respectively (if \( q \leq 1 \)). The exact expressions are given by Eqs. (3.8), (3.9), and (3.10), respectively, in terms of the composition-independent virial coefficients of the binary mixture.
While in Eq. (3.8) all the coefficients are known analytically, in Eqs. (3.9) and (3.10) one needs to resort to numerical MC evaluations listed in Table I.

The comparison between the exact and approximate coefficients is carried out in Fig. 1. We see that the influence of three-body interactions on \( B_3^{(1)} \) and \( B_3^{(2)} \) is practically negligible in the range \( q_0 \leq q \lesssim 0.4 \) but becomes quite important, especially in the case of \( B_3^{(1)} \), if \( q \gtrsim 0.6 \). A similar conclusion can be drawn from \( B_4^{(1)} \): the role played by three- and four-body interactions is irrelevant if \( q \leq 0.4 \) but becomes essential as \( q \) increases. We observe that the non-pairwise contributions to the true effective many-body colloid potential tend to increase the values of \( B_3^{\text{eff}} \) and \( B_4^{\text{eff}} \) with respect to the depletion-potential estimates, thus partially compensating for the attractive character of the depletion potential. For instance, while the depletion approximation predicts a monotonic decrease of \( B_3^{(1)} \) with increasing \( q \), the exact coefficient presents a non-monotonic behavior with a minimum at \( q \approx 0.54 \). Also, \( B_4^{(1)} \) is negative definite in the depletion approximation, while it actually changes from negative to positive at \( q \approx 0.74 \).

Assuming sufficiently small values of \( \eta_{p,r} \), the expansion (3.4) can be truncated to obtain the approximate forms \( B_3^{\text{eff}}(\eta_{p,r}) \approx B_3^{\text{HS}} + B_3^{(1)}(1) \eta_{p,r} + B_3^{(2)}(1) \eta_{p,r}^2 \) and \( B_4^{\text{eff}}(\eta_{p,r}) \approx B_4^{\text{HS}} + B_4^{(1)}(1) \eta_{p,r} + B_4^{(2)}(1) \eta_{p,r}^2 \). The resulting curves for \( q = 0.154 \lesssim q_0 \) and \( q = 0.8 \) in the range \( 0 \leq \eta_{p,r} \leq 0.1 \) are plotted in Fig. 2. Figure 2(a) is qualitatively analogous to Fig. 3 of Ref. 24. We observe that three- and four-body interactions become relevant for \( \eta_{p,r} \gtrsim 0.1 \) if \( q = 0.8 \).

VI. CONCLUDING REMARKS

Using the available results for the virial coefficients of the AO binary-mixture model, in this paper we have
assessed, for size ratios $0 < q < 1$, the effect of neglecting three- and four-body interactions on the values of the effective one-component virial coefficients $B_3^{\text{ff}}$ and $B_4^{\text{ff}}$ that follow from the depletion pair potential derived in the coarse-grained version of such a model. While it was already known that the coarse-grained version is exact for $q \leq q_0 = 2/\sqrt{3} - 1 \simeq 0.1547$, the mapping between the virial coefficients of the true mixture and the effective ones that we have presented here, together with the corresponding analytical results, have allowed us to explicitly quantify the differences for the partial contributions $B_3^{(1)}$, $B_3^{(2)}$, and $B_4^{(1)}$ for $q > q_0$. As an extra bonus of this mapping, exact analytical expressions for the binary-mixture coefficients $E_{11122}$ and $E_{11112}$ were derived for any size ratio $q < q_0$. The same was in turn useful to check the accuracy of our numerical results for those coefficients, which were proven to be reliable.

The results indicate that the pair depletion approximation is very accurate for $q_0 < q \lesssim 0.4$ but one must certainly take into account the influence of three-body interactions on $B_3^{\text{ff}}$ and $B_4^{\text{ff}}$ if $q > 0.6$, their role becoming essential as $q$ increases. While it is not possible at this stage to disentangle the roles of three- and four-body interactions on $B_4^{\text{ff}}$, it is reasonable to expect that four-body terms could be important at least for values of $q$ close to unity. All these facts should be especially noteworthy when dealing with dense systems. Also, for small values of $\eta_{p,r}$, such an influence has been shown here to be relevant. In fact, as already pointed out in the case of three-body interactions by the numerical studies of Ashton and Wilding, the deviation between the exact and depletion values of $B_3^{\text{ff}}$ significantly increases as $\eta_{p,r}$ becomes larger. Therefore, care must be exercised when drawing conclusions from the coarse-grained version of the AO model if either $q$ or $\eta_{p,r}$, or both, are large.

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**Appendix A: Derivation of Eqs. (3.5)–(3.10)**

We start by rewriting Eq. (2.2) to fifth order as

$$
\beta p(\rho_c, \rho_p) = \rho_c + \rho_p + B_{11} \rho_c^2 + 2B_{12} \rho_c \rho_p + C_{111} \rho_c^3 \\
+ 3C_{112} \rho_c^2 \rho_p + D_{1111} \rho_c^4 + 4D_{1112} \rho_c^3 \rho_p \\
+ 6D_{1122} \rho_c^2 \rho_p^2 + E_{11111} \rho_c^5 + 5E_{11112} \rho_c^4 \rho_p \\
+ 10E_{11122} \rho_c^3 \rho_p^2 + 10E_{11222} \rho_c^2 \rho_p^3 + O(\rho^6),
$$

(A1)

where we have used Eqs. (2.3)–(2.6). Next, from Eq. (2.1) and the thermodynamic relation $\mu_p = (\partial u/\partial \rho_p)_{\rho_c}$, we obtain

$$
\beta \mu_p = \ln (\rho_p \Lambda_p^3) + 2B_{12} \rho_c + \frac{3}{2} C_{112} \rho_c^2 + \frac{4}{3} D_{1112} \rho_c^3 \\
+ 4D_{1122} \rho_c^2 \rho_p + \frac{5}{4} E_{11112} \rho_c^4 + 5E_{11122} \rho_c^3 \rho_p \\
+ \frac{15}{2} E_{11222} \rho_c^2 \rho_p^2 + O(\rho^5).
$$

(A2)

Consequently, the fugacity (3.2) can be written as

$$
\tilde{z}_p = 1 + 2B_{12} \rho_c + \left(2B_{12}^2 + \frac{3}{2} C_{112}\right) \rho_c^2 + \left(\frac{4}{3} B_{12}^3 \right) \rho_c^3 \\
+ 3B_{12} C_{112} + \left(\frac{4}{3} D_{1112}\right) \rho_c^3 + 4D_{1122} \rho_c^2 \rho_p \\
+ \left(\frac{2}{3} B_{12}^4 + 3B_{12}^2 C_{112} + \frac{8}{3} B_{12} D_{1112} + \frac{9}{8} C_{1112}\right) \rho_c^4 \\
+ \frac{5}{4} E_{11112} \rho_c^4 + (8B_{12} D_{1112} + 5E_{11122}) \rho_c^3 \rho_p \\
+ \frac{15}{2} E_{11222} \rho_c^2 \rho_p^2 + O(\rho^5).
$$

(A3)

This can be inverted to express $\rho_p$ as a series expansion in powers of $\rho_c$ and $z_p$:

$$
\rho_p = 1 - 2B_{12} \rho_c + \left(2B_{12}^2 - \frac{3}{2} C_{112}\right) \rho_c^2 - \left(\frac{4}{3} B_{12}^3 \right) \rho_c^3 \\
- 3B_{12} C_{112} + \left(\frac{4}{3} D_{1112}\right) \rho_c^3 - 4D_{1122} \rho_c^2 z_p \\
+ \left(\frac{2}{3} B_{12}^4 - 3B_{12}^2 C_{112} + \frac{8}{3} B_{12} D_{1112} + \frac{9}{8} C_{1112}\right) \rho_c^4 \\
- \frac{5}{4} E_{11112} \rho_c^4 + (16B_{12} D_{1112} - 5E_{11122}) \rho_c^3 z_p \\
- \frac{15}{2} E_{11222} \rho_c^2 \rho_p^2 + \cdots,
$$

(A4)

where the ellipsis denotes terms of order $\rho_c^n z_p^j$ with $n+j \geq 6$.

Inserting Eqs. (A1) and (A4) into Eq. (3.1) one can easily identify the coefficients shown in Eqs. (3.5)–(3.10).

**Appendix B: Expressions for $B_4^{(1)}$ in the depletion-potential approximation**

In the range of interest $1 < r < 1 + q < 2$, the expressions for the contributions of $g^{\text{HS}}(r)$ in Eq. (4.23) are

$$
\varphi(r) = \frac{\pi^2 (r - 3)^4}{36} (r^3 + 12r^2 + 27r - 6),
$$

(B1)

$$
\psi(r) = \frac{\pi^2 (r - 2)^2}{36} (r^5 + 4r^4 - 51r^3 - 10r^2 + 479r - 81).
$$

(B2)
\[
\chi(r) = \pi \Theta \left( \sqrt{3} - r \right) \left[ -r^2 \left( \frac{3r^2}{280} - \frac{41}{420} \right) \sqrt{3 - r^2} - \left( \frac{23}{15} r - \frac{36}{35r} \right) \cos^{-1} \frac{r}{\sqrt{3(4 - r^2)}} \right.
\]
\[
+ \left( \frac{3r^6}{500} - \frac{r^4}{15} + \frac{r^2}{2} + \frac{2r}{15} - \frac{9}{35r} \right) \cos^{-1} \frac{r^2 + r - 3}{\sqrt{3(4 - r^2)}}
\]
\[
+ \left( \frac{3r^6}{500} - \frac{r^4}{15} + \frac{r^2}{2} - \frac{2r}{15} + \frac{9}{35r} \right) \cos^{-1} \frac{-r^2 + r + 3}{\sqrt{3(4 - r^2)}} \right].
\] (B3)

Use of Eqs. (B1)–(B3) into Eq. (4.22) gives

\[
B^{(1)}_4 = B^{(1)}_{4,\chi} + B^{(1)}_{4,\psi},
\] (B4)

where

\[
B^{(1)}_{4,\chi} = -\frac{\pi^3}{3} \left( 1 + \frac{q}{8} - q^2 - \frac{7q^3}{24} + \frac{29q^4}{140} + \frac{41q^5}{560} - \frac{79q^6}{5040} \right.
\]
\[
- \frac{37q^7}{16800} + \frac{q^8}{2100} + \frac{q^9}{25200},
\] (B5)

with

\[
B^{(1)}_{4,\chi A} = -\frac{\pi^2}{22400q^3} \left[ \frac{2\sqrt{2}}{105} (375323 + 1710828q + 548814q^2 - 204400q^3) - \pi (23669 + 76404q + 56562q^2
\]
\[
+ 12240q^3) + 135 (387 + 1164q + 990q^2 + 272q^3) \cos^{-1} \frac{1}{3} \right],
\] (B7)

\[
\Delta B^{(1)}_{4,\chi} = -\frac{\pi^2}{11200q^3} \left[ \frac{\sqrt{2 - 2q - q^2}}{105} (375323 + 1599922q + 413153q^2 - 465800q^3 - 241510q^4 - 108524q^5 - 40954q^6
\]
\[
- 4760q^7 + 2555q^8 + 1050q^9 + 105q^{10}) + \frac{(1 - q)^5}{2} (1603 + 2243q + 1479q^2 + 855q^3 + 405q^4 + 117q^5
\]
\[
+ 17q^6 + q^7) \cos^{-1} \frac{2q - 1}{\sqrt{3(1 - q)}} - 8(1 + q)^3 (1373 - 336q - 72q^2 + 96q^3 + 24q^4) \cos^{-1} \frac{1 + q}{\sqrt{3}}
\]
\[
+ \frac{(3 + q)^5}{2} (111 + 171q - 117q^2 + 135q^3 + 25q^4 - 3q^5 - 3q^6 + q^7) \cos^{-1} \frac{5 + 2q}{\sqrt{3(3 + q)}} \right].
\] (B8)

Taking into account that (B6) is exact for \( q < q_0 \), and using Eqs. (2.7), (2.8), (2.12), and (3.10), one can obtain the following exact expression of \( E_{11112} \) for \( q < q_0 \):

\[
E_{11112} = \left( \frac{\pi}{6} \right)^4 \frac{1}{5} \left[ 1 + 12q + 66q^2 + 40q^3 + 81q^4 + \frac{108q^5}{5} - 144q^6 - \frac{6516q^7}{35} - \frac{1521q^8}{10} - \frac{338q^9}{35} - \frac{6858q^{10}}{175} \right.
\]
\[
- \frac{1458q^{11}}{175} - \frac{243q^{12}}{350} \right] + \frac{2\pi q^3}{45} \left( B^{(1)}_{4,\chi A} + \Delta B^{(1)}_{4,\chi} \right).
\] (B9)

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