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Theory of asymmetric nonadditive binary hard-sphere mixtures

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It is shown that the formal procedure of integrating out the degrees of freedom of the small spheres in a binary hard-sphere mixture works equally well for nonadditive as it does for additive mixtures. For highly asymmetric mixtures (small size ratios) the resulting effective Hamiltonian of the one-component fluid of big spheres, which consists of an infinite number of many-body interactions, should be accurately approximated by truncating after the term describing the effective pair interaction. Using a density functional treatment developed originally for additive hard-sphere mixtures the zero, one, and two-body contribution to the effective Hamiltonian are determined. It is demonstrated that even small degrees of positive or negative nonadditivity have significant effect on the shape of the depletion potential. The second virial coefficient B_2, corresponding to the effective pair interaction between two big spheres, is found to be a sensitive measure of the effects of nonadditivity. The variation of B_2 with the density of the small spheres shows significantly different behavior for additive, slightly positive and slightly negative nonadditive mixtures. Possible repercussions of these results for the phase behavior of binary hard-sphere mixtures are discussed and it is suggested that measurements of B_2 might provide a means of determining the degree of nonadditivity in real colloidal mixtures.

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I. INTRODUCTION

Mixtures of hard spheres play a pivotal role in the statistical mechanics of liquids. Not only do they provide a realistic reference system for describing the structure and thermodynamics of simple atomic mixtures and mixtures of colloidal particles, they are also of considerable intrinsic interest. In particular, investigating the properties of asymmetric binary hard-sphere mixtures became a topic of much activity when it was recognized by Biben and Hansen [1] that such athermal mixtures might afford important examples of pure entropy-driven fluid-fluid phase separation. The most studied model is that of *additive* hard spheres, where the cross diameter $\sigma_{bs}=(\sigma_{bb}+\sigma_{ss})/2$ and σ_{bb} refers to the big-big and σ_{ss} to the small-small diameters. There is now compelling evidence to suggest that additive mixtures, with sufficiently small size ratios σ_{ss}/σ_{bb}, do undergo fluid-fluid phase separation but this transition remains metastable with respect to the fluid-solid transition [2]. The other well studied model is the so-called Asakura-Oosawa (AO) model [3,4] of a colloid-polymer mixture in which the colloid-colloid interaction is hard-sphere like, with diameter σ_{cc}, and the colloid-polymer interaction is also hard-sphere like with diameter σ_{cp}, whereas the polymer-polymer interaction is zero, i.e., $\sigma_{pp}=0$, corresponding to ideal interpenetrating coils. The cross diameter $\sigma_{cp}=(\sigma_{cc}+2R_g)/2$, where R_g is the radius of gyration of the polymer. Various approximate theories [5–7] and some simulation studies for simplified versions of the AO model [7,8] showed that when the size ratio $2R_g/\sigma_{cc}$ is larger than about 0.35 fluid-fluid phase separation is stable with respect to the fluid-solid transition. The AO model can be regarded as an extreme *nonadditive* mixture with $\sigma_{cp}>(\sigma_{cc}+\sigma_{pp})/2$.

One can, of course, investigate mixtures with arbitrary nonadditivity and recent studies of binary hard-sphere mixtures have indicated that a small degree of positive nonadditivity in the cross diameter σ_{bs} might be sufficient to induce a fluid-fluid transition [9,10]. By employing an effective one-component treatment and a variety of liquid state perturbation theories, Louis *et al.* [11] have demonstrated that nonadditivity should have a profound effect on both the fluid-fluid and fluid-solid transition in highly asymmetric hard-sphere mixtures. However, their treatment is based on an empirical approximation [12] for the effective (depletion) potential between two big spheres rather than any systematic derivation of an effective one-component Hamiltonian for the nonadditive hard-sphere mixture. In this paper we develop such an approach following the path that was trodden in the recent studies of the additive mixture [2] and in the special case of the AO model [7]. We show that the same formal technique of integrating out the degrees of freedom of the smaller species, used in Ref. [2], applies equally well to nonadditive mixtures (see Sec. II A).

We were motivated toward such an approach by the following considerations: (a) treating highly asymmetric mixtures by brute force simulation is beset by ergodicity problems and slow equilibration when the packing fraction of the small species is substantial, (b) for small size ratios three and higher body potentials in the effective Hamiltonian do not have a significant effect on the phase behavior of the additive hard-sphere model [2] or of the AO [7,8] model, i.e., in both models phase transitions are determined primarily by the effective pairwise potential between the big particles and we expect the same to be true for small size ratios in systems

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with intermediate degrees of nonadditivity. (c) the effective pairwise potential that arises in the formal development of the theory is the depletion potential, introduced into colloid science by Asakura and Oosawa, and now much studied by theory, simulation [13,14] and experiment. Indeed a variety of experimental techniques [15] have been developed to measure the depletion potential between a colloidal particle, immersed in a sea of small colloids or nonadsorbing polymer, and a wall or another big colloid. Interpreting the results of such experiments requires a reliable theory. Recently we have shown [16,17] that a density functional approach (DFT) provides an accurate means of calculating the depletion potential for additive hard spheres. In the present paper we show (Sec. II B) that the same DFT approach remains valid for the nonadditive case and can, therefore, be used to investigate a much wider class of depletion potentials than one might have suspected *a priori*. We find that even very small degrees of nonadditivity can have a very pronounced effect on the shape of the depletion potential, which leads to significant changes of the magnitude, and sometimes the sign, of the second virial coefficient B_2 associated with the total effective potential between two big spheres. Such changes in B_2 may, in turn, have repercussions for the phase behavior, and may be directly accessible by experiments.

We begin by defining what we mean by nonadditivity. A nonadditive binary hard-sphere mixture is characterized by the diameters (distances of closest approach of the centers of the spheres) σ_{bb}, σ_{ss}, and σ_{bs}, where the subscripts b and s denote big and small. These diameters describe the (pairwise) interaction potentials between two spheres

$$\Phi_{ij}(r)=\begin{cases}\infty & r<\sigma_{ij}\\ 0 & \text{otherwise,}\end{cases} \tag{1}$$

with $i,j\in\{s,b\}$. We follow the usual convention and introduce the nonadditivity parameter Δ via

$$\sigma_{bs}=\tfrac{1}{2}(\sigma_{bb}+\sigma_{ss})(1+\Delta), \tag{2}$$

and allow Δ to be positive or negative. Additive hard-sphere mixtures have $\Delta=0$.

In the following we consider two different routes to introducing nonadditivity into a binary hard-sphere mixtures. In both routes we keep the diameter of the big spheres σ_{bb} and the number density of the small spheres in the reservoir ρ_s^r fixed but allow for (i) changes in the diameter of the small spheres σ_{ss} while keeping the cross diameter σ_{bs} constant or (ii) changes in the cross diameter σ_{bs} while keeping the diameter of the small spheres σ_{ss} constant. These two types of changes are illustrated in Figs. 1 and 2, respectively.

In the first route (i), which was introduced in an earlier paper by two of us [18], we can smoothly follow a path that connects the additive hard-sphere mixture to the Asakura-Oosawa model [3,4]. As mentioned above, in the Asakura-Oosawa model, the small particles are modeled as ideal gas particles with zero diameter $\sigma_{ss}^{AO}\equiv 0$ and $\Delta\equiv\Delta^{AO}>0$, keeping the same cross diameter as in the additive case, i.e., we require

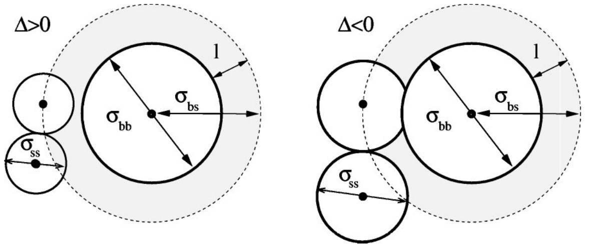

FIG. 1. The centers of the small spheres are excluded from the shaded depletion layer around each big sphere of diameter σ_{bb}. When changing the nonadditivity Δ by route (i), the big-small diameter σ_{bs} is kept constant. For a fixed σ_{bb} this implies that the depletion layer thickness $l=\sigma_{bs}-\sigma_{bb}/2$ is also held constant. The small sphere diameter $\sigma_{ss}(\Delta)$ is decreased for $\Delta>0$ and increased for $\Delta<0$, and since the number density ρ_s^r is fixed, the small sphere packing fraction $\eta_s^r(\Delta)$ also changes.

$$\sigma_{bs}=\tfrac{1}{2}[\sigma_{bb}+\sigma_{ss}(\Delta)](1+\Delta)=\text{const}=\sigma_{bs}^{add}\equiv\tfrac{1}{2}(\sigma_{bb}+\sigma_{ss}^{add}), \tag{3}$$

so that

$$\sigma_{ss}(\Delta)=\frac{\sigma_{ss}^{add}-\sigma_{bb}\ \Delta}{1+\Delta}. \tag{4}$$

The AO limit, defined by $\sigma_{ss}(\Delta^{AO})=0$, implies $\Delta^{AO}=\sigma_{ss}^{add}/\sigma_{bb}\equiv q$, the (fixed) size ratio. Within route (i) choosing $\Delta>\Delta^{AO}$ would give rise to $\sigma_{ss}(\Delta)<0$, which is unphysical, of course. For a given value of the nonadditivity parameter Δ and a fixed number density of the small spheres ρ_s^r it follows that their packing fraction $\eta_s^r(\Delta)=\pi\sigma_{ss}^3(\Delta)\rho_s^r/6$ also varies with Δ,

$$\eta_s^r(\Delta)=\eta_s^{add}\left(\frac{q-\Delta}{q(1+\Delta)}\right)^3, \tag{5}$$

where $\eta_s^{add}\equiv\eta_s^r(0)$. Clearly $\eta_s^r(\Delta)$ decreases with increasing Δ in the range $0<\Delta<\Delta^{AO}=q$. On the other hand, for negative nonadditivity, $\Delta<0$, $\eta_s^r(\Delta)$ increases rapidly with increasing $|\Delta|$ and for studies of the fluid phase we should restrict $\eta_s^r(\Delta)<\eta_s^{freez}=0.494$, the value of the packing fraction at the bulk freezing transition of hard spheres.

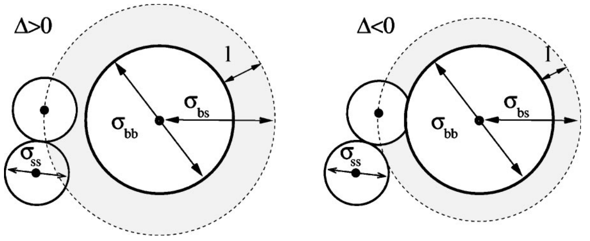

FIG. 2. When changing Δ by route (ii), the big-small diameter σ_{bs} changes. For a fixed σ_{bb} this implies that the depletion layer thickness $l=\sigma_{bs}-\sigma_{bb}/2$ also changes. The small-particle diameter σ_{ss} is kept constant, and since ρ_s^r is fixed, the small sphere packing fraction η_s^r is also constant.

If we consider route (ii), the route used by most previous authors [9–11], both σ_{bb} and σ_{ss} are kept fixed and the cross diameter σ_{bs} becomes a function of Δ through Eq. (2). Note that this case is very different from case (i) as the packing fraction η_s^r of the small spheres remains constant through the whole range of nonadditivity and the Asakura-Oosawa limit can only be reached in the limit of $\rho_s^r \to 0$ in which the depth of the depletion potential approaches zero as well.

Examples of depletion potentials and second virial coefficients calculated from both routes are given in Sec. III. We conclude in Sec. IV with a summary of our results and a discussion of their possible relevance for experiments.

II. MAPPING A BINARY MIXTURE ONTO AN EFFECTIVE ONE-COMPONENT SYSTEM

In this section we map the binary mixture of nonadditive hard spheres onto an effective one-component system of big particles. To this end we begin by formally integrating out the degrees of freedom of the small spheres and determine the form of the effective Hamiltonian of the one-component fluid. We demonstrate that each term of the effective Hamiltonian of the nonadditive system can be determined using a theory for an additive mixture. In a second step we calculate explicitly the leading contributions to the effective Hamiltonian for the binary mixture of nonadditive hard spheres using a DFT designed for the additive hard-sphere mixture.

A. Formal mapping for additive and nonadditive mixtures

We follow the procedure developed by McMillan and Mayer [19] to formally integrate out the degrees of freedom of the small spheres in a homogeneous mixture of N_b big and N_s small spheres in a macroscopic volume V. The Hamiltonian of our mixture is given by

$$H = K + H_{bb} + H_{ss} + H_{bs}, \tag{6}$$

with K the total kinetic energy of the mixture, leading to a trivial contribution to the free energy, and three potential energy contributions

$$H_{bb} = \sum_{i<j}^{N_b} \Phi_{bb}(\mathbf{r}_i^b - \mathbf{r}_j^b), \qquad H_{ss} = \sum_{i<j}^{N_s} \Phi_{ss}(\mathbf{r}_i^s - \mathbf{r}_j^s),$$

$$H_{bs} = \sum_{i=1}^{N_b} \sum_{j=1}^{N_s} \Phi_{bs}(\mathbf{r}_i^b - \mathbf{r}_j^s), \tag{7}$$

where the pairwise hard-sphere interaction potentials Φ_{ij} are defined in Eq. (1). $\mathbf{r}_i^b$, $\mathbf{r}_j^s$ denote the coordinates of big particle i and small particle j, respectively. The thermodynamic potential $F(N_b, z_s, V)$ of a general binary mixture in the semigrandcanonical ensemble can be written in terms of an effective Hamiltonian H^{eff} via the relation

$$\exp(-\beta F) = \mathrm{Tr}_b \exp(-\beta H^{eff}), \tag{8}$$

where $\beta = 1/k_B T$, and $z_s = \Lambda_s^{-3} \exp(\beta\mu_s)$ is the fugacity of the (small) species s, fixed by the reservoir. Tr_ν is shorthand for $1/N_\nu! \Lambda_\nu^{3N_\nu}$ times the volume integral over the coordinates of species ν. In Eq. (8) it denotes the classical trace over the degrees of freedom of the (big) species b. The effective Hamiltonian H^{eff} is given, in the notation of Ref. [2], by

$$H^{eff} = H_{bb} + \Omega, \tag{9}$$

with $\Omega = \Omega(N_b, z_s, V; \{\mathbf{r}^b\})$, the grandcanonical potential of the fluid of species s subjected to the external potential of a fixed configuration $\{\mathbf{r}^b\}$ of N_b particles of species b, defined by

$$\exp(-\beta\Omega) = \sum_{N_s=0}^{\infty} \exp(\beta\mu_s N_s) \mathrm{Tr}_s \exp[-\beta(H_{ss} + H_{bs})]. \tag{10}$$

Using a Mayer cluster expansion it was shown [2] that Ω can be written as a sum of terms Ω_n, which describe the simultaneous interaction of n particles of species b with the ‘‘sea’’ of species s, i.e.,

$$\Omega = \sum_{n=0}^{N_b} \Omega_n. \tag{11}$$

This result is valid for arbitrary (integrable) pairwise potentials. We emphasize that in Eq. (9) all direct interactions between species b, the big particles, are contained in H_{bb} while Ω describes interactions between species s, small spheres, and between the big and small ones. It is precisely this separation into a term that contains just the big-big interactions and those that contain small-small and big-small interactions that allows us to calculate the leading terms Ω_n for nonadditive hard-sphere mixtures using a theory for an *additive* mixture. More specifically, for a given fixed configuration of large particles, Ω is completely determined by the parameters z_s, σ_{ss}, and σ_{bs}. In other words all the terms Ω_n would have an identical form for an additive or a nonadditive system. The only differences arise in H_{bb}, where σ_{bb} constrains the possible positions of the big particles to $|\mathbf{r}_i^b - \mathbf{r}_j^b| > \sigma_{bb}$ for all i,j. For the additive case $\sigma_{bb} = 2\sigma_{bs} - \sigma_{ss}$, while in the nonadditive case σ_{bb} can vary more widely depending on the value of Δ.

1. Zero-body term Ω_0

The first term, Ω_0, is the grandcanonical potential of a sea of small spheres with fugacity z_s *without* any big sphere present and it follows that [2]

$$\Omega_0(z_s, V) = -p_s(z_s) V, \tag{12}$$

with $p_s(z_s)$ the pressure of the reservoir of small spheres. Since this term is intrinsic to the small-sphere fluid it is not affected by introducing nonadditivity.

2. One-body term Ω_1

For a homogeneous system the one-body term Ω_1 is of the form

$$\Omega_1(N_b, z_s) = N_b \omega_1(z_s), \tag{13}$$

with [2]

$$\exp[-\beta\omega_1(z_s)] = \langle \exp(-\beta H_{bs}^{(1)})\rangle_{z_s}, \tag{14}$$

where $H_{bs}^{(n)}$ denotes the interaction between N_s small spheres and $n \geqslant 1$ big spheres and the brackets $\langle \cdots \rangle_{z_s}$ refer to an ensemble average in the reservoir of small spheres. $\omega_1(z_s)$ can be identified as the difference in grandcanonical potential between a sea of small spheres at fugacity z_s with and without a single big sphere. By considering the potential distribution theorem and the definition of the one-body direct correlation function $c_b^{(1)}(\mathbf{r}^b)$ one can show [20,16] that this difference in grandcanonical potential can be expressed as

$$\beta\omega_1(z_s) = -\lim_{\mu_b \to -\infty} c_b^{(1)}(\infty), \tag{15}$$

where $c_b^{(1)}(\infty)$ denotes the direct correlation function of a big sphere evaluated in the bulk mixture. The limit $\mu_b \to -\infty$ implies that the chemical potential μ_b of species b is made sufficiently negative that only one big sphere is present. $c_b^{(1)}(\infty)$ is proportional to the excess (over ideal) chemical potential of species b, i.e., $-c_b^{(1)}(\infty) = \beta\mu_b^{ex}$ and, in general, depends on the density of both species. However, in the limit $\mu_b \to -\infty$, $c_b^{(1)}(\infty)$ depends only on the fugacity z_s. Since only one big sphere is involved [this is explicit in Eq. (14)] nonadditivity plays no role in determining Ω_1. One merely specifies σ_{ss} and then σ_{bs} describes the interaction between small spheres and a fixed big one.

As noticed in Ref. [21], the one-body term $\omega_1(z_s)$ determines the Henry's law constant $h(z_s)$ of the fluid. The latter can be defined by [22]

$$h(z_s) = \lim_{\rho_b \to 0} \frac{\rho_b}{z_b(\rho_b)}, \tag{16}$$

where $z_b = \Lambda_b^{-3}\exp(\beta\mu_b)$ is the fugacity of species b. It follows that

$$h(z_s) = \exp[-\beta\omega_1(z_s)]. \tag{17}$$

$h(z_s)$ does not depend on b-b interactions; deviations of $h(z_s)$ from unity reflect the average effect of b-s interactions at a fixed fugacity z_s of small spheres. Thus, given some means of calculating $c_b^{(1)}(\infty)$, in the limit $\rho_b \to 0$, one can determine the Henry's law constant.

3. Two-body term $\boldsymbol{\Omega_2}$

The two-body term Ω_2 is given by

$$\Omega_2(N_b, z_s; \{\mathbf{r}^b\}) = \sum_{i<j}^{N_b} \omega_2(z_s; |\mathbf{r}_i^b - \mathbf{r}_j^b|), \tag{18}$$

where the pair potential ω_2 is defined by [2]

$$\exp[-\beta\omega_2(z_s; r_{ij}^b)] = \frac{\langle \exp(-\beta H_{bs}^{(2)})\rangle_{z_s}}{\langle \exp(-\beta H_{bs}^{(1)})\rangle_{z_s}^2}, \tag{19}$$

with $r_{ij}^b \equiv |\mathbf{r}_i^b - \mathbf{r}_j^b|$ the distance between the centers of the big spheres. Equivalently we can use the variable $h \equiv r_{ij}^b - \sigma_{bb}$, i.e., the distance between the surfaces of two big spheres. $\omega_2(z_s; r_{ij}^b) \equiv W(h = r_{ij}^b - \sigma_{bb})$ is the grand potential difference between a sea of small spheres, at fugacity z_s, containing two big spheres at finite separation r_{ij}^b and one in which the separation $r_{ij}^b = \infty$. Although the positions of two big particles are involved, the big-big interaction does not enter explicitly into the calculation of ω_2; the diameter σ_{bb} merely acts as an external parameter that restricts the minimum separation to $r_{ij}^b = \sigma_{bb}$. In other words, for a given z_s, σ_{bs}, and σ_{ss}, the calculation of ω_2 is the same for both additive and nonadditive systems.

ω_2 can be identified with the well-known depletion potential between the two big spheres [2,16] and expressed in terms of the one-body direct correlation function

$$\beta\omega_2(z_s; \mathbf{r}) = \lim_{\mu_b \to -\infty} [c_b^{(1)}(\infty) - c_b^{(1)}(\mathbf{r})], \tag{20}$$

where $c_b^{(1)}(\mathbf{r})$ refers to an inhomogeneous situation in which a big sphere fixed at the origin exerts its field on the small spheres and a big (test) particle is inserted at $\mathbf{r}$ [16].

4. Three-body and higher-order terms $\boldsymbol{\Omega_{n\geqslant 3}}$

The three-body term Ω_3 can be written as a sum of three-body potentials $\omega_3(z_s; \mathbf{r}_{i,j,k}^b)$, which can, in turn, be expressed in terms of ensemble averages $\langle \exp(-\beta H_{bs}^{(n)})\rangle_{z_s}$ with $n = 1,2,3$ [2]. Once again big-big interactions are not involved in the calculation and σ_{bb} simply specifies the physically allowed configurations of the three big spheres. Clearly nonadditivity plays no role. The same argument applies for the higher-body ($n > 3$) contributions to Ω, although the specification of the allowed configurations of the big spheres becomes increasingly complicated as n increases.

In practice, the calculation of Ω_n for $n \geqslant 3$ is tedious and determining the phase behavior for effective Hamiltonians that include these and higher-body interactions would be very cumbersome. Contributions to the many-body terms arise from two mechanisms: (1) Directly, if for a given σ_{bb}, σ_{bs} is large enough to allow the overlap of more than two depletion layers. (2) Indirectly, if correlations between the small particles, present for all nonzero σ_{ss}, induce interactions between more than two particles. Contributions from mechanism (1) to Ω_n with $n \geqslant 3$ are identically zero for $(2\sigma_{bs} - \sigma_{bb})/\sigma_{bb} \leqslant 2/\sqrt{3} - 1 = 0.1547$ [7], while for $(2\sigma_{bs} - \sigma_{bb})/\sigma_{bb} \leqslant \sqrt{3/2} - 1 = 0.2247$ the contributions to Ω_n with $n \geqslant 4$ terms are zero [23], etc., . . . If $\sigma_{ss} > 0$, then mechanism (2) will induce additional contributions to the many-body terms at all values of σ_{bs} and σ_{bb}.

For the extreme nonadditive AO model, where $\sigma_{ss} = 0$ but σ_{bs} is nonzero, only mechanism (1) contributes to the many-body terms. An explicit form for the three-body term can be calculated [24], but this is still very tedious to evaluate.

For *additive* binary hard-sphere mixtures with $q = \sigma_{ss}/\sigma_{bb} \leqslant 0.1$, where only the indirect mechanism (2) contributes, three-body contributions seem to be small [13]. Recent DFT calculations [24,25] of the three-body potentials show that these are still much smaller than the two-body potentials for $q=0.2$, where both mechanisms contribute, and that the indirect mechanism (2) can have an important effect on their shape.

There is strong evidence from direct simulation studies of the additive binary system that retaining only two-body contributions in the effective Hamiltonian provides a very good account of the equilibrium phase behavior for $q\leqslant 0.2$ [2]. Similar conclusions were reached for a lattice version of the AO model [8]. In this study we shall focus on such highly asymmetric systems and neglect three and higher-body contributions to the effective Hamiltonian. With this assumption it follows that the structure of the homogeneous fluid (equilibrium correlation functions of the big spheres) is determined solely by the effective pairwise potential

$$\Phi_{eff}(z_s;r)=\Phi_{bb}(r)+\omega_2(z_s;r), \tag{21}$$

since Ω_0 and Ω_1 do not depend on the coordinates of the big particles [21]. It is also straightforward to show that the *phase equilibria* of the binary mixture do not depend on the zero and one-body term [2]. However, these two terms do influence the total pressure and compressibility of the mixture [21].

To complete this section it is necessary to explain how to convert from ρ_s^r, the number density of the small spheres in the reservoir to ρ_s, the actual value of the small sphere density in the mixture. The average number of small spheres in the mixture is given by the thermodynamic relation

$$\langle N_s\rangle_{z_s}=-\frac{\partial F(N_b,V,z_s)}{\partial \mu_s}=-\left\langle \frac{\partial\beta\sum_{n=0}^{\infty}\Omega_n}{\partial \ln z_s}\right\rangle_{z_s}. \tag{22}$$

In Ref. [2] it was shown that an accurate approximation for the conversion can be obtained for additive hard spheres with high asymmetry, $q\leqslant 0.1$, by truncating the expansion after the one-body term so that the average number of small spheres can be evaluated approximately from the formula

$$\langle N_s\rangle_{z_s}\approx-\left(\frac{\partial\beta(\Omega_0+\Omega_1)}{\partial \ln z_s}\right)_{N_b,V}. \tag{23}$$

The required density $\rho_s=\langle N_s\rangle_{z_s}/V$. We shall revisit this approximation in the next section.

B. Evaluation of Ω_0, Ω_1, and Ω_2 within DFT

1. Rosenfeld's fundamental measure DFT

In order to make the mapping presented in Sec. II A explicit for the model of interest, namely, the binary mixture of nonadditive hard spheres, we calculate the terms Ω_0, Ω_1, and Ω_2 within the framework of Rosenfeld's fundamental measure DFT [26]—a theory constructed for additive hard-sphere mixtures. As mentioned earlier, the reason why we can apply a theory constructed for *additive* binary mixtures is that only the interaction potentials Φ_{ss}, between two small spheres, and Φ_{bs}, between a big and a small sphere, enter into the calculation of Ω_n. This argument substantiates further the intuitive picture presented in Ref. [18].

What is required for calculating Ω_1 and Ω_2 is some means of determining $c_b^{(1)}$ in the limit of vanishing density of big spheres. DFT provides a suitable route since [27]

$$c_b^{(1)}(\mathbf{r})=-\beta\frac{\delta\mathcal{F}_{ex}[\rho_b,\rho_s]}{\delta\rho_b(\mathbf{r})}, \tag{24}$$

where $\mathcal{F}_{ex}[\rho_b,\rho_s]$ is the excess (over ideal) intrinsic Helmholtz free energy functional of the mixture [16]. Thus, given some prescription for the mixture functional one can calculate all the necessary ingredients. Rosenfeld's fundamental measure theory [26] supplies an approximate functional $\mathcal{F}_{ex}$ for an additive mixture of hard spheres of the form

$$\beta\mathcal{F}_{ex}[\rho_b(\mathbf{r}),\rho_s(\mathbf{r})]=\int d^3r\,\Psi(\{n_\alpha\}), \tag{25}$$

with weighted densities n_α that depend on the fundamental geometrical measures of the spheres constituting the mixture. There are four scalar and two vector weight functions w_α^i, with $1\leqslant\alpha\leqslant 6$. Details can be found in Ref. [26]; the weights depend on the radii R_i of each species. For a binary mixture the weighted densities are

$$n_\alpha(\mathbf{r})=\sum_{i=s,b}\int d^3r'\,\rho_i(\mathbf{r}')\mathrm{w}_\alpha^i(\mathbf{r}-\mathbf{r}'). \tag{26}$$

It is important to realize that once the reduced free energy density $\Psi(\{n_\alpha\})$ is specified the mapping described in Sec. II A is completely determined within this (approximate) DFT framework. We choose to apply the *original* Rosenfeld functional [26]

$$\Psi(\{n_\alpha\})=-n_0\ln(1-n_3)+\frac{n_1n_2-\mathbf{n}_1\cdot\mathbf{n}_2}{1-n_3}+\frac{n_2^3-3n_2\mathbf{n}_2\cdot\mathbf{n}_2}{24\pi(1-n_3)^2}. \tag{27}$$

Recall that the two-body direct correlation functions $c_{ij}^{(2)}$, with $i,j\in b,s$, obtained by taking two functional derivatives of this functional reduce to the Percus-Yevick (PY) $c_{ij}^{(2)}(|\mathbf{r}-\mathbf{r}'|)$ for a homogeneous hard-sphere mixture. The Rosenfeld functional has proven to be extremely successful in describing the structure of the inhomogeneous fluid phases of hard-sphere mixtures. If solid phases are to be considered, modifications to the original Rosenfeld functional should be made [28].

2. Calculating Ω_0 from DFT

We begin the explicit mapping by noting that the equation of state underlying the Rosenfeld functional [26] is p_{PY}^c, the Percus-Yevick compressibility equation of state for additive hard-sphere mixtures. In order to calculate the zero-body term, however, we need only the equation of state for a one-component fluid so we set

$$\beta p_s(z_s)=\beta p^{c}_{PY}(z_s)\equiv\rho^r_s\frac{1+\eta^r_s+(\eta^r_s)^2}{(1-\eta^r_s)^3}, \tag{28}$$

with $\eta^r_s\equiv\pi\sigma^3_{ss}\rho^r_s/6$, the reservoir packing fraction of the small spheres. Ω_0 follows directly from Eq. (12).

3. Calculating Ω_1 from DFT

Using the Rosenfeld functional the direct one-body correlation function $c^{(1)}_b$ can be written as [16]

$$c^{(1)}_b(\mathbf{r})=-\sum_\alpha\int d^3r'\left(\frac{\partial\Psi(\{n_\alpha\})}{\partial n_\alpha}\right)_{\mathbf{r}'} \mathrm{w}^b_\alpha(\mathbf{r}-\mathbf{r}'). \tag{29}$$

In the dilute limit in which the density of the big spheres $\rightarrow 0$, the weighted densities depend only on the density profile $\rho_s(\mathbf{r})$ of the small spheres

$$n^{dilute}_\alpha(\mathbf{r})=\int d^3r'\,\rho_s(\mathbf{r}')\mathrm{w}^s_\alpha(\mathbf{r}-\mathbf{r}'). \tag{30}$$

Note that $\rho_s(\mathbf{r})$ then corresponds to a one-component fluid of species s [16]. In *bulk* the density profile of the small spheres $\rho_s(\mathbf{r})$ is constant and equal to ρ^r_s, the vector weighted densities $\mathbf{n}_\alpha$ vanish and scalar weight functions reduce to those of a one-component fluid, i.e., $n_3\rightarrow\eta^r_s$, $n_2\rightarrow 6\eta^r_s/\sigma_{ss}$, $n_1\rightarrow 3\eta^r_s/(\pi\sigma^2_{ss})$, and $n_0\rightarrow 6\eta^r_s/(\pi\sigma^3_{ss})$. $c^{(1)}_b(\infty)$ can be evaluated explicitly and the result expressed as

$$\beta\omega_1(z_s)=\lim_{\mu_b\rightarrow-\infty}-c^{(1)}_b(\infty)=\frac{4\pi R^3_b}{3}\beta p_s(z_s)+4\pi R^2_b\beta\gamma(z_s)+\frac{R_b}{\sigma_{ss}}\frac{6\eta^r_s}{1-\eta^r_s}-\ln(1-\eta^r_s), \tag{31}$$

where the first term corresponds to the partial derivative $\partial/\partial n_3$, the second to $\partial/\partial n_2$, and so on. As the first term is proportional to the pressure of the reservoir of small spheres, given by Eq. (28) and the second term is proportional to the planar ''surface tension''

$$\beta\gamma(z_s)=\frac{3\eta^r_s(2+\eta^r_s)}{2\pi\sigma^2_{ss}(1-\eta^r_s)^2}, \tag{32}$$

these have a natural interpretation as $p_s\Delta V$ and $\gamma\Delta A$ terms, respectively. Although it is more difficult to give a physical interpretation of the last two terms in Eq. (31) they are important, for example, in obtaining the correct low density limit—see below. Since $-\beta^{-1}c^{(1)}_b(\infty)$ is the excess chemical potential of species b in a uniform (bulk) mixture we can also determine this quantity starting from the bulk excess free energy density, differentiating with respect to the bulk density ρ_b and then taking the limit $\rho_b\rightarrow 0$. The result is identical to that in Eq. (31).

Although we have derived this result starting from a theory developed for an additive mixture once we have a taken the limit $\rho_b\rightarrow 0$ the big-big interaction is not relevant. It follows that for an arbitrary nonadditive mixture, R_b entering Eq. (31) should be defined as $R_b\equiv\sigma_{bs}-\sigma_{ss}/2$. In the particular case of an additive mixture R_b reduces to $\sigma_{bb}/2$.

Note that the *form* of Eq. (31) is the same as that given by Henderson [20] in a scaled particle theory for $c^{(1)}_b(\infty)$. However, in Henderson's treatment $c^{(1)}_b(\infty)$ is expressed in powers of the variable $R\equiv\sigma_{bs}$. If one converts his Eq. (54) to an expression in terms of $R_b=R-\sigma_{ss}/2$ one recovers *precisely* Eq. (31). In other words, his scaled particle analysis agrees completely with the present DFT approach, attesting further to the consistency of the latter. Note also that in the low density limit $\rho^r_s\rightarrow 0$, Eq. (31) implies $\beta\omega_1(z_s)\rightarrow 4\pi\sigma^3_{bs}\rho^r_s/3$ which is the *exact* limiting value—see Appendix.

4. Converting from the reservoir packing fraction η^r_s to the packing fraction η_s in the mixture

Given explicit formulas for Ω_0 and Ω_1 we can employ Eq. (23) to obtain an explicit conversion between η_s, the packing fraction of the small spheres in the system, and η^r_s, the packing fraction in the reservoir. To this end we first determine the fugacity $z_s=\rho^r_s\exp(\beta\mu^{ex}_s)$ of the small spheres within the framework of the Rosenfeld DFT approach. μ^{ex}_s, the excess chemical potential of the pure small sphere fluid, is given by the Percus-Yevick (compressibility) result, so that

$$z_s=\frac{6\eta^r_s}{\pi\sigma^3_{ss}(1-\eta^r_s)}\exp\left(\frac{14\eta^r_s-13(\eta^r_s)^2+5(\eta^r_s)^3}{2(1-\eta^r_s)^3}\right). \tag{33}$$

Using the expressions for Ω_0 and Ω_1 given in this section together with Eqs. (23) and (33) we obtain for the packing fraction of small spheres in the system $\eta_s=\pi\sigma^3_{ss}\rho_s/6$,

$$\eta_s=(1-\eta_b)\eta^r_s-3q_{eff}\eta_b\eta^r_s\frac{1-\eta^r_s}{1+2\eta^r_s}-3q^2_{eff}\eta_b\eta^r_s\frac{(1-\eta^r_s)^2}{(1+2\eta^r_s)^2}-q^3_{eff}\eta_b\eta^r_s\frac{(1-\eta^r_s)^3}{(1+2\eta^r_s)^2}, \tag{34}$$

where $q_{eff}\equiv\sigma_{ss}/2R_b$ is the effective size ratio. In the limit $\eta^r_s\rightarrow 0$ this result reduces to

$$\eta_s/\eta^r_s=[1-\eta_b(1+q_{eff})^3], \tag{35}$$

which is the standard excluded volume expression, appropriate to an ideal gas of small particles [2]. However, for nonzero densities of small spheres Eq. (34) predicts a nonlinear dependence of η_s on η^r_s. This is illustrated in Fig. 3 where we plot η_s versus η^r_s for *additive* hard-sphere mixtures with (a) $q=0.1$ and (b) $q=0.05$. Our results are compared with those of direct Monte-Carlo simulations of the binary mixture [2]. The agreement between theory and simulation is excellent, with a small deviation occurring at $\eta_b=0.74$ and 0.10 for $q=0.1$. Note that the free-volume theory of Lekkerkerker and Stroobants [29], which asserts that $\eta_s/\eta^r_s=\alpha(z_s=0;\eta_b)$, where $\alpha(z_s=0;\eta_b)$ is the free-volume frac-

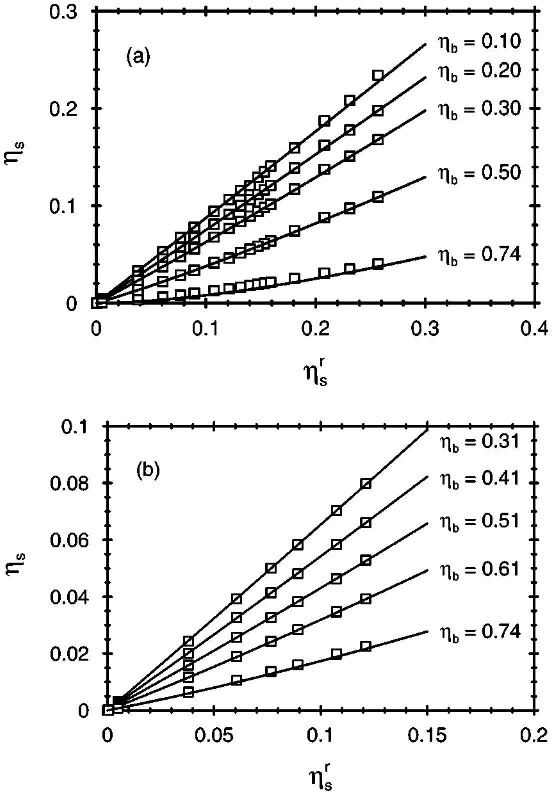

FIG. 3. The small sphere packing fraction η_s of an additive binary hard-sphere mixture, with size ratio (a) 0.10 and (b) 0.05, versus that of the reservoir η_s^r for several big sphere packing fractions η_b. The squares denote the direct simulation data of Ref. [2] while the lines denote the results of Eq. (34). Note the significant deviations from linearity in both theory and simulations.

tion evaluated for zero fugacity of the small spheres, significantly underestimates η_s/η_s^r at higher values of η_s^r [2]. We conclude that retaining only the two leading terms Ω_0 and Ω_1 and employing PY theory for these quantities provides an accurate approximation for the free volume fraction η_s/η_s^r, at least for small values of q.

For completeness, we should mention that the theory employed in Ref. [2] to calculate η_s/η_s^r used the Carnahan-Starling result for z_s and Henderson's expression for $c_b^{(1)}(\infty)$ but with an empirical modification of the leading (R_b^3) term. It is now clear that there was no need to make such a modification; the confusion arose from the improper identification of the parameter R in Henderson's theory. Fortunately the numerical results presented in Fig. 13 of Ref. [2] are very close to those given by the present, fully consistent theory. For future applications we recommend that Eq. (34) should be used.

5. Calculating Ω_2 from DFT

The two-body contribution Ω_2, given in Eq. (18), requires the calculation of the depletion potential $\omega_2(z_s;r)$ given by Eq. (20). This can be carried out using the procedure described in Ref. [16]. We first calculate the (inhomogeneous) equilibrium density profile $\rho_s(r)$ of the small spheres near a fixed big sphere of radius R_b. This is used in Eq. (30) to determine the relevant weighted densities, which then determine $c_b^{(1)}(r)$ via Eq. (29).

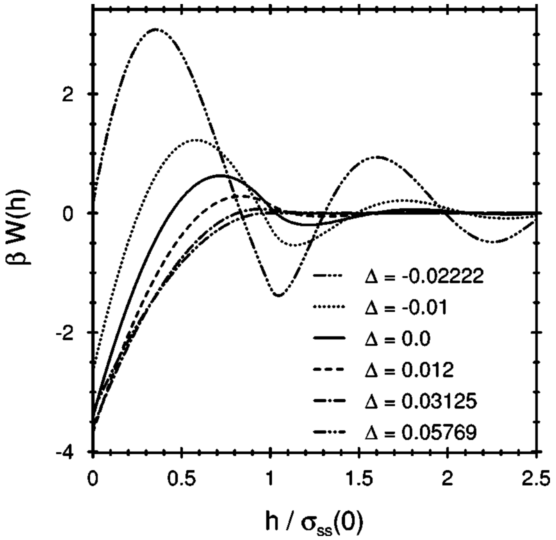

FIG. 4. The depletion potential $W(h) \equiv \omega_2(z_s;\sigma_{bb}+h)$ between two big hard spheres in a sea of small hard spheres calculated for a size ratio $q=0.1$ and a range of nonadditivities Δ treated according to route (i). The number density of the small spheres, ρ_s^r, is fixed with packing fraction $\eta_s^{add} \equiv \rho_s^r \pi(\sigma_{ss}^{add})^3/6 = 0.2$. $\Delta=0$ corresponds to an additive hard-sphere mixture. h is the separation between the surfaces of the big spheres and $\sigma_{ss}(0)=q\sigma_{bb}$.

We emphasize that the mapping of a depletion potential in a nonadditive system onto one in an additive mixture is exact and has been applied in a recent study of generalized effective potentials [30].

III. APPLICATIONS

A. Effect of nonadditivity on the shape of depletion potentials

1. Changes of type (i): σ_{ss} varies, but σ_{bs} is fixed

Following the procedure of Ref. [18] we follow route (i) and demonstrate that for a given (fixed) size ratio q and packing fraction η_s^{add} of the additive mixture the effects of nonadditivity Δ on the shape of the depletion potential are very strong.

Choosing a size ratio $q=0.1$ and a fixed packing fraction in the additive mixture of $\eta_s^{add}=0.2$, we can vary the nonadditivity parameter Δ between $\Delta=-0.031$, corresponding to the packing fraction $\eta_s^r(\Delta)$ of the small spheres, given by Eq. (5), reaching the freezing packing fraction $\eta^{freez}=0.494$, and $\Delta=\Delta^{AO}=q$, in which case $\sigma_{ss}\equiv 0$ and hence $\eta_s^r(\Delta^{AO})\equiv 0$. Results for the depletion potentials are given in Fig. 4. For $q=0.1$ and $\eta_s^{add}=0.2$ the depletion potential obtained from DFT for additive hard spheres ($\Delta=0$) is in excellent agreement with the results of computer simulations [13]—see the comparison in Ref. [16]. Moreover, for $\Delta=\Delta^{AO}=0.1$ we find that our calculated depletion potential is indistinguishable from the analytic AO result [18].

For small degrees of positive nonadditivity the main effects observed in the depletion potential are a weakening of

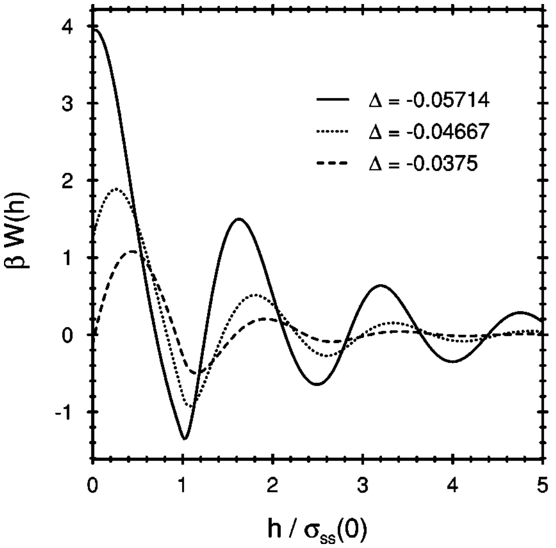

FIG. 5. As in Fig. 4 but now the packing fraction η_s^{add} is fixed at 0.1. For these negative values of the nonadditivity Δ the depletion potential is repulsive near contact and for $\Delta=-0.057\,14$ the depletion force is repulsive near contact.

the first repulsive potential barrier, due to a decreased packing fraction [given by Eq. (5)], and an increase in the range of attraction, i.e., the maximum of the potential shifts to larger separations h. Both effects tend to increase the net attraction and this is reflected in the second virial coefficient, as we shall see later.

For negative values of Δ the packing fraction $\eta_s^r(\Delta)$ of the small spheres increases rapidly and the contact value of the depletion potential increases sharply—see Fig. 4. For sufficiently negative values of Δ the depletion potential can become positive at contact while the force near contact remains attractive. If the density ρ_s^r of the small spheres is small enough to permit a high degree of negative nonadditivity the depletion force near contact can even become repulsive. This is illustrated in Fig. 5 for parameters $\eta_s^{add}=0.1$ and $q=0.1$. Now Δ can take values as low as -0.060 whilst $\eta_s^r(\Delta)$ remains smaller than η_s^{freez}. Depletion potentials for $q=0.1$ and $\eta_s^{add}=0.3$ were presented in Fig. 3 of Ref. [18] and for $q=0.2$ and $\eta_s^{add}=0.1$ were presented in Fig. 2 of Ref. [30]; these display similar trends with Δ as those shown here.

2. Changes of type (ii): σ_{bs} varies, but σ_{ss} is fixed

In Fig. 6 we show the effect of changing Δ according to route (ii). Now the packing fraction in the reservoir η_s^r is fixed at 0.2 for all values of Δ and σ_{bs} varies. The results are very different from those in Fig. 4 that correspond to the same size ratio $q=0.1$ and the same η_s^{add}. In the present case increasing Δ shifts the depletion potential almost rigidly along the h axis to larger separations h leading to much deeper and longer ranged attractive wells than for $\Delta=0$. Making Δ increasingly more negative corresponds to shifting the potential to smaller separations, thereby reducing the attraction and the height of the potential barrier. Depletion potentials for $q=0.2$, $\eta_s^r=0.2$ were presented in Fig. 3 of Ref. [30]; these display similar trends with Δ as those shown here.

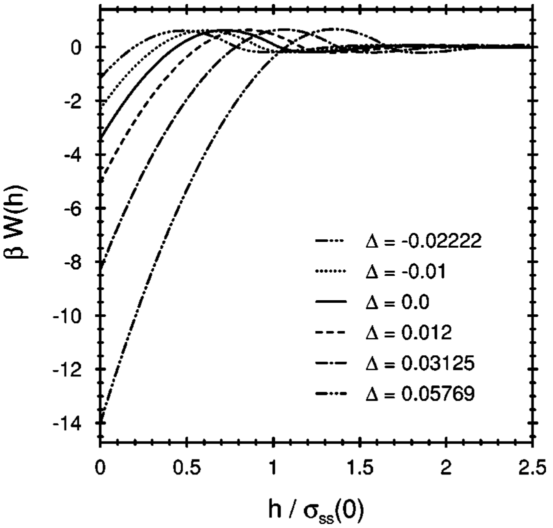

FIG. 6. The depletion potential $W(h)\equiv\omega_2(z_s;\sigma_{bb}+h)$ between two big hard spheres in a sea of small hard spheres calculated for a size ratio $q=0.1$ and a range of nonadditivities Δ treated according to route (ii). The packing fraction in the reservoir $\eta_s^r=0.2$ remains constant for all values of Δ. $\Delta=0$ corresponds to an additive hard-sphere mixture. h is the separation between the surfaces of the big spheres and $\sigma_{ss}(0)=q\sigma_{bb}$. These results should be contrasted with those in Fig. 4—note the difference between the vertical scales.

B. Effect of nonadditivity on the second virial coefficient

1. Changes in B_2 as a function of Δ

In Sec. III A we demonstrated that introducing a rather small degree of either positive or negative nonadditivity has a profound effect on the shape of the depletion potential. Here we investigate the effect of nonadditivity on the second virial coefficient B_2 that measures the net attraction between two big particles in the sea of small ones. B_2 corresponds to the total effective pair potential $\Phi_{eff}(z_s;r)$ defined in Eq. (21). It follows that

$$B_2=B_2^{HS}+2\pi\int_{\sigma_{bb}}^{\infty} dr r^2\{1-\exp[-\beta\omega_2(z_s;r)]\}, \quad (36)$$

with $B_2^{HS}=2\pi\sigma_{bb}^3/3$, the second virial coefficient of the pure hard-sphere system. If the depletion potential $\omega_2(z_s;r)$ generates enough attraction between the two big spheres B_2 can become negative [31]. Note that B_2 is a function of Δ and z_s.

In Fig. 7 B_2 is plotted as a function of Δ for $\eta_s^{add}=0.2$ and $q=0.1$. For an intermediate value of $\Delta_{min}\approx0.0279$ we find that B_2 takes its minimum value of $B_2(\Delta_{min})/B_2^{HS}\approx-0.5$. The variation of B_2 with Δ is similar to that of $W(h=0)=\omega_2(z_s;\sigma_{bb})$, the contact value of the depletion potential, although the latter has its minimum at a slightly lower value $\Delta\approx0.016$ – see inset of Fig. 7. Provided η_s^r is sufficiently high to generate significant packing effects the presence of a minimum in B_2 in the range $0>\Delta_{min}>\Delta^{AO}$ is

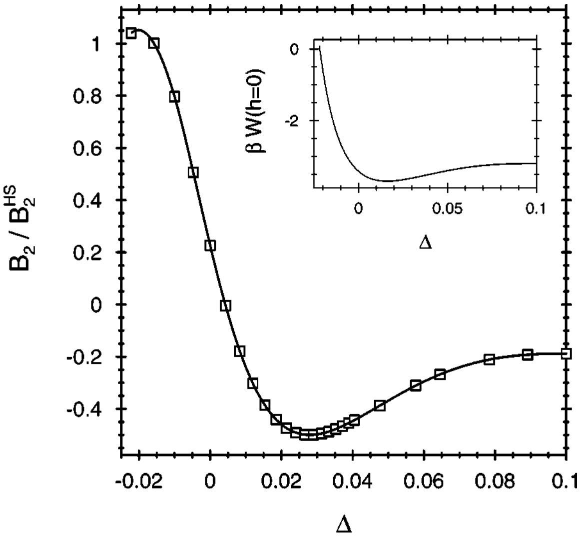

FIG. 7. The reduced second virial coefficient of the big spheres B_2 in units of $B_2^{HS} \equiv 2\pi\sigma_{bb}^3/3$ as a function of the nonadditivity Δ. These results correspond to the depletion potentials of Fig. 4, i.e., $\eta_s^{add} = 0.2$ and $q = 0.1$, for which the maximum nonadditivity is $\Delta^{AO} = 0.1$. The inset shows the contact value $\beta W(h=0) \equiv \beta\omega_2(z_s;\sigma_{bb})$ of the depletion potential as a function of Δ.

easily understood [18]. For a given size ratio q and density of small particles $\rho_s^r > 0$ the Asakura-Oosawa depletion potential given by

$$W(h) \equiv W^{AO}(h) = -p_{id}(z_s)\Delta V(h), \tag{37}$$

where $p_{id}(z_s) = \rho_s^r k_B T$ is the ideal gas pressure and $\Delta V(h)$ is the overlap volume excluded to the centers of the small spheres. h denotes the separation between the surfaces of the two big spheres so that $\Delta V(h) = 0$ for $h > \sigma_{ss}(0) = q\sigma_{bb}$. W^{AO} is purely attractive and should always generate more net attraction than the depletion potential of an additive hard-sphere mixture—provided η_s^r is large enough that packing effects become significant. Then the depletion potential consists of an attractive part close to contact and an oscillatory tail for larger separation. Packing effects of the small spheres reduce the range of the initial attractive part of the hard-sphere depletion potential compared to the Asakura-Oosawa potential and for the same value of q and ρ_s^r we find $B_2^{AO} < B_2^{add}$, at least for the parameters we studied. Very close to the Asakura-Oosawa limit, i.e., $\Delta \lesssim \Delta^{AO}$, where the packing fraction of the small spheres, Eq. (5), is small but nonzero, packing effects are minor and the depletion potential is still determined by excluded volume considerations. For a nonzero packing fraction, however, the pressure of the small sphere fluid is higher than in an ideal gas so that to first order in η_s^r, the virial expansion of this pressure yields

$$W^{AO1}(h) = [1 + 4\eta_s^r(\Delta)]W^{AO}(h). \tag{38}$$

In Ref. [18] we showed that this modified AO approximation is very accurate for $\eta_s^r(\Delta) < 0.01$. According to this approximation the depletion potential, Eq. (38), is more attractive than in the Asakura-Oosawa limit so that we can conclude that for an intermediate value of Δ the second virial coefficient B_2 must have a minimum. It is, however, surprising and striking that this minimum is found to be deep, $[B_2^{HS} - B_2(\Delta_{min})]/[B_2^{HS} - B_2(\Delta^{AO})] \approx 1.26$, and located at a rather low degree of nonadditivity.

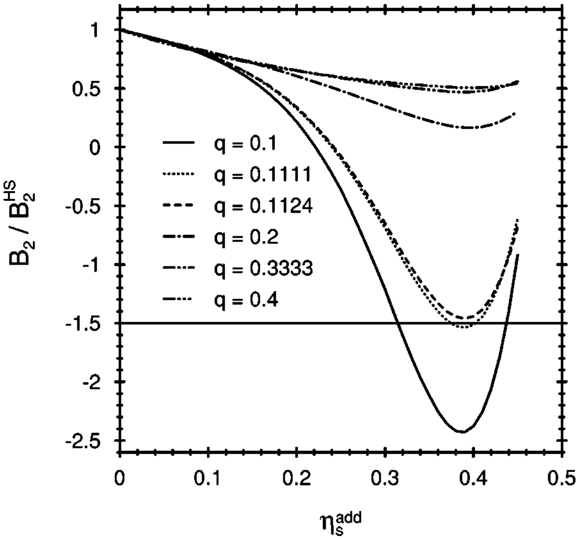

FIG. 8. The reduced second virial coefficient of the big spheres in *additive* hard-sphere mixtures ($\Delta = 0$) for various size ratios q versus η_s^{add}, the packing fraction of small spheres in the reservoir. According to the criterion of Ref. [32], (metastable) fluid-fluid phase separation can only occur if $B_2/B_2^{HS} < -1.5$ (horizontal line).

In the additive limit B_2 is already positive for this particular mixture and a very small degree of negative nonadditivity is sufficient to make B_2 strongly positive.

2. Changes in B_2 as a function of η_s^r and a criterion for fluid-fluid phase separation

In an experimental situation Δ is not an easily controllable or tunable parameter and, therefore, it is most interesting from an experimental point of view to consider a fixed value of Δ and investigate the depletion potential and B_2 when the reservoir density of the small spheres ρ_s^r, a quantity that can be controlled easily in an experiment, is changed.

If one were to take any real (asymmetric) binary mixture of hard-sphere like colloidal particles and have some means of determining the three interparticle pairwise potentials one could, in principle, assign three effective hard-sphere diameters σ_{bb}, σ_{bs}, and σ_{ss} using standard liquid state theories [30]. In general, one would not expect these diameters to be perfectly additive although the magnitude and sign of the nonadditivity might be difficult to ascertain by any direct measurement. In this section we demonstrate that a very small degree of nonadditivity reveals itself very clearly in the dependence of B_2 on the packing fraction of the small spheres η_s^r.

To this end we start with an additive mixture and plot in Fig. 8 B_2 expressed in units of the second virial coefficient of a pure hard-sphere system B_2^{HS} as a function of $\eta_s^r \equiv \eta_s^{add}$ for various size ratios q. The qualitative behavior of B_2 is the same for all size ratios: for small values of η_s^r the reduced second virial coefficient decreases from unity in approximately linear fashion while for high packing fractions, $\eta_s^r > 0.3$, the decreasing range of attraction and the increasing height of the repulsive potential barrier in the depletion potential hinder a further decrease of B_2 and we find a minimum of the second virial coefficient at roughly $\eta_s^r \lesssim 0.4$ and an increase of B_2 upon further increase of η_s^r.

The quantitative behavior, however, depends very strongly on the value of q. For large size ratios, $q > 0.2$ we find that for all packing fractions η_s^r the depletion potential cannot generate enough net attraction to make B_2 negative. This observation helps us to understand, in terms of the depletion potential, the fact that in additive binary hard-sphere mixtures with large size ratios q even metastable fluid-fluid phase separation does not occur [2].

For smaller size ratios the minimum of B_2 becomes more pronounced and B_2 takes on negative values for a range of η_s^r. At a size ratio 1:9 ($q = 0.1111$) the minimum value of B_2 falls below $-1.5B_2^{HS}$. By analyzing a large series of simulation results for a variety of (one component) model fluids, Vliegenthart and Lekkerkerker [32] have shown recently that the second virial coefficient evaluated at the gas-liquid critical temperature T_c takes values that lie in a fairly narrow range around $-1.5B_2^{HS}$. For the model fluids considered in Ref. [32] gas-liquid coexistence can only occur if $B_2/B_2^{HS} < -1.5$. If we assume that this empirical criterion is applicable to the effective one-component system described by our pairwise potentials Φ_{eff} it follows that only systems with B_2/B_2^{HS} lying below the horizontal line in Fig. 8 could exhibit (metastable) fluid-fluid coexistence. It is important to emphasize that the criterion is empirical and that it was developed for model fluids in which the attractive part of the pairwise potential is monotonically increasing with interparticle separation r, unlike our present effective potentials. Moreover, the criterion does not predict whether the gas-liquid coexistence is stable or metastable with respect to fluid-solid coexistence. Recall that the shorter range of the attractive potential the more likely is the gas-liquid transition to become metastable [32]. In a simulation study of the effective one-component Hamiltonian for an additive hard-sphere mixture, metastable fluid-fluid phase separation was found for $q = 0.1$ and $q = 0.05$ [2]. For $q = 0.1$ fluid-fluid coexistence occurred for $\eta_s^r \gtrsim 0.29$, whereas for $q = 0.05$ this occurred for $\eta_s^r \gtrsim 0.165$. These results are in keeping with the predictions of the empirical criterion. Note that the second intersection of B_2/B_2^{HS} with the horizontal line for $q = 0.1$ in Fig. 8 suggests a possible upper critical point near $\eta_s^r = 0.43$ [30].

If we introduce a very small degree of *positive* nonadditivity according to route (i), i.e., we keep σ_{bb} and σ_{bs} constant so that $\sigma_{ss}(\Delta)$ becomes smaller than for the additive case [see Eq. (4)], we find a dramatically different situation. In order to be of relevance to an experimental situation, where it might be impossible to rule out a small degree of nonadditivity, we set $\Delta = q/20$ for each choice of q.

As expected, positive nonadditivity leads to a slight increase in the width of the depletion layer and, therefore, *more* net attraction than in the additive case. The behavior of B_2 as a function of $\eta_s^r(\Delta)$, however, changes qualitatively as can be seen in Fig. 9. For all size ratios considered here the second virial coefficient becomes negative and B_2/B_2^{HS} falls below the -1.5 line prior to freezing of the small particles. The smaller q, the smaller the value of η_s^r when this line is crossed. There is no minimum in B_2. Thus according to the empirical criterion all the mixtures considered here should exhibit (metastable) fluid-fluid coexistence. Once again, we cannot say whether this transition is stable with respect to the fluid-solid transition.

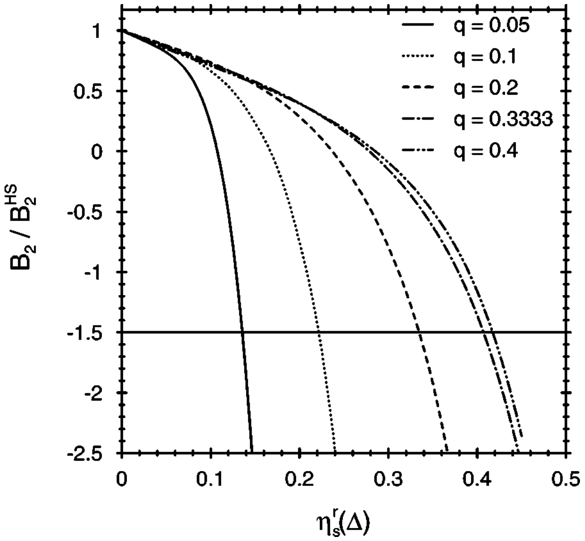

FIG. 9. The reduced second virial coefficient of the big spheres in hard-sphere mixtures with a small *positive* nonadditivity $\Delta = +q/20$ for various size ratios q versus $\eta_s^r(\Delta)$, the packing fraction of small spheres in the reservoir. In contrast to the additive case, Fig. 8, B_2/B_2^{HS} always falls below -1.5 indicating that (metastable) fluid-fluid phase separation could occur for all size ratios shown here.

Our results provide some understanding, in terms of the depletion potential description, of why only small degrees of positive nonadditivity might lead to fluid-fluid phase separation in asymmetric binary hard-sphere mixtures. We recall that Biben and Hansen [9] found for $q = 0.1$, on the basis of the Barboy-Gelbart [33] equation of state, that a value $\Delta = 0.01$ was sufficient to produce a fluid-fluid transition at a total packing fraction < 0.5. Later Dijkstra [10] carried out a series of Gibbs ensemble Monte-Carlo simulations of the binary mixture for $q = 0.1$ and varying degrees of positive nonadditivity. She found that it was possible to have fluid-fluid demixing for a total packing fraction < 0.5, provided Δ was sufficiently large.

On the other hand, introducing a small degree of *negative* nonadditivity [again via route (i)] decreases the width of the depletion layer compared to the additive case so that the net attraction should also decrease. We set $\Delta = -q/20$ for each q and find that these small negative values of Δ are sufficient to change significantly the shape of B_2 versus $\eta_s^r(\Delta)$ from that of the additive case.

This is illustrated in Fig. 10 where we show that for size ratios $q \gtrsim 0.2$ the second virial coefficient changes little as function of $\eta_s^r(\Delta)$. For large values of η_s^r we even find that

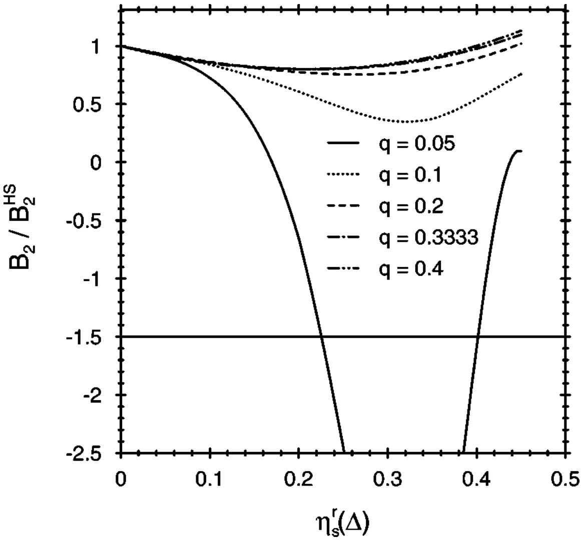

FIG. 10. The reduced second virial coefficient of the big spheres in hard-sphere mixtures with a small *negative* nonadditivity $\Delta = -q/20$ for various size ratios q versus $\eta_s^r(\Delta)$, the packing fraction of small spheres in the reservoir. Note that B_2/B_2^{HS} falls below -1.5 only for the smallest ratio, $q = 0.05$, considered here.

$B_2 > B_2^{HS}$. For a size ratio of $q = 0.1$, which in the additive case was sufficiently small for B_2 to become strongly negative, B_2 remains positive for all packing fractions. Only for very small q can the depletion potential in nonadditive mixtures with negative Δ generate sufficient net attraction to drive B_2 negative.

We conclude this discussion by emphasizing how sensitive B_2 is to changes in the depletion potential. In Fig. 11 we show the depletion potentials calculated for $q = 0.1$ and fixed $\eta_s^r(\Delta) = 0.3$ for three values of Δ. Although the three potentials appear rather similar, they yield very different values of B_2. From Figs. 8–10 we see that B_2/B_2^{HS} is about -1.21 for $\Delta = 0$, is strongly negative ($B_2/B_2^{HS} < -9$) for $\Delta = 0.005$ (the empirical criterion would predict fluid-fluid phase separation) and is positive ($B_2/B_2^{HS} = 0.36$) for $\Delta = -0.005$.

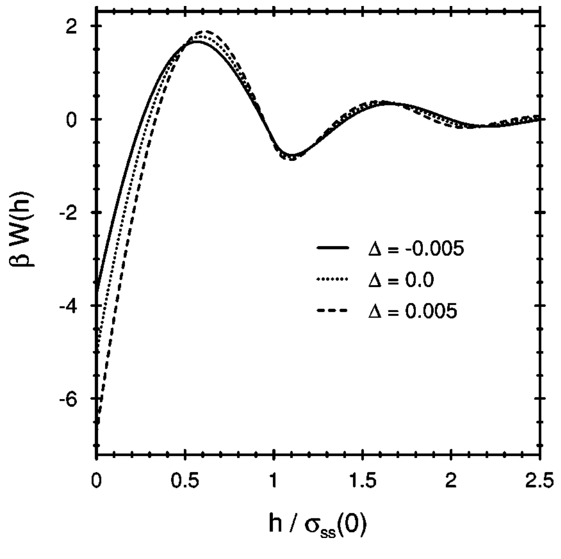

FIG. 11. Depletion potentials for $q = 0.1$ and fixed $\eta_s^r(\Delta) = 0.3$ for $\Delta = -0.005$, 0 and $+0.005$. Although these potentials do not differ drastically from each other the corresponding B_2, see Figs. 8–10, take very different values: $B_2/B_2^{HS} = 0.36$, -1.21, and < -9 for $\Delta = -0.005$, 0, and $+0.005$, respectively.

IV. DISCUSSION

The main results of our study of the equilibrium statistical mechanics of nonadditive binary hard-sphere mixtures may be summarized as follows:

1. The formal technique of integrating out the degrees of freedom of the small spheres in order to obtain an effective Hamiltonian H^{eff} for the big spheres is equally valid for nonadditive as for additive mixtures, where it has proved particularly useful [2] for determining the phase behavior of asymmetric systems. We have provided expressions for zero, Ω_0, one, Ω_1, and two-body contributions to H^{eff}, which can be evaluated in simulations of the small sphere fluid (Sec. II A).

2. We showed that the same contributions are readily calculated using the fundamental measure DFT of Rosenfeld, a theory developed originally for additive hard spheres (Sec. II B). By calculating Ω_0 and Ω_1 we were able to derive an explicit approximation (34) for the packing fraction η_s of small spheres in the mixture at given reservoir fraction η_s^r and big-sphere fraction η_b. Comparison with a previous simulation study for additive mixtures with small size ratios q showed that the approximation is very accurate (Fig. 3).

3. The two-body contribution to H^{eff} is a sum of effective pairwise potentials $\Phi_{eff}(z_s;r) = \Phi_{bb}(r) + \omega_2(z_s;r)$. Our DFT approach provides a powerful means of determining the depletion potential $\omega_2(z_s;r)$ for nonadditive mixtures. Provided three and higher body terms are small, as is expected for small q, it is solely ω_2 that determines big-big correlation functions and the phase equilibria of the mixture.

4. We described two different routes to introducing nonadditivity Δ and gave examples of the depletion potentials and the second virial coefficient B_2 associated with the corresponding effective potential Φ_{eff} obtained from both routes (Sec. III). Although the depletion potential depends upon only the bare potentials and ρ_s^r, the pattern of the variation with Δ (see Figs. 4–6) does depend on whether route (i) σ_{bs} fixed, σ_{ss} varies or route (ii) σ_{ss} fixed, σ_{bs} varies, is employed. B_2 is a sensitive indicator of the shape and range of the effective potential and exhibits considerable variation with q, Δ and η_s^r (Figs. 7–10).

5. On the basis of the empirical criterion $B_2/B_2^{HS} < -1.5$ [32], we showed that fluid-fluid phase separation is much more likely to occur for a small degree of positive nonadditivity, $\Delta > 0$, than in additive mixtures, $\Delta = 0$, with the same size ratio. Our results provide a guide to which binary hard-sphere mixtures might exhibit fluid-fluid separation which is stable with respect to fluid-solid separation and we hope that these might stimulate further computer simulation studies.

We conclude by turning to the question of whether the strong effect of nonadditivity on the depletion potentials and on the virial coefficients found in Secs. III A and III B has any implications for experiments on colloidal systems.

One-component colloidal suspensions that mimic very closely a hard-sphere system can be created because any small residual short-range interactions remaining after refractive index matching are very well approximated by hard spheres with an effective hard-sphere diameter [34]. But creating a truly additive binary colloidal suspension is much more difficult, since this implies an additional constraint on the value of the effective hard-sphere diameters, namely, that $2\sigma_{bs}=\sigma_{bb}+\sigma_{ss}$. The small residual interactions in an experimental system designed to mimic binary hard-sphere mixtures can easily introduce nonadditivity [30]; nonadditivity is probably the rule and perfect additivity the exception. For example, in an earlier paper [11], one of us has shown by a simple argument that for both sterically and electrostatically stabilized asymmetric binary colloids, $2\sigma_{bs}$ is likely to be smaller than $(\sigma_{bb}+\sigma_{ss})$, which implies a small negative nonadditivity. This in turn suggests that the well depth at contact $W(h=0)$ is smaller than what would be expected for an additive system. For short-ranged depletion systems the location of a fluid-solid liquidus line can be roughly correlated to $W(h=0)$ [11,23]; one would, therefore, expect the experimental liquidus line to occur at larger values of η_s than what is predicted for a purely additive binary hard-sphere system. Experimental results do seem to follow this trend [35]. However, since the experimental phase boundaries are typically plotted with the small-particle packing fraction η_s on the *y* axis, it is not always clear whether discrepancies with the additive theory arise from nonadditivity, or from small errors in the measurement of σ_{ss}, which enters η_s as σ_{ss}^3.

Instead of focusing on phase boundaries, we propose that direct measurements of the osmotic second virial coefficient B_2 as a function of η_s should be a much more sensitive measure of the existence of nonadditivity, and may even provide an independent way to ascertain the value of σ_{bs}, which is otherwise very hard to determine. As illustrated in Figs. 8, 9, and 10, different degrees of nonadditivity induce clear qualitative differences in the dependence of B_2 on η_s, implying that one does not require a high level of quantitative accuracy in measurements of B_2 in order to distinguish clearly between negative and positive nonadditivity.

For colloidal suspensions B_2 is typically extracted from the low density limit of the osmotic equation of state, measured by static light scattering. This is nontrivial since it requires extracting the contribution from the big particles to the total scattering intensity. Such measurements were first carried out by de Hek and Vrij in 1982 [36] for a colloid-polymer mixture with a size ratio $2R_g/\sigma_{cc}\approx 1$ (here R_g is the radius of gyration of the polymers); they found a clear trend towards negative values of B_2 upon increasing the polymer concentration, which is consistent with the expected positive nonadditivity in such colloid-polymer systems. In contrast, the results in Sec. III B imply that for an additive binary colloid mixture, size ratios of $\sigma_{ss}/\sigma_{bb}\lesssim 0.2$ are required to drive B_2 negative. For negative nonadditivity even smaller size ratios are required. Such qualitative effects should be visible in experiments.

We note in passing that the effect of increasing the polymer concentration on the second osmotic virial coefficient of a globular protein-polymer solution has been measured recently [37]. However, these experiments are in the protein limit $2R_g/\sigma_{cc}\gg 1$, where the concepts of negative and positive nonadditivity are less useful.

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APPENDIX: LOW DENSITY LIMIT OF ω_1

Here we demonstrate that the one-body term $\beta\omega_1(z_s)$, given in Eq. (31), reduces in the limit $\rho_s^r\to 0$ to the *exact* low density limit, i.e.,

$$\lim_{\rho_s^r\to 0}\beta\omega_1(z_s)=\rho_s^r V_{b+s}, \tag{A1}$$

with $V_{b+s}=4\pi\sigma_{bs}^3/3$ the volume of a spherical cavity of radius σ_{bs}, which is excluded to the centers of the small spheres. Recall that $\omega_1(z_s)$ is the excess chemical potential of a big hard sphere in a sea of small ones.

In order to take the low density limit we note that to leading order in powers of ρ_s^r the equation of state, Eq. (28), reduces to

$$\lim_{\rho_s^r\to 0}\beta p=\rho_s^r, \tag{A2}$$

the surface tension, Eq. (32), to

$$\lim_{\rho_s^r\to 0}\beta\gamma=\frac{\sigma_{ss}}{2}\rho_s^r, \tag{A3}$$

the coefficient of the term in $\beta\omega_1$ linear in R_b reduces to

$$\lim_{\rho_s^r\to 0}\frac{6\eta_s^r}{\sigma_{ss}(1-\eta_s^r)}=\pi\sigma_{ss}^2\rho_s^r, \tag{A4}$$

and, finally

$$\lim_{\rho_s^r\to 0}-\ln(1-\eta_s^r)=\frac{\pi}{6}\sigma_{ss}^3\rho_s^r. \tag{A5}$$

It follows that

$$\lim_{\rho_s^r\to 0}\beta\omega_1=\frac{4\pi}{3}R_b^3\rho_s^r+4\pi R_b^2\frac{\sigma_{ss}}{2}\rho_s^r+4\pi R_b\left(\frac{\sigma_{ss}}{2}\right)^2\rho_s^r+\frac{4\pi}{3}\left(\frac{\sigma_{ss}}{2}\right)^3\rho_s^r. \tag{A6}$$

Recalling that $R_b\equiv\sigma_{bs}-\sigma_{ss}/2$ we find $\lim_{\rho_s^r\to 0}\beta\omega_1=(4\pi/3)\sigma_{bs}^3\rho_s^r$, which is Eq. (A1).

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