Is the binary hard-sphere mixture a good reference system for sterically stabilized colloids?

Ph. Germain,* C. Regnaut, and S. Amokrane

Groupe de Physique des Milieux Denses, Faculté des Sciences et de Technologie, Université Paris XII, 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France

The relevance of the hard-sphere mixture model as a starting point for the study of sterically stabilized colloids is discussed. Two physical situations are distinguished: true molecular solvent-colloid mixtures, and pseudobinary mixtures of two supramolecular objects. For the former, the limitation of the hard-sphere mixture model are recalled. Its potential use as a reference system for perturbation treatments is then analyzed. The accuracy of the latter is tested numerically. This study shows that the hard-sphere mixture is, in general, not a good reference system for sterically stabilized colloids in molecular solvents. For pseudobinary mixtures, the potential of mean force between the bigger solutes induced by the smaller ones is considered. The influence of a very short-range heteroattraction is discussed.

I. INTRODUCTION

The model of a binary mixture of hard spheres (HS) with large difference in size has been extensively studied in recent years, in view to clarifying the microscopic mechanisms that govern the phase behavior of sterically stabilized colloids. By incorporating in the simplest way the granularity of the solvent, it indeed made possible the understanding of basic features such as the short-range behavior of the effective interaction between large solute particles. It is precisely in this manner that Asakura and Oosawa predicted [1], in the context of a study of polymer induced floculation of colloidal particles, the so-called depletion force between large particles immersed in a medium of much smaller ones. Being a signature of the geometrical asymmetry between the microscopic components, this effect constitutes a remarkable specificity (and a generic property) of colloidal suspensions. It is thus considered as one of the fundamental features that explain their thermodynamics.

The HS mixture model is entirely characterized by the size ratio $q = \sigma_2/\sigma_1 \gg 1$, the two independent thermodynamic variables being usually the packing fractions $\eta_i = (\pi/6)\rho_i\sigma_i^3$ (ρ_i and σ_i are, respectively, the number density and the diameter of component i; hereafter $i=1$ will refer to the small spheres). It is currently investigated following two routes: either the treatment of the true (binary) mixture [2–8] or the effective one-component fluid approach [8–15]. From various theoretical methods and numerical simulations, a number of fundamental features have been established: the existence of a stable isostructural solid-solid (S-S) transition for very large size asymmetry [8], and the unstability of the fluid-fluid (F-F transition) with respect to the F-S one (the possibility of phase separation at sufficiently large q was first pointed out by Biben and Hansen [16]). These features are a consequence of the very short-range attractive tail of the depletion potential for $q \gg 1$.

The asymmetric binary HS mixture is thus an original model that should provide a unified insight into the phase

behavior of colloidal systems in which the interactions are truly dominated by the hard core repulsion. Now, the question is to know which experimental systems belong to this category. Indeed, several theoretical studies considered HS mixtures without always specifying the physical systems to which this model is relevant. To this end, two classes of (sterically stabilized) colloidal suspensions need to be distinguished: true colloid-solvent mixtures, that is, colloidal particles suspended in a molecular solvent and pseudobinary mixtures consisting of two supramolecular hard objects (colloid-colloid or colloid-polymer mixtures; see, for example, Ref. [17]) in a molecular solvent. From the modelistic point of view, it is mainly the range of the interactions between the different species—as compared with their size—that decides to which physical systems the model applies.

(1) In colloid-solvent mixtures, the indirect potential between the big particles mediated by the smaller ones varies at the scale of the microscopic components of the mixture. For this situation, several theoretical studies have underlined important modifications with respect to the pure depletion effect: On the one hand, solvent-solvent and solvent-solute attractive forces can have a strong impact on the potential of mean force. As a result, the phase behavior of the solute particles may be qualitatively different and far more complex than that relative to pure HS mixtures (for related works, see Ref. [18] and references therein). On the other hand, the variation of the direct solute-solute interaction at short range must also be considered, as this occurs in a region of similar extension to that of the indirect potential [19]. This effect should play an important role for the determination of the effective potential, especially for $q \sim 20$–100 [20], which is typical of (molecular) solvent-solute mixtures.

The insufficiency of the HS mixture model in the context of pure solvent-colloid mixtures is actually evidenced by many experimental observations. For instance, numerous mixtures exhibit stable fluid phases rich in solute particles in a liquid solvent [21] (see also Ref. [22] for a review on microemulsions). This feature, as well as the strong influence on the phase diagram of the temperature [22] and of the physicochemical characteristics of the solute [23] and solvent particles [24] are by definition foreign to the pure hard

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*Corresponding author. Email: germain@univ-paris12.fr

core scenario. The latter is thus clearly too primitive to describe correctly solvent-solute mixtures. The only remaining question is thus to know wether the HS mixture may provide a good reference system for the perturbative treatment of nonhard core effects. This is the main problem that we will examine in this work.

(2) In pseudobinary mixtures, a possible short-range structure in the effective interaction induced by the solvent is likely to be masked by the other contributions due to the smaller colloids. The solvent is thus completely ignored in the model. Now, the indirect potential between the bigger colloids induced by the smaller ones has a much longer range than the size of the microscopic components of the mixture. The range of the attractive forces between the bigger colloidal species is in this case also much smaller than that of the depletion one, induced by the smaller colloids. These forces may thus be expected to have a much weaker influence than for true solute-solvent mixtures. To our knowledge, however, this point has not yet been clearly assessed in the litterature. It will also be partly addressed in this work.

The asymmetric HS mixture model appears thus to be more appropriate to pseudobinary mixtures than to solvent-colloid ones. *A priori*, the former provide the main experimental motivation of the persistent and difficult investigations in view of establishing its complete phase behavior together with simple parametrization of the pair distribution functions (PDFs) and the equation of state (for recent work, see, for example, Refs. [25–27] and references therein). For these systems, the colloid-colloid size ratio usually lies in the range $q = 1-10$. Greater values of q correspond more likely to true colloid-solvent mixtures. However, values of $q > 10$ are commonly considered in theoretical studies of the HS mixture: for instance, the phase behavior was computed for $q = 1-33$ in Ref. [8], $q = 1-20$ in Ref. [28]. The question is thus to which physical systems these results are relevant. This point is not always made explicit in the theoretical studies as stressed above. Hence, the only justification of the HS mixture model for $q \gg 1$ would be its potential use as a reference system for more realistic interactions in the context of solvent-colloid binary mixture. One indeed frequently finds the general argument that the HS mixture should play a role similar to that of the HS fluid for one-component systems in perturbation treatments.

The perturbation theory (PT) [29] has already been applied successfully to moderately asymmetric mixtures (see, for example, Ref. [30]), but it has been seldom used for true mixtures in the colloidal regime. For instance, nonadditivity in the solvent-solute hard core potential (which might model solvatation forces) was studied in Ref. [31] by first-order perturbation and its effect on the stability of the liquid phase was examined. A thorough test of this approach was, however, not performed. This was done, for instance, by Gazzillo [32] for the nonadditivity, but with HS spheres of equal diameter. It is thus necessary to consider the validity of the PT in the high asymmetry regime and in situations more general than the mere nonadditivity.

The main scope of this paper is thus to investigate the PT for asymmetric mixtures, by extending our previous analysis

of the perturbation treatment in one-component systems [33]. The paper is presented as follows: in Sec. II, we present the PT with HS mixture reference system. The principle of the approximation of the effective one-component fluid is briefly recalled. The PT is then presented formally for the true mixture and its efffective fluid representation. The choice of the latter is justified and the numerical method is described. The results are then presented in Sec. III for different models of attractive forces. Finally, an exemple of interaction parameters appropriate to colloid-colloid mixtures will be analyzed. Section IV is the conclusion.

II. PERTURBATION THEORY WITH HS MIXTURE REFERENCE SYSTEM

A. Hamiltonian for non-hard-sphere particles

We consider a binary mixture of particles interacting with some model potential u_{ij}, assumed here with spherical symmetry. The total interaction potential H is

$$H = \frac{1}{2} \sum_{i=1}^{N_1} \sum_{j=1}^{N_1} u_{11}(r_{ij}) + \frac{1}{2} \sum_{i=1}^{N_2} \sum_{j=1}^{N_2} u_{22}(r_{ij})$$
$$+ \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} u_{12}(r_{ij}), \tag{1}$$

where N_i is the total number of particles of species i.

When all the interactions are hard-sphere-like, one has

$$u_{ij}^{HS}(r) = \begin{cases} \infty, & r < \sigma_{ij} \\ 0, & r \geq \sigma_{ij} \end{cases}$$

with $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ for additive HS (thus $\sigma_{11} = \sigma_1$ and $\sigma_{22} = \sigma_2$).

As emphasized in the introduction, some correction to the HS interaction might be necessary for some specific systems:

$$\Delta u_{ij}(r) = u_{ij}(r) - u_{ij}^{HS}(r), \tag{2}$$

so that one writes

$$H = H_{HS} + H_1, \tag{3}$$

where H_{HS} and H_1 correspond, respectively, to the HS interaction u_{ij}^{HS} and to Δu_{ij} in Eq. (1). By assuming that the latter lead only to small modifications with respect to the pure HS case, one can use standard methods of the perturbation theory [29], the reference system being the HS mixture.

The question of the choice of the ''true'' interactions $u_{ij}(r)$ in real colloidal suspensions and hence of Δu_{ij} is actually not a simple one. It will be partially examined in Sec. IV, where a few typical cases will be studied numerically. In what follows, we examine the aspects of the perturbation treatment that do not require specification of these corrections.

B. Thermodynamic potentials

To discuss the validity of the PT, the effective one-component representation will prove more convenient: first, because it is numerically simpler; second, because it is the most transparent way to capture the impact of the perturbation potentials on the properties of the solutes. The suitable thermodynamic ensemble is then the semigrand one. The mixture has a fixed number of solute particles N_2, and is in thermodynamic equilibrium with a reservoir of solvent particles with temperature T and chemical potential μ_1. The associated thermodynamic potential $F(N_2,V,T;\mu_1)$ reads

$$F = -kT \ln Z(N_2,V,T;\mu_1) \qquad (4)$$

with

$$Z = \frac{1}{N_2! \Lambda_2^{3N_2}} \sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int \int d\mathbf{r}^{N_1} d\mathbf{r}'^{N_2}$$

$$\times \exp[-\beta H(\mathbf{r}^{N_1}, \mathbf{r}'^{N_2})], \qquad (5)$$

where $\beta = 1/kT$, $z_1 = \Lambda_1^{-3} \exp(\beta\mu_1)$ is the solvent fugacity with $\Lambda_i = h/\sqrt{2\pi m_i kT}$, and V is the volume of the mixture. Equivalently, Z reads

$$Z = \frac{1}{N_2! \Lambda_2^{3N_2}} \int_V d\mathbf{r}^{N_2} \exp\{-\beta[H_{22}(\mathbf{r}^{N_2}) + \Omega]\}, \qquad (6)$$

with

$$\Omega = -kT \ln \sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int_V d\mathbf{r}'^{N_1} \exp\{-\beta[H_{11}(\mathbf{r}'^{N_1})$$

$$+ H_{12}(\mathbf{r}'^{N_1}, \mathbf{r}^{N_2})]\}, \qquad (7)$$

where H_{ij} is the sum of the pair interaction terms u_{ij} between species i and j. Equations (6) and (7) are exact. They constitute the starting point of the effective one-component representation, Z appearing as the canonical partition function of a one-component system with thermodynamic variables (N_2,T,V) interacting through the effective N_2-body interaction potential:

$$H^{eff} = H_{22} + \Omega. \qquad (8)$$

In this treatment, the effect of the solvent on the solute particles is entirely contained in the indirect potential Ω. The latter depends on μ_1 and is a functional of the interaction potentials u_{11} and u_{12} through Eq. (7). It is not, in general, a pairwise additive potential. The following step is to write expansion of Ω at high dilution. At second order, this reads (see, for example, Ref. [8])

$$\bar{\Omega} = \Omega_0(\mu_1,T,V) + N_2 \omega_1(\mu_1,T,V)$$

$$+ \frac{1}{2} \sum_{i=1}^{N_2} \sum_{j=1}^{N_2} \omega_2(\mathbf{r}_{ij};\mu_1,T,V) \qquad (9)$$

with

$$\Omega_0 = -kT \ln[Z_0(\mu_1,T,V)], \qquad (10)$$

$$\omega_1(\mu_1,T,V) = -kT \ln\left[\frac{Z_1(\mu_1,T,V)}{Z_0(\mu_1,T,V)}\right], \qquad (11)$$

$$\omega_2(\mathbf{r};\mu_1,T,V) = -kT \left\{ \ln\left[\frac{Z_2(\mathbf{r};\mu_1,T,V)}{Z_0(\mu_1,T,V)}\right] - 2\ln\left[\frac{Z_1(\mu_1,T,V)}{Z_0(\mu_1,T,V)}\right] \right\} \qquad (12)$$

and

$$Z_0 = \sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int_V d\mathbf{r}^{N_1} \exp[-\beta H_{11}(\mathbf{r}^{N_1})], \qquad (13)$$

$$Z_1 = \sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int_V d\mathbf{r}^{N_1} \exp\left[-\beta\left(H_{11}(\mathbf{r}^{N_1}) + \sum_{i=1}^{N_1} u_{12}(r_i)\right)\right], \qquad (14)$$

$$Z_2 = \sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int_V d\mathbf{r}^{N_1} \exp\left[-\beta\left(H_{11}(\mathbf{r}^{N_1}) + \sum_{i=1}^{N_1} [u_{12}(r_i) + u_{12}(|\mathbf{r}_i - \mathbf{r}|)]\right)\right]. \qquad (15)$$

Equation (9) may be interpreted as follows: the first term Ω_0 is the grand potential of the solvent at μ_1 and T without interaction with the solute (one has indeed $\Omega = \Omega_0$ for $u_{12} = 0$). The following terms ω_1 and ω_2 are the one-body and two-body contributions to $\bar{\Omega}$ induced by the solvent-solute interaction. The one-body term $N_2\omega_1$ is the grand potential difference obtained by considering as independant the contribution of each solute particle in the solvent sea [from Eqs. (9), (11), (13), and (14), one has for $N_2=1$: $\bar{\Omega} = \Omega_0 + \omega_1 = -kT \ln Z_1$]. The two-body term containing ω_2 is the lowest-order correction due to the solute-solute correlation. Note that for $N_2=2$ one recovers exactly $\bar{\Omega} = \Omega_0 + 2\omega_1 + \omega_2 = -kT \ln Z_2$ [see Eqs. (9)–(15)]. The interaction term ω_2 is the potential of mean force. In this approximation, it contains the whole effective contribution of the solvent to the phase behavior of the solute. From Eqs. (8) and (9), one has indeed

$$\bar{H}^{eff} = \Omega_0(\mu_1, T, V) + N_2 \omega_1(\mu_1, T, V)$$

$$+ \frac{1}{2} \sum_{i=1}^{N_2} \sum_{j=1}^{N_2} u^{eff}(r_{ij}; \mu_1, T, V) \quad (16)$$

with

$$u^{eff}(r; \mu_1, T, V) = u_{22}(r) + \omega_2(r; \mu_1, T, V). \quad (17)$$

In Eq. (16), the first term Ω_0 refers only to the solvent, which is assumed to remain homogeneous (as we are interested in conditions in which only the solutes are concerned by the phase transition, the thermodynamic variables have to be chosen, for a fixed potential u_{11}, either in the supercritical region for the solvent or outside the F-F binodal). The second term $N_2 \omega_1(\mu_1, T, V)$ is also irrelevant for the solutes phase behavior because its contribution to the grand potential is linear in N_2. Therefore, u^{eff} is the sole relevant term of $\bar{H}^{eff}$ for the thermodynamics of the solutes. It contains the direct part u_{22} of the solute-solute interaction and the indirect one ω_2, which is mediated by the solvent sea. In the pure HS mixture, ω_2 reduces to the depletion potential, which we will denote ω_{dep} in the rest of the paper. For a given size ratio, ω_{dep} depends only on r and μ_1 or, equivalently, on r and ρ_1^* the solvent density in the reservoir.

C. Perturbation treatment

1. Perturbation free energy

Starting from Eq. (1) and using the HS mixture reference system one obtains the thermodynamic potential at first order as

$$F^{pert} = F_{HS} + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \rho_{11}^{HS}(\mathbf{r}, \mathbf{r}') \Delta u_{11}(|\mathbf{r} - \mathbf{r}'|)$$

$$+ \int \int d\mathbf{r} d\mathbf{r}' \rho_{12}^{HS}(\mathbf{r}, \mathbf{r}') \Delta u_{12}(|\mathbf{r} - \mathbf{r}'|)$$

$$+ \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \rho_{22}^{HS}(\mathbf{r}, \mathbf{r}') \Delta u_{22}(|\mathbf{r} - \mathbf{r}'|), \quad (18)$$

where F_{HS} is the thermodynamic potential of the HS reference system and $\rho_{ij}^{HS}(\mathbf{r}, \mathbf{r}')$ the corresponding two-body density for species i and j. This approximation amounts to neglecting the variations of the pair correlation functions during the charging process. The part of the grand potential neglected in this approximation is

$$\Delta F = \int_0^1 \frac{d\lambda}{2} \int \int d\mathbf{r} d\mathbf{r}' \left[\sum_{i,j} [\rho_{ij}^\lambda(\mathbf{r}, \mathbf{r}') - \rho_{ij}^{HS}(\mathbf{r}, \mathbf{r}')] \right.$$

$$\left. \times \Delta u_{ij}(|\mathbf{r} - \mathbf{r}'|) \right] \quad (19)$$

with $\rho_{ij}^\lambda(\mathbf{r}, \mathbf{r}')$ the pair density computed for $H_\lambda = H_{HS}$

$+ \lambda H_1$ [see Eq. (2)]. The same approximation in the one-component representation is deduced from Eqs. (16) and (17):

$$\bar{F}^{pert} = \bar{F}_{HS} + \Delta[\Omega_0 + N_2 \omega_1] + \int \int d\mathbf{r} d\mathbf{r}' \bar{\rho}^{dep}(\mathbf{r}, \mathbf{r}')$$

$$\times [\Delta \omega_2(|\mathbf{r} - \mathbf{r}'|) + \Delta u_{22}(|\mathbf{r} - \mathbf{r}'|)], \quad (20)$$

where

$$\Delta \omega_2(r) = \int dr' \left(\frac{\delta \omega_2(r)}{\delta u_{11}(r')} \bigg|_{(u_{ij} = u_{ij}^{HS})_{ij}} \Delta u_{11}(r) \right.$$

$$\left. + \frac{\delta \omega_2(r)}{\delta u_{12}(r')} \bigg|_{(u_{ij} = u_{ij}^{HS})_{ij}} \Delta u_{12}(r) \right) \quad (21)$$

and where $\bar{F}_{HS}$ is the free energy of the (N_2, T, V) effective one-component system computed from Eq. (16); $u^{eff} = u_{22}^{HS} + \omega_{dep}$, $\bar{\rho}^{dep}(\mathbf{r}, \mathbf{r}')$ is the corresponding pair density and $\Delta[\Omega_0 + N_2 \omega_1]$ the variation of $(\Omega_0 + N_2 \omega_1)$ induced by the perturbation potential. In this scheme, the effect of the PT is to neglect the variations induced by the charging process on the one-component pair density $\bar{\rho}^\lambda(\mathbf{r}, \mathbf{r}')$ and on the two terms $[\delta \omega_2(r)/\delta u_{ij}(r')]|_\lambda$ leading to $\Delta \omega_2$. We will now explain why the effective one-component fluid representation is preferable for our study.

2. Choice of the one-component representation

We consider here a perturbation involving only Δu_{11} and Δu_{12} since the direct solute-solute interaction potential u_{22} plays the same role in the mixture and in the effective fluid. The accuracy of the perturbation free energy F^{pert} depends on the magnitude of the term $\beta \Delta F$ that is neglected. For our present concern, the latter reads [see Eq. (19)]

$$\beta \Delta F = \int_0^1 \frac{d\lambda}{2} \int \int d\mathbf{r} d\mathbf{r}' \{ [\rho_{11}^\lambda(\mathbf{r}, \mathbf{r}') - \rho_{11}^{HS}(\mathbf{r}, \mathbf{r}')] \Delta u_{11}(|\mathbf{r}$$

$$- \mathbf{r}'|) + [\rho_{12}^\lambda(\mathbf{r}, \mathbf{r}') - \rho_{12}^{HS}(\mathbf{r}, \mathbf{r}')] \Delta u_{12}(|\mathbf{r} - \mathbf{r}'|) \}. \quad (22)$$

From this expression, one would naively expect the PT to be valid when the two-body densities ρ_{11} and ρ_{12} computed for the total potential do not differ much from their reference values. This would indeed lead to a small value of the ratio $\beta \Delta F / \beta(F - F_{HS})$, that expresses the relative weight of the neglected part. This reasoning is, in fact, incorrect since only a very small fraction of the total thermodynamic potential is actually relevant to the phase behavior of the solute particles. This appears more clearly in the one-component representation. Indeed, from Eq. (16) the effective free energy $\bar{F}^{eff}$ reads

$$\bar{F}^{eff} = \Omega_0(\mu_1, T, V) + N_2 \omega_1(\mu_1, T, V) + \bar{F}(N_2; \mu_1, T, V), \quad (23)$$

where $F'(N_2;\mu_1,T,V)$ is given by

$$\bar{F} = -kT \ln \frac{1}{N_2! \Lambda_2^{3N_2}} \int_V d\mathbf{r}^{N_2} \exp\left[-\frac{\beta}{2} \sum_{i \neq j} \left[u_{22}(\mathbf{r}_{ij})\right.\right.$$

$$\left.\left. + \omega_{22}(\mathbf{r}_{ij})\right]\right]. \tag{24}$$

As already emphasized, the phase behavior of the solutes is determined only by $\bar{F}$. This is a small quantity when compared with Ω_0 and $N_2\omega_1$. One has indeed $|\bar{F}| \sim N_2^2$, while $|\Omega_0| \sim N_1^2$ [see Eqs. (10) and (13)] and $|N_2|\omega_1| \sim N_1 N_2$ [see Eqs. (11), (13), and (14)] which, with $N_2 \ll N_1$, leads to $|\bar{F}| \ll |\Omega_0 + N_2\omega_1|$. Therefore, even a deviation ΔF that would be small with respect to the total perturbation $(F - F_{HS})$ could have a very strong impact on $\bar{F}$. This would also hold with a more exact expression of $\bar{F}^{eff}$, integrating the indirect potential Ω beyond the two-body term ω_2, since one has in any case $|\Omega - \Omega_0 - N_2\omega_1| \ll |\Omega_0 + N_2\omega_1|$. The one-component expression (24) of the free energy is, therefore, more appropriate to test the PT than that of the mixture [Eq. (18)]. From Eqs. (20) and (21), we see that the validity of the PT is, in fact, linked to the choice of the depletion potential (plus the HS direct repulsion) as a reference for the effective potential u^{eff}. Equation (20) shows that this amounts to neglecting the effect on the solute pair distribution $\bar{\rho}^{eff}$ of the attractive contributions Δu_{11} and Δu_{12} [for the discussion of Eq. (21) see Sec. II D].

To conclude this section, we wish to emphasize the main point of the previous discussion: in many physical situations, the effect of Δu_{11} and Δu_{12} on the associated pair densities ρ_{11} and ρ_{12} is moderate (for example, see Figs. 3 and 4 in Ref. [34]). These "small perturbations" may nevertheless have a strong impact on the potential of mean force ω_2, or equivalently on the solute-solute correlations at infinite dilution. This means that the situation is completely different from that of simple fluids or slightly asymmetric mixtures: in highly asymmetric ones indeed, moderate changes of the interaction potentials with respect to the HS mixture ones may strongly modify the structural properties of the solute. In the following section, numerical results with realistic interactions u_{11} and u_{12} will illustrate the quantitative and in some case even qualitative inaccuracy of the perturbation treatment in the fluid state.

D. Outline of the numerical method

The accuracy of the PT with HS mixture reference system for mixtures with attractive forces has been tested by comparing the PT free energy to the "exact" one, both being computed in the one-component representation. Two models of perturbation potentials have been investigated (see Sec. III). To avoid possible effects of pair additivity assumption involved in the effective one-component approach, we have considered the region of the phase diagram where this approximation has been tested successfully by direct simulations of the mixture in the case of pure HS potentials.

For the PT free energy, we have kept in Eq. (20) only the interaction terms that are relevant for the phase behavior. This gives:

$$F'^{pert} = \bar{F}^{HS} + \rho^2 V \int_V d\mathbf{r}\, g_{dep}(\mathbf{r}) \Delta\omega(\mathbf{r}). \tag{25}$$

where g_{dep} is the PDF of the fluid of solute particles at (N_2,T,V) computed for the potential $\phi_{dep} = \omega_{dep} + u_{22}^{HS}$, ρ is the solute number density, and $\Delta\omega(r) \equiv \Delta\omega_2(r)$. The direct interaction has been taken as the HS one: $u_{22} = u_{22}^{HS}$. For the sake of simplicity, the dependance of $\bar{F}^{HS}$, $\Delta\omega$, and g_{dep} on η_1^* and q will be specified only when necessary.

The depletion potential ω_{dep} has been computed from the Ornstein-Zernike equations (OZE) of the HS mixture at infinite dilution with the HNC closure as in Ref. [36]. An improved RHNC closure with bridge functions from Rosenfeld's DFT [3] has been used more recently by Amokrane and Malherbe [35]. However, as the aim of the present work paper was to test the PT rather than to study a specific physical system, the effective potentials from the much simpler HNC closure are sufficient.

To compute the exact free energy $\bar{F}$, the total potential of mean force ω_{22} was also needed. We used the same method as for ω_{dep}, that is, the OZE/HNC for the actual potentials u_{11} and u_{12}. Next, the reference free energies $\bar{F}^{HS}$ and $\bar{F}$, for the effective one-component fluid, were computed by applying the RHNC method with optimized reference system [37] with the respective potentials ϕ_{dep} and $\phi_{tot} = u_{22} + \omega_{22}$. The accuracy of this method for the HS mixture model for the densities considered in this work has been shown in Refs. [18,36]. Thus, $\bar{F}^{HS}$ and $\bar{F}$ will be considered as "exact."

The RHNC free energy uses also the one-component HS fluid reference system but the additional part of the interaction is treated in a nonperturbative way [37]. We used the version proposed in Ref. [33], which takes as unique imput the HS bridge function $B_0(r)$ proposed by Malijevsky and Labik [38] (the RHNC/OZE were solved with the algorithm of Labik, Malijevski, and Vonka [39]). The HS reference PDF $g_0(r)$ is next deduced from $B_0(r)$ by solving the OZE for the HS potential (for more details read Sec. III of Ref. [33]). Although this method is computationally less convenient than that using directly the Verlet-Weiss PDF [40], it is necessary to solve the numerical convergence problems arising at high density, when the parametrized $g_0(r)$ does not strictly correspond to $B_0(r)$.

As a last step, the PT free energy F'^{pert} was deduced from $\bar{F}^{HS}$ and g_{dep} (also provided by the RHNC computation) by applying Eq. (25). However, in contrast with a strict perturbative treatment of $\Delta u_{11}(r)$ and $\Delta u_{12}(r)$, we used for $\Delta\omega$ the exact relation $\Delta\omega = \omega_2 - \omega_{dep}$, instead of the aproximate one given by Eq. (21). Thus, in our version, F'^{pert} is just the PT free energy of a one-component fluid with potential ϕ_{tot}, computed for the reference potential ϕ_{dep}. This choice was, in fact, the simplest one since both ω_2 and ω_{dep} are already necessary inputs for the computation of $\bar{F}^{HS}$ and F'^{pert}. Moreover, it provides an improved version of the PT

by accounting for the exact changes of ω_2 induced by the perturbation potentials. This point is established in the appendix by comparing the free energy F'^{pert} obtained following the two routes. Note that, in both cases, the PT has a variational foundation since the free energy satisfies the Gibbs-Bogoliubov inequality.

III. RESULTS AND DISCUSSION

A. Molecular solvent-colloid mixture

The numerical results presented below were obtained for a few examples of u_{ij} typical of molecular solvent—sterically stabilized colloid mixtures. As recalled in the Introduction, at least two physical effects may lead to strong modifications of the total effective potential between the solutes, in comparison with the depletion one plus a hard-sphere interaction u_{22}^{HS}. The first one is the influence of the solvent-solute and the solvent-solvent attractive forces. For this specific point, the study by integral equations and simulation made in Ref. [18] of the influence of the range of the solvent-solvent attraction clearly shows how critical this influence might be. A somewhat less recognized effect is that of the direct interaction between the solute particles: it must be considered at the same scale as the short-range structure in the indirect interaction (that mediated by the solvent). When both show a comparable spatial variation, the image of a near-hard-sphere solute may indeed become insufficient [19]. It was shown in Ref. [20] that the direct potential is predominant with respect to the indirect one for $R\sim100$ (coated silica particles in inorganic solvent provide a typical example of this situation). On the contrary, the latter is still relevant for $R\sim20$, which corresponds rather to the case of water-in-oil microemulsion. We will thus consider this situation. Although the fine structure of the direct potential also proves to be significant in this regime [19], we will only focuss on the influence of the solvent-solvent and solvent-solute attraction forces, the direct potential being a HS one. We use for the heteroattraction u_{12} a Yukawa potential

$$\beta u_{12}(r)$$
$$= \begin{cases} -\dfrac{\sigma_{12}}{r}\varepsilon_{12}^* \exp[-\lambda_{12}(r-\sigma_{12})/\sigma_1], & \infty, \quad r\geq\sigma_{12} \\ \infty, & r<\sigma_{12} \end{cases}$$

and for the solvent-solvent interaction, a Lennard-Jones (L-J) one:

$$\beta u_{11}(r)=4\varepsilon_{11}^*\left[\left(\frac{d_1}{r}\right)^{12}-\left(\frac{d_1}{r}\right)^6\right].$$

In these expressions, ε_{ij}^* characterizes the magnitude of the potential (in units of k_BT). The inverse λ_{12}^{-1} of the dimensionless parameter λ_{12} is the reduced range of the Yukawa potential, in unit of the solvent "effective" HS diameter σ_1. This is chosen such that $u_{11}(\sigma_1)=0$, that is, $\sigma_1=d_1$. Another choice could be made, for instance, $u_{11}(\sigma_1)=\frac{3}{2}kT$ (see

TABLE I. Parameters of the binary mixture model: q is the HS diameter ratio; ε_{11}^* the solvent-solvent L-J parameter; $(\varepsilon_{12}^*,\lambda_{12})$ the solute-solvent Yukawa parameters.

Model	q	ε_{11}^*	ε_{12}^*	λ_{12}
A	10	0.5	8	2.5
B	10	0.1	13	2.5

Ref. [36]), but as the term $(d_1/r)^{12}$ increases very quickly for $r<d_1$ this would not change the indirect potential in a significant way.

Even in this restricted framework, the joint effect of u_{11} and u_{12} is subtle and can produce a quite complex behavior of the potential of mean force. The accuracy of the PT with HS reference mixture will thus be investigated in two specific situations, hereafter referred to as model (A) and model (B) (see Table I).

With model A a fluid suspension rich in solute particles was found to be stable in Ref. [18]. This case is particularly relevant for real solvent-colloid mixtures as it provides a microscopic insight into the solvation effect, which is usually addressed on more phenomenological grounds.

Model B corresponds to solvophilic macroparticles in a weakly attracting L-J fluid. While leading at large η_1^* to the expected solvation effect, such potentials induce more surprisingly a phase separation at very low η_1^* (see Ref. [41] and hereafter). This situation is thus numerically appropriate for testing the ability of the PT with HS mixture reference system to predict correctly a F-F transition.

1. Model A

In the first case, ϕ_{dep} and ϕ_{tot} were computed for the following values of the density ρ^* of the solvent in the reservoir: $\rho^*=0.15,0.3,0.4$ (for greater values of ρ^*, one crosses the nonconvergence region of the RHNC equations for the depletion potential). The deviation $\beta\Delta F=\beta(F'^{pert}-\bar F)$ that measures the inaccuracy of the PT was next computed for the same densities as a function of the solute packing fraction η. The results are shown in Fig. 1: we see that the total potential of mean force is repulsive in the region of contact, the depletion effect being completely masked by the solvation one (see Refs. [18,19,34,35,42] for a similar discussion). As a result, the F-F transition predicted above $\rho^*\sim0.5$ for the pure HS case is shifted to much higher solvent density (the F-F transition is then due to the attractive tail of the interaction for $r/\sigma_1\gtrsim11$). A finer analysis shows that the magnitude of $\Delta\phi=\phi_{tot}-\phi_{dep}$ at contact increases when ρ^* increases in the range 0.15–0.4. One has, for instance, $\Delta\phi(r=\sigma_2)\sim6.5kT$ for $\rho^*=0.4$. The deviation $\beta\Delta F$ [Fig. 1(b)] shows a variation with ρ^* and η similar to that already obtained in our previous study of one-component systems [33]: at fixed ρ^*, $\beta\Delta F$ increases first with η, reaches a maximum at some value η_{max}, and then decreases. Thus, the variation of $\beta\Delta F$ with η is clearly nonlinear. This is an important point because it means that the deviation observed is thermodynamically relevant. To confirm this
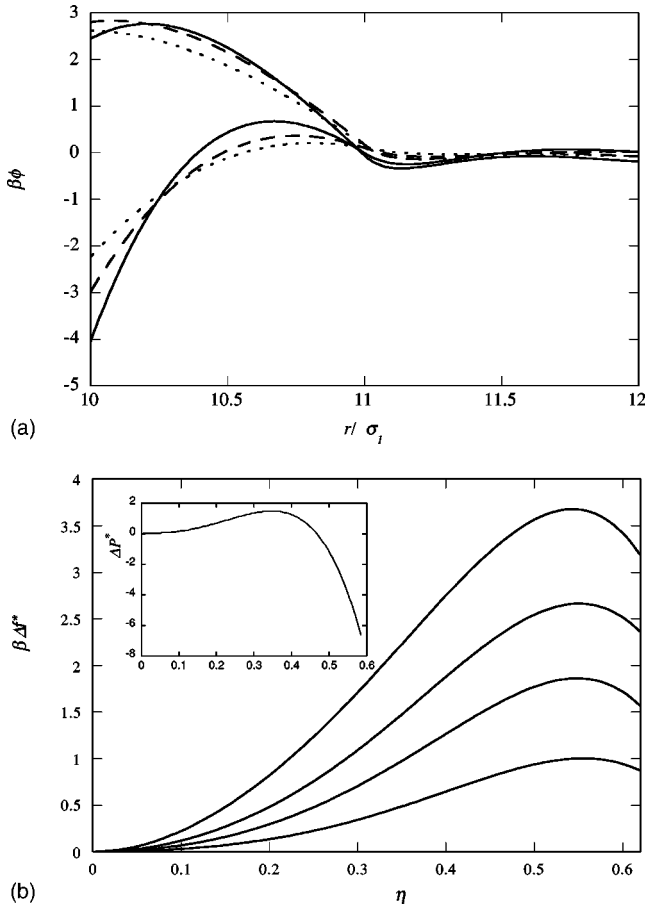
FIG. 1. (a) HNC potential of mean force at infinite dilution for $q = 10$ and different solvent bulk densities $\rho^* = \rho_1 \sigma_1^3$. First set (negative at contact): pure HS mixture; second set (positive at contact): HS+attractions (model A). Dotted line: $\rho^* = 0.23$; dashed line: $\rho^* = 0.3$; solid line: $\rho^* = 0.4$. r is the distance between the centers of the solute particles. (b) Free energy difference $\beta \Delta f^* = (\sigma_2^3/V)\beta(F'^{pert} - \bar{F})$ in model A vs solute packing fraction $\eta = (\pi/6)\rho_2 \sigma_2^3$. The solvent density is from bottom to top: $\rho^* = 0.15, 0.23, 0.3, 0.4$. Inset: Pressure difference $\Delta P^* = \beta \sigma_2^3 (\partial F'^{pert}/\partial V - \partial \bar{F}/\partial V) = (\beta/\sigma_2^3)[\Delta f^* - \eta(\partial \Delta f^*/\partial \eta)]$ vs η for $\rho^* = 0.4$.

point, the pressure difference $\Delta P = -\partial(F'^{pert} - \bar{F})/\partial V$ was computed for $\rho^* = 0.4$ (see inset): we do not observe improvement after derivation.

It was shown in Ref. [33] that the location of η_{max} depends, in fact, on the respective widths on $\Delta \phi$ and of the correlation peak of g_{ref} in the contact region. To understand this feature, one has to consider that the reference PDF can correctly reproduce the behavior of the true one only when the spatial variation of the perturbation potential is smooth enough within the separation range corresponding to the peak of g_{ref}. In this case, indeed, the perturbation forces are weak enough in this region and do not modify this peak too strongly. This explains why, for $\Delta \phi$ fixed, $\beta \Delta F$ decreases at very high density, when the width of the correlation peak is small enough. However, the effective potentials in colloids are of very short range. Therefore, one does not observe the region—at very high density—where the PT should be valid
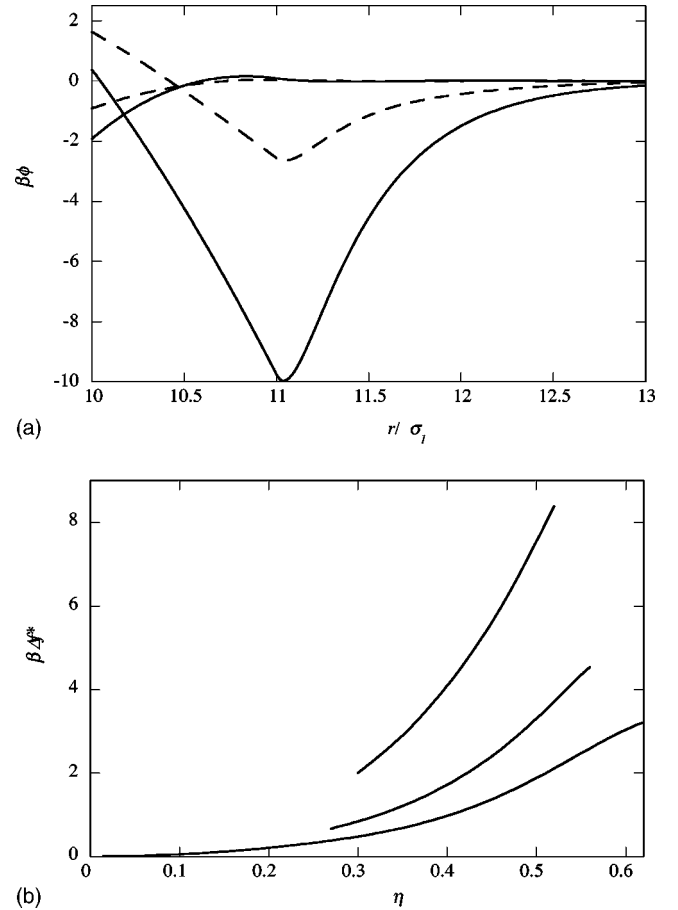

FIG. 2. (a) Same as Fig. 1(a) with model A. Dashed lines: $\rho^* = 0.1$; solid lines $\rho^* = 0.2$. (b) Same as Fig. 1(b) with model B. From bottom to top: $\rho^* = 0.09, 0.13, 0.23$.

again, as in simple fluids (for $R = 20$, η_{max} is greater than the close packing limit). On the contrary, the variation of ΔP (see inset) show that the PT tends to induce an artificial transition towards a very dense state. In Ref. [33], we already found that the PT is pathological for very short-range potentials, as it may lead to unphysical F-F transitions, which are pure artefacts of the method.

For η fixed, $\beta \Delta F$ increases with ρ^* (this is the direct consequence of the increase of $\Delta \phi$). For $\rho^* = 0.4$, we found $\Delta F \cong \bar{F} - \bar{F}^{HS}$ for $\eta = 0.5$. For greater values of ρ^*, as those corresponding to the F-F transition of the system with attractions, the situation would even be worse. The PT is thus very inaccurate for this choice of potentials.

2. Model B

The behavior of $\beta \Delta F$ for $\rho^* = 0.09–0.13$ is shown in Fig. 2(b). This range of density was chosen because it corresponds to a metastable F-F coexistence region [15,36] (a stable transition is obtained for $\varepsilon_{12}^* \gtrsim 13$ [15] but this is irrelevant for the present analysis). The variations of $\beta \Delta F$ with ρ^* and η are similar to those in Fig. 1(b) and those reported in our previous paper [33]. However, $\beta \Delta F$ increases more quickly in the present case, and η_{max} is outside the fluid regime. Thus, the PT is even more inaccurate than for model
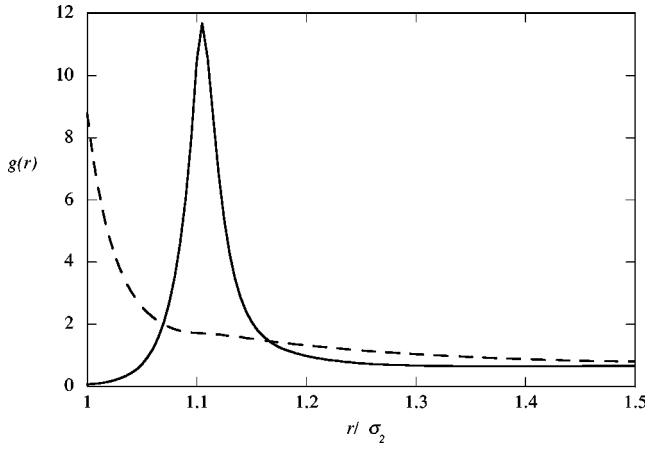
FIG. 3. Solute pair distribution function $g(r)$ in the effective fluid with $\eta = 0.4$. The potential of mean force is computed for $q = 10$, $\rho^* = 0.13$, and two models of the mixture: pure HS (dashed line); model B (solid line). r is the distance between the centers of the solute particles.

A. This result may be easily understood from the comparison of ϕ_{dep} and ϕ_{tot} [Fig. 2(a)]: the sign of the contact value is again reversed by the attractive forces. But ϕ_{tot} has this time a sizeable attractive (and nonoscillatory) tail with a much longer range than ϕ_{dep}. The comparison of g_{dep} and g_{tot}, computed for $\rho^* = 0.13$ and $\eta = 0.4$, shows the complete inadequacy of the HS mixture model for approximating the solute PDF in the region of contact when attractive forces are present (Fig. 3). Note that in this case, the PDF $g_0(r)$ of the one-component HS fluid with suitable diameter provides a much better estimate of g_{tot} than g_{dep}.

Now, we compare the phase behavior computed for the same u_{ij} in the PT and in the "exact" treatment (at one-component level). In the latter, the onset a F-F transition is observed for $\rho_c^* \simeq 0.11$. This is a consequence of the particular shape of ϕ_{tot} discussed above. The PT was then tested near ρ_c^*. It is found to fail in predicting the phase transition. This is shown in Fig. 4, for $\rho^* = 0.12$, that is just above ρ_c^*: one observes that the change of concavity of $F(\eta)$ obtained in the exact treatment [see Fig. 4(a) and inset] is absent in the pertubative one. More specifically, the inability of the PT for estimating the excess part $F_1 = F - \bar{F}^{HS}$ of F is shown in Fig. 4(b). To complete this test, $F'^{pert}(\eta)$ has been computed up to $\rho^* = 0.5$ (for greater ρ^* one encounters again the nonconvergence region of the RHNC equations for ϕ_{dep}): the failure of the PT is complete since the F-F transition is never observed in this approximation.

3. Nonadditivity

As a final illustration, we consider here nonadditive HS mixtures defined by $\sigma_{12} = [(\sigma_{11} + \sigma_{12})/2](1 + \Delta)$. Their phase diagram was studied by perturbation by Louis, Finken, and Hansen [31] both for positive and negative nonadditivity. $\Delta = 0 - 0.25$, $q = 5$ and $\Delta = -0.01$, $q \approx 9.3$. For the fluid phase, the free energy of the reference system was taken from the Mansoori *et al.* [43] equation of state. The free energy of the nonadditive HS was computed by the PT for
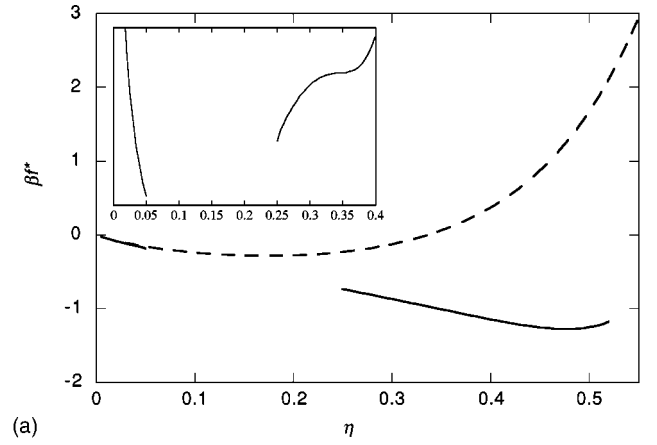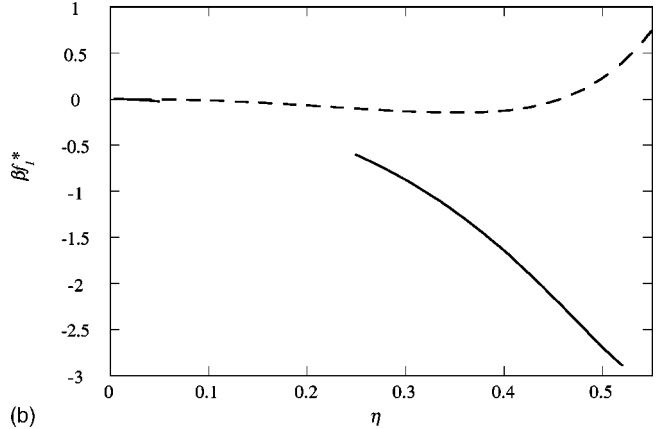
FIG. 4. (a) Reduced free energy $f^* = (\sigma^3/V)\beta F$ of model B for $\rho^* = 0.12$. Dashed line: PT; solid line: RHNC. The inset shows the RHNC reduced free energy after substraction of the linear component. (b) Same as Fig. 4(a) for the reduced excess free energy $f_1^* = (\sigma_2^3/V)\beta(F - \bar{F}^{HS})$.

the true mixture. In this case, this amounts to using a simple version of Eq. (18), in which only the PDF $g_{12}^{HS}(\sigma_{12})$ of the additive mixture is required. To assess the accuracy of this method, it is still necessary to consider the quantities that are relative to the solute only. The effective one-component potentials ϕ_{dep} and ϕ_{tot} were thus computed at $\rho^* = 0.4$. Figure 5 shows some results for different values of q and Δ. One observes that ϕ_{tot} quickly departs from ϕ_{dep} when Δ increases (see also Ref. [44]). The accuracy of the PT with additive HS reference system may therefore be questioned in some cases. This is shown in Table II where $\beta\Delta F/V$ and $\Delta F/(F - \bar{F}^{HS})$ are reported for $\eta = 0.4$. The ratio $\Delta F/(F - \bar{F}^{HS})$ is never negligible, even for $\Delta = -0.01$. For $\Delta = -0.04$ it is greater than 100%.

B. Pseudobinary mixture

In this last section, we briefly consider a mixture of two differently sized colloids. As stressed in the Introduction, the role of the solvent is usually ignored in this case. We thus do not considered it either. The indirect potential between the bigger colloids induced by the smaller ones has a range comparable to the size of the latter. On the contrary, the attractive
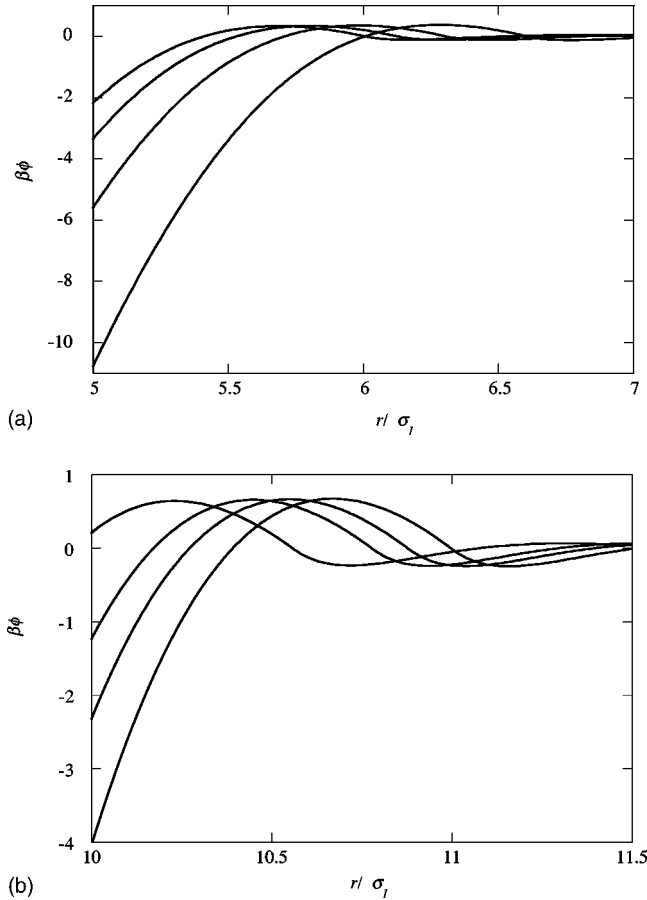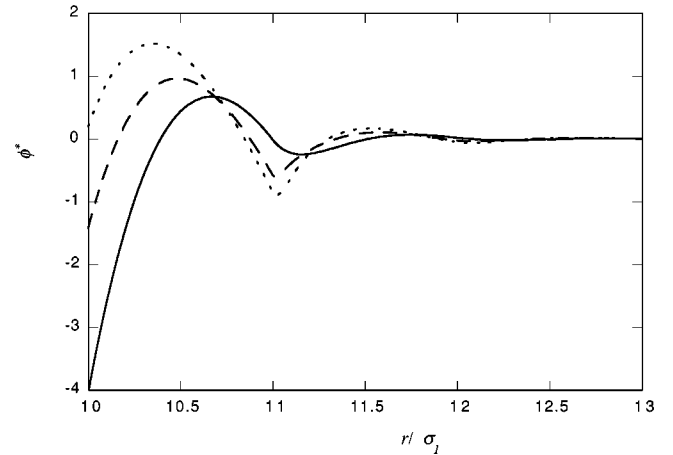
FIG. 6. Influence of a very short-range Yukawa heteroattraction on the HNC potential of mean force at infinite dilution for $q=10$, $\rho^*=0.4$. Yukawa parameters: $\varepsilon_{12}^*=8$; $\kappa_{12}=10$ (dotted line), 20 (dashed line). Solid line: depletion potential.

being weaker than in the previous situations (see, for instance, Fig. 1(a) at the same density), the difference between ϕ_{tot} and ϕ_{dep} is far from being negligible: $\Delta\phi(r=\sigma_2)$ $\sim 4.2kT$ and $2.6kT$ for $\kappa=10$ and 20, respectively. For $\kappa=10$, the depletion well is completely removed, while its depth is still significantly reduced for $\kappa=20$. These results suggest that the question of the relevance of the HS model to colloid-colloid mixtures deserves further examination. The actual answer should depend on the respective sizes of the components of the mixture and of the range of the direct interactions, as suggested by our results and those of Ref. [34]. Finally, we observed that the inaccuracy of the PT free energy with ϕ_{dep} as a reference potential can also be significant in this situation, albeit somehow less than for true molecular solvent-colloid mixtures.

IV. CONCLUSION

In this paper we have investigated the relevance of the HS mixture model as a starting point for the study of sterically stabilized colloids. Two different situations were distinguished. In the first one relative to polymer-colloid or colloid-colloid mixtures, the HS mixture model is usually considered as appropriate, and if present, non-hard-core interactions are considered as small perturbations. On the contrary, several experimental and theoretical facts underline the limitations of this model for the case of colloidal particles in a molecular solvent. However, the numerous theoretical works devoted to its study considered both the regimes of moderate and high size asymmetry, without always specifying the physical system under study. As the latter regime corresponds to pure solvent-colloid mixtures, it is necessary to discuss the potential use of the HS model as a reference system for investigating more realistic interactions. We thus studied numerically the PT with HS mixture reference system in the effective one-component representation, for two typical models of attractions between the solvent particles and between the solvent and the solute ones. In comparison with the "exact" RHNC free energy, the perturbation treat-

FIG. 5. (a) Influence of the nonadditivity parameter Δ on the HNC potential of mean force at infinite dilution for $q=5$; $\rho^*=0.4$. From top to bottom at contact: $\Delta=0,0.02,0.05,0.1$. (b) Same as Fig. 5(a) for $q=10$; $\rho^*=0.4$ From bottom to top at contact: $\Delta=0,-0.01,-0.02,-0.04$.

potentials between the colloidal particles have a much smaller range, characteristic of their specific structure (surface layer for example). A rapid insight on the effect of these forces may be obtained by modeling the colloidal particles as a binary mixture of hard spheres with a very short-range Yukawa heteroattraction. We took $q=10$ for the big to small colloid size ratio, and $\varepsilon_{12}^*=8$ and $\kappa_{12}=10,20$ for the Yukawa tail (inverse range in units of the diameter of the smaller colloid). $\kappa=20$ should be appropriate, for instance, to colloidal particles with diameters of 10 nm and 100 nm. $\kappa=10$ would rather correspond to the microemulsion range ($\sigma_1 \sim 2$ nm). The effect of the heteroattraction on the potential of mean force is shown in Fig. 6 for $\rho^*=0.4$. Although

TABLE II. Influence of the nonadditivity HS parameter Δ on the free energy deviation $\delta=\beta\sigma_2^3\Delta F/V$ and on the relative imprecision $R=\Delta F/(F-\bar{F}^{HS})$ of the PT, for $q=10$, $\rho^*=0.4$, $\eta=0.4$ [with $\eta=(\pi/6)\rho_2\sigma_2^3$ the solute packing fraction].

Δ	-0.01	-0.02	-0.04
δ	0.25	0.65	1.37
R(%)	28	56	106

ment was shown to be inaccurate for both models. The comparison quickly worsens when the solvent density increases. This discrepancy of the PT may be easily understood from the comparison of the solute-solute effective potentials computed for the reference HS potential (depletion potential) and for the total one. These results are very similar to those observed in a previous work on one-component hard particle fluids with very short-range attractions. For the second model the F-F transition could be studied numerically: the PT failed completely to predict the phase transition in the wide domain of solvent density that can be explored by the numerical algorithm. The excess free energy with respect to that of the depletion potential is indeed poorly estimated by the perturbation theory. As a last example, the model of nonadditive HS recently studied in a similar perturbative way was considered. The difference in excess free energy between the PT and the RHNC is found to increase quickly with the nonadditivity parameter. These results suggest that the binary HS mixture, with large difference in size, is in general not a good reference system for sterically stabilized suspensions of colloids in a molecular solvent. In this respect, efforts for improving the computation of the effective potential to be used in the effective fluid approach seem worth being continued. A clarification of the role of manybody effects is then necessary. Alternatively the treatment of the true mixture with improved closures of the OZE remains to be developed. Furthermore, a fine analysis of the direct interaction potential between the solutes would be necessary for studying any specific mixture.

Finally, we briefly considered the case of pseudobinary mixtures of colloidal particles. To model this situation, we considered the colloidal particles as hard sphere but the interarction between unlike species had a very short-range Yukawa attraction. We observed that in this situation, the potential of mean force may still be significantly modified with respect to the pure depletion one. This suggests that even for these kinds of mixtures, the question of the adequacy of the binary HS model needs again a carefull analysis.

APPENDIX

Let us consider the total potential $H = H_{HS} + \Delta H$. The perturbation free energy F^{pert} of Eq. (18) may also be written as

$$F^{pert} = F^{HS} + \langle \Delta H \rangle_{HS} \tag{A1}$$

with

$$\langle \Delta H \rangle_{HS} = \frac{1}{Z_{HS}} \sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int \int d\mathbf{r}^{N_1} d\mathbf{r}'^{N_2} \{ \Delta H \exp[-\beta H_{HS}] \}, \tag{A2}$$

where

$$Z_{HS} = \sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int \int d\mathbf{r}^{N_1} d\mathbf{r}'^{N_2} \exp[-\beta H_{HS}]. \tag{A3}$$

For $\Delta H = \Delta H_{11} + \Delta H_{12}$ (and $\Delta H_{22} = 0$), Eq. (A2) leads to

$$\langle \Delta H \rangle_{HS} = \frac{1}{Z_{HS}} \int_V d\mathbf{r}^{N_2} \Bigg[\exp[-\beta H_{22}^{HS}]$$
$$\times \Bigg(\sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int_V d\mathbf{r}^{N_1} \{ (\Delta H_{11} + \Delta H_{12})$$
$$\times \exp[-\beta(H_{12}^{HS} + H_{12}^{HS})] \} \Bigg) \Bigg]. \tag{A4}$$

By multiplying the numerator and the denominator by $\exp[-\beta \Omega^{HS}]$, with Ω^{HS}, the indirect potential corresponding to the HS mixture reference system, and by using Eq. (7) for the denominator, one gets

$$\langle \Delta H \rangle_{HS} = \frac{1}{Z_{HS}} \int_V d\mathbf{r}^{N_2} \{ \overline{\Delta \Omega} \exp[-\beta(H_{22}^{HS} + \Omega^{HS})] \}, \tag{A5}$$

where

$$\overline{\Delta \Omega} = \frac{\displaystyle\sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int_V d\mathbf{r}^{N_1} (\Delta H_{11} + \Delta H_{12}) \exp[-\beta(H_{11}^{HS} + H_{12}^{HS})]}{\displaystyle\sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int_V d\mathbf{r}^{N_1} \exp[-\beta(H_{11}^{HS} + H_{12}^{HS})]}. \tag{A6}$$

One has thus $\overline{\Delta \Omega} = \langle \Delta H_{11} + \Delta H_{12} \rangle_1^{HS}$, where the symbol $\langle \ \rangle_1^{HS}$ denotes the statistical average over the solvent components for the reference potential. Equations (A5) and (A6) are equivalent to Eqs. (20) and (21) when Ω is a pairwise additive potential.

Now, let us write the exact expression of $\Delta \Omega = \Omega - \Omega^{HS}$, with Ω the total indirect potential corresponding to H. This reads

$$\Delta \Omega = -kT \ln \Bigg\{ \sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int_V d\mathbf{r}^{N_1} \{ \exp[-\beta(\Delta H_{11}$$
$$+ \Delta H_{12})] \exp[-\beta(H_{11}^{HS} + H_{12}^{HS})] \} /$$
$$\Bigg\{ \sum_{N_1} \frac{z_1^{N_1}}{N_1!} \int_V d\mathbf{r}^{N_1} \exp[-\beta(H_{11}^{HS} + H_{12}^{HS})] \Bigg\}. \tag{A7}$$

Thus, $\Delta\Omega$ also reads $\Delta\Omega = -kT \ln \langle \exp[-\beta(\Delta H_{11} + \Delta H_{12})] \rangle_1^{HS}$. Comparing Eqs. (A6) and (A7), and applying the relation $\exp(X) \geq X$, one gets:

$$\Delta\Omega \leq \overline{\Delta\Omega}. \tag{A8}$$

Then, calling $\widetilde{\langle \Delta H \rangle}_{HS}$ the free energy correction obtained

by using in Eq. (A5) the exact $\Delta\Omega$ instead of $\overline{\Delta\Omega}$, one has

$$\widetilde{\langle \Delta H \rangle}_{HS} \leq \langle \Delta H \rangle_{HS}. \tag{A9}$$

Let us compare also $\widetilde{\langle \Delta H \rangle}_{HS}$ to the exact free energy difference ΔF defined by Eq. (19). This one may also read

$$\Delta F = -kT \ln \left\{ \frac{\int_V d\mathbf{r}^{N_2} \{ \exp[-\beta\Delta\Omega] \exp[-\beta(H_{22}^{HS} + \Omega^{HS})] \}}{\int_V d\mathbf{r}^{N_2} \exp[-\beta(H_{22}^{HS} + \Omega^{HS})]} \right\}. \tag{A10}$$

As the denominator of Eq. (A10) is equal to Z_{HS}, one gets the usual Gibbs-Bogoliubov relation:

$$\Delta F \leq \widetilde{\langle \Delta H \rangle}_{HS}. \tag{A11}$$

Relations (A9) and (A11) show that the choice of $\Delta\Omega$

instead of $\overline{\Delta\Omega}$ in Eq. (A5) leads to a more accurate computation of the free energy, the Gibbs-Bogoliubov criterium being satisfied in both cases. This conclusion is independent of the approximation used for the indirect potential, provided this approximation is the same for the reference potential and for the total one.

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