

Phase behavior of binary hard-sphere mixtures from perturbation theory

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Using a first-order perturbation theory, we have studied the phase diagram of a binary mixture of hard spheres for different values of the size ratio. Recent models for the two-body depletion potential between large spheres are used to take into account the role of the small spheres. The theory predicts a complex phase diagram including a fluid-solid transition at high packing fraction of small spheres, metastability of fluid-fluid demixing, an isostructural solid-solid transition at high packing fraction of the large spheres for sufficiently small values of the size ratio q of the spheres, and the tendency to sticky-sphere behavior in the limit $q \rightarrow 0$. The agreement with recent simulation results is quite good. We also show that this phenomenology was already implicit in the pioneering work of Asakura and Oosawa. [S1063-651X(99)10009-6]

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I. INTRODUCTION

An extensive research effort has been devoted in recent years to the study of phase transitions and the topology of the phase diagram of model colloidal systems [1]. These are relevant issues not only because of their important technological implications, but also from a fundamental point of view. For example, mixtures of colloidal particles consisting of hard spheres (HS) with a small amount of nonadsorbing polymer have been shown experimentally to present a rich variety of phase behaviors [2]. Simulation [3] and theoretical [4,5] studies have shown that these behaviors can be qualitatively well understood by considering the mixture as an effective system formed by HS colloidal particles with an attractive interaction tail due to a depletion mechanism.

Mixtures of colloidal particles and polymers are not the only possibility and very recently the study of the phase diagram of an even simpler model of colloidal mixture, namely a mixture of large and small hard spheres, has gained renewed interest. So far the main unsolved issue and topic of debate has been the existence of a fluid-fluid demixing transition which, in case it exists, will be an entropically driven transition that, in principle, could be described theoretically as a liquid-gas transition occurring in the system of large spheres and induced by the attractive depletion interaction due to the small spheres. However, very recent simulation results [6,7] have shown that the phenomenology is more complex and that, consistent with experimental results [8], demixing is strongly associated with the freezing transition.

Different theoretical studies have been reported [9–11], aimed at elucidating the existence and nature of the demixing transition. The conclusion that can be extracted from these studies is that theoretical predictions for the phase behavior depend on fine details of the approximations and are, therefore, inconclusive.

In this paper we obtain theoretically the phase diagram of an effective system of hard spheres interacting via a variety of depletion interactions based on different approximations published recently in the literature. For this purpose we use a *consistent* perturbation theory, applicable to both fluid and solid phases: as it turns out, it is crucial to use an accurate

perturbation theory for the solid phase in order to obtain an accurate description of phase equilibria. In line with recent simulation work, our results indicate the existence of a fluid-fluid transition, but this transition is metastable with respect to a direct fluid-solid transition. In addition, solid-solid demixing is observed for low values of the size ratio q . Finally, we show how the topology of the phase diagram of the mixture evolves with respect to q down to the limit $q \rightarrow 0$, which corresponds to the sticky-sphere limit. One important conclusion of this paper is that, despite the high degree of sophistication of all the recently obtained depletion potentials, the basic physics of this system was already implicit in the early Asakura and Oosawa potential [12], which possesses a phase diagram that essentially does not differ from those obtained using the more elaborate potentials.

II. DEPLETION MODELS

A number of authors [6,13] have recently studied the phase behavior of a mixture of hard spheres with respect to the size ratio $q \equiv \sigma_s / \sigma_l$, where σ_s and σ_l are the diameters of the small and large spheres, respectively. Phase equilibria were obtained by performing Monte Carlo (MC) simulations on an effective system made up of large spheres which interact via a hard core of diameter σ_l plus an attractive tail. The origin of this attraction is a depletion mechanism [14]: the small spheres have more free volume available (and the system as a whole increases its entropy) when the large spheres approach each other in such a way that there is no room left for small spheres in the space between the large ones.

This depletion mechanism gives an effective potential whose range is controlled by the size of the smaller particles and, therefore, suggests the possibility of having real systems which behave as simple systems with a tunable range of the interaction potential, an interesting avenue for fundamental research. Recently, several depletion-potential approximations have been proposed in order to improve on pioneering work by Asakura and Oosawa [12], who, using excluded-volume arguments, derived the potential

$$\beta\phi_{\text{dep}}^{\text{AO}}(r) = -\frac{1+q}{2q}3\lambda^2\eta_s\left[\frac{1+(1+\lambda/3)q}{1+q}\right], \quad -1 < \lambda < 0, \quad (1)$$

where $\lambda = r/q - 1/q - 1$, η_s is the small-sphere packing fraction, $\beta = 1/kT$, and r is in units of σ_l . On the other hand, use of the classical Derjaguin or flat-interface approximation [14] leads to

$$\beta\phi_{\text{dep}}^D(r) = -\frac{1+q}{2q}\pi\left[\frac{1}{2}P(\eta_s)\lambda^2 + 2\Gamma(\eta_s)\lambda\right], \quad -1 < \lambda < 0, \quad (2)$$

where $P(\eta_s) = \beta p(\eta_s)\sigma_s^3$ is the (reduced) hard-sphere pressure and $-\Gamma(\eta_s) = \beta\gamma(\eta_s)\sigma_s^2/2$ is the (reduced) surface tension of a fluid of hard spheres close to a planar hard wall. Mao *et al.* [15] derive a virial expansion of the potential, within the Derjaguin approximation, which is exact up to third order in η_s . A simplified version, obtained by Götzelmann *et al.* [16] using the Carnahan-Starling pressure and the expression for the surface tension from scaled particle theory [17], is

$$\beta\phi_{\text{dep}}^G(r) = -\frac{1+q}{2q}[3\lambda^2\eta_s + (9\lambda + 12\lambda^2)\eta_s^2 + (36\lambda + 30\lambda^2)\eta_s^3], \quad -1 < \lambda < 0. \quad (3)$$

This expression is exact to second order in η_s and does not differ significantly from Mao *et al.*'s expression. Note that the (exact) first-order term in η_s is different from that of Asakura and Oosawa; this difference is numerically quite small and we have chosen to use the modified version (1) since it has been used previously in the work of Gast *et al.* [9], which we discuss later. In [16], a so-called *wedge* approximation is considered whereby the free volume available to a small sphere in the presence of two large spheres is

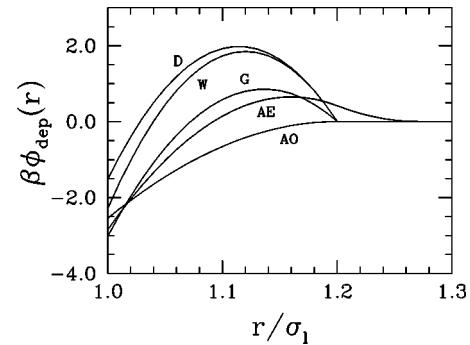


FIG. 1. Behavior of the different depletion potentials $\phi_{\text{dep}}(r)$ with distance r , for $q=0.2$ and $\eta_s=0.3$. The potentials are expressed in thermal energy units kT (with $\beta=1/kT$). Labels are as follows: D , full Derjaguin approximation; W , wedge approximation; G , third-order approximation of Götzelmann *et al.*; AE , potential derived by Almarza and Enciso; AO , potential of Asakura and Oosawa.

computed in a more sophisticated way than in the classical Derjaguin approximation. The explicit expression for this potential is

$$\beta\phi_{\text{dep}}^W(r) = -\frac{1+q}{2q}\pi\left[\frac{1}{2}P(\eta_s)\lambda^2 + 2\Gamma(\eta_s)\lambda\frac{1+q(1+\lambda/2)}{1+q}\right], \quad -1 < \lambda < 0. \quad (4)$$

Almarza and Enciso [13] consider an approach similar to that of [16] leading to Eq. (3) but use different approximations, writing

$$\beta\phi_{\text{dep}}^{AE}(r) = f_1(r, q)\eta_s + f_2(r, q)\eta_s^2, \quad (5)$$

where

$$f_2(r, q) = \begin{cases} 8f_1(r, q) + \frac{2}{q^3}[(1+q)f_0(q) - r]^2[2(1+q)f_0(q) + r], & 1 < r < (1+q)f_0(q) \\ 0, & r > (1+q)f_0(q), \end{cases} \quad (6)$$

$$f_1(r, q) = -\frac{1}{2q^3}\begin{cases} (1+q-r)^2[2(1+q)+r], & 1 < r < 1+q \\ 0, & r > 1+q, \end{cases} \quad (7)$$

and

$$f_0(r, q) = \left[1 + \frac{9}{8}\left(\frac{q}{1+q}\right) - \frac{1}{4}\left(\frac{q}{1+q}\right)^3\right]^{1/3}. \quad (8)$$

The behavior of the different depletion potentials with distance r , for $q=0.2$ and $\eta_s=0.3$, is displayed in Fig. 1. Included in the figure are potentials derived from the full Derjaguin (D) and wedge approximations (W), the third-order

Götzelmann *et al.* potential (G), the potential derived by Almarza and Enciso (AE), and that of Asakura and Oosawa (AO). These potentials are not intended to be valid for these values of q and η_s as far as an accurate description of the real hard-sphere mixture is concerned; however, they show most clearly the difference between the potentials, this being the only reason why we choose these particular values. In fact, for the range of values of q and η_s ($q < 0.2$ and $\eta_s < 0.2$), where these potentials should be expected to describe the mixture accurately, they do not differ significantly and give quantitatively similar phase diagrams, as will be discussed later.

Let us review the MC results obtained using the Götzelmann *et al.* potential. In [6], two cases were considered,

namely $q=0.1$ and 0.05 , and it was found that there exists a fluid-fluid demixing transition, but that it is *metastable* with respect to a direct fluid-solid transition. This is in qualitative agreement with possible interpretations of experimental results [8] and with previous theoretical studies [18] and it would seem to put an end to the discussion concerning the fluid-fluid demixing transition. In addition, an isostructural solid-solid transition was found which, for $q=0.1$, is also metastable with respect to the melting transition but becomes stable for $q \leq 0.05$. This is a very interesting result because it suggests a simpler experimental way for observing the solid-solid transition than in the case of mixtures of colloidal particles and polymers since it should be easier to reduce the value of q . From the theoretical point of view this result demands that any approximation be able to take into account the solid phase in an accurate (and consistent with the approach for the liquid phase) way along the entire solid density range, i.e., from the melting density up to the close-packing limit.

Despite those findings, some caution should be taken because it might be argued that the depletion potential approximation is very crude. In principle, many-body contributions to the depletion potential are expected to be important, and these contributions should play a crucial role in the clustering mechanism behind a demixing transition. Direct simulations of the HS mixture are difficult due to equilibration problems, especially when the sizes of the spheres are very dissimilar ($q \ll 1$), because then there appear two very different relaxation times in the system. Therefore, only scarce direct simulation data are available that can be used as a justification for the depletion potential approximation. Buhot and Krauth [19] have recently used a so-called cluster algorithm to simulate a binary mixture of HS. They have considered only one thermodynamic state ($\eta_l = \eta_s = 0.1215$, where η_l is the large-sphere packing fraction) and three size ratios ($q=0.1$, 0.05 , and 0.033) finding evidence for demixing in the two latter cases. However, the clustering observed in this study is most likely associated with freezing rather than fluid-fluid demixing given the thermodynamic state considered by Buhot and Krauth.

More recently, Dijkstra *et al.* [7] have been able to perform such a direct simulation in the region of a moderately low small-sphere packing fraction, where the richest part of the phase diagram takes place. They have found quite a good agreement with the results from the MC simulations based upon the description of the mixture in terms of the depletion potential (3). This is the case even for a value of q as large as 0.2 , for which a description in terms of the depletion potential could be expected to fail.

Finally, Almarza and Enciso [13] have also used MC techniques to obtain the phase diagram of a system of spheres interacting via the depletion potential derived by them. Their phase diagrams are quite similar; interestingly, they do not find any fluid-fluid equilibria for the cases studied.

III. THEORY AND RESULTS

Our theoretical approximation is a first-order perturbation theory for the Helmholtz free energy $F(\rho)$, which can be applied to both the fluid and the solid phases. The expression

for $F(\rho)$, exact up to first order, is [20]

$$F(\rho) = F_{\text{HS}}(\rho) + 2\pi\rho^2 \int_{\sigma_l}^{\infty} dr r^2 \tilde{g}_{\text{HS}}(r) \phi_{\text{dep}}(r), \quad (9)$$

where ρ is the mean density, F_{HS} is the free energy of the HS reference system, and \tilde{g}_{HS} is an angle average of the two-body distribution function of the reference system $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$. In the solid phase, \tilde{g}_{HS} can be very accurately obtained, provided that the thermodynamics and the local density $\rho(\mathbf{r})$ of the solid reference system are known [21], while in the liquid phase it reduces consistently to the radial distribution function [21]: Equation (9) reduces to the usual perturbation scheme for uniform liquids [21]. For this latter case we have used the Carnahan-Starling prescription for the free energy of the HS fluid and the Verlet-Weiss approximation for its radial distribution function.

The thermodynamic properties, free energy, and local density $\rho(\mathbf{r})$ of the face-centered-cubic (fcc) phase of HS can be accurately obtained from any of the density functionals available [22] or may be calculated using a recently proposed extension of the well-known free-volume approximation, which is capable of giving not only the equation of state of ordered phases of HS, but also their microscopic structure, in a very accurate way [23]. The results presented here were obtained using the second route but are practically indistinguishable from those obtained using, e.g., the Tarazona functional [24].

It is worth mentioning that it is crucial to implement an accurate scheme for the angle-averaged $\tilde{g}_{\text{HS}}(r)$ of the solid phase; in this respect the scheme proposed in [21] and used in the present paper can be used with advantage over most of the theories used by other workers, which give very poor results for extremely short-ranged potentials. Our theoretical scheme is quite similar to, but, we believe, more consistent than, that used by Gast *et al.* [9], in their work on polymer-induced phase separation, where solid correlations obtained from simulations on the HS system are included in the perturbation theory. In addition, some of the higher-order terms in the perturbative expansion used by these authors are included in a manner proposed by Stell and co-workers [25] for the solid phase. We will comment on these results later.

Figure 2 shows our theoretical results for the phase diagram using the Götzelmann *et al.* potential. The figure includes calculations for different size ratios, $q = 0.2$, 0.1 , 0.05 , 0.0001 , and 0.00001 . Also included are simulation results of Dijkstra *et al.* using both the depletion potential approximation and the results from their direct simulations of the binary mixture at moderately low small-sphere packing fractions. The overall agreement between theoretical and computer simulation results is quite good. Our perturbation theory reproduces satisfactorily the change of topology that occurs in the phase diagram when the size ratio q is progressively reduced. Also, the theory is quantitatively correct as regards the solid-solid transition, present for $q \leq 0.1$, and becomes more accurate in the case of the fluid-solid transition as q is reduced. The theory is also able to find a fluid-fluid demixing transition (metastable with respect to the fluid-solid transition), though shifted to high densities. This is an interesting result which contrasts with recent at-

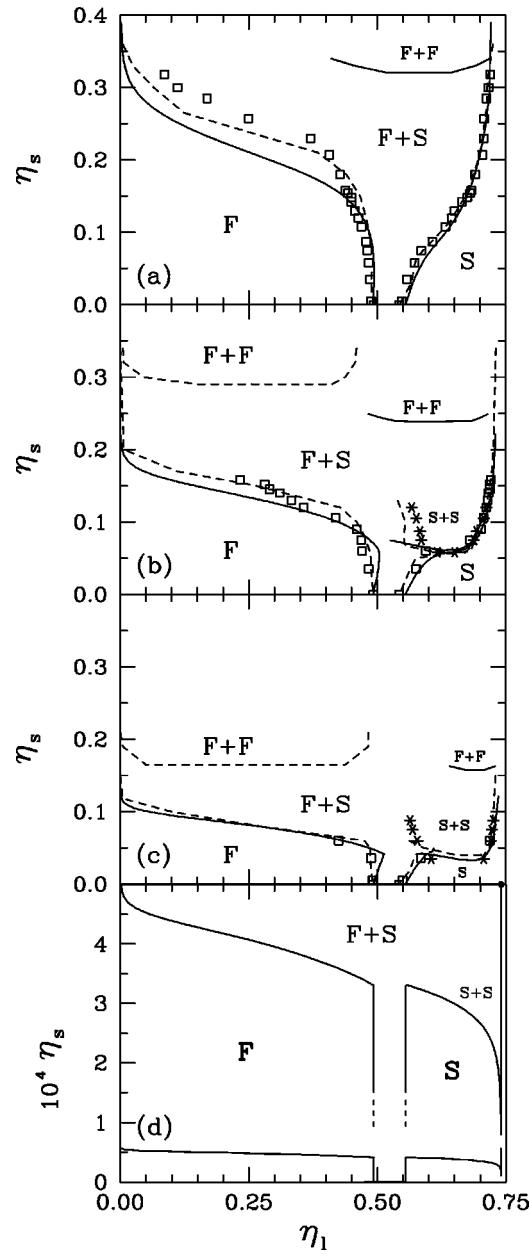


FIG. 2. Theoretically predicted phase diagram for binary HS mixtures, using the Götzelmann *et al.* depletion potential. Size ratios are, from top to bottom, $q=0.2$, 0.1 , 0.05 , and 0.0001 (in the last graph the case $q=0.00001$ is also included). F and S denote the stable fluid and solid (fcc) phases. $F+S$, $F+F$, and $S+S$ denote, respectively, the stable fluid-solid, the metastable fluid-fluid, and (meta)stable solid-solid coexistence regions. Solid lines are results from the present theory. Dashed lines are results from MC simulations of the effective depletion model. Symbols are results from the direct MC simulation of the mixture: the squares and the asterisks denote, respectively, the fluid-solid and the solid-solid transition.

tempts to find the fluid-fluid demixing by perturbation theory [6,16]. The main difference between our theory and that in Ref. [16] is the approximation used for the radial distribution function (rdf). While in Ref. [16] the authors consider a constant rdf (taken to be the contact value of the Percus-Yevick approximation) within the range of the depletion potential, we use the full Verlet-Weiss [26] approximation, which is known to predict the correct contact value. Since the deple-

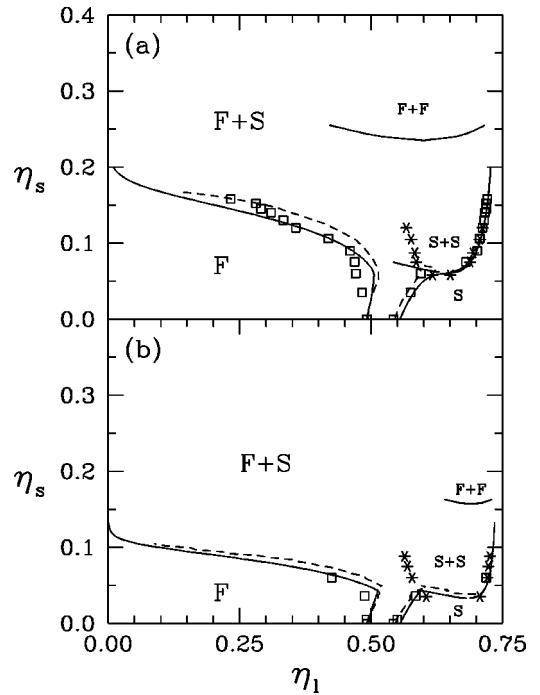


FIG. 3. Same as Fig. 2 but for the Almarza and Enciso potential. Size ratios are $q=0.1$ (top) and $q=0.05$ (bottom).

tion potential presents a deep well near contact and a slightly positive region, this difference turns out to be crucial. However, some caution is needed because the Verlet-Weiss approximation for the rdf breaks down in the high-density regime, close to where the theory finds the demixing transition.

We now present our theoretical results for the phase diagram corresponding to the Almarza-Enciso depletion potential [13], which are contained in Fig. 3. MC data obtained in [13] have been included in the figure. In the two cases studied, $q=0.05$ and 0.1 , the agreement of the theoretical results with simulation is similar to that found for the Götzelmann *et al.* potential. Note that all features of the phase diagrams predicted from the theory are completely similar, as expected from the similarity between the potentials for low values of q and η_s . For the same reason, one should expect the Asakura-Oosawa potential to lead to a quantitatively similar phase diagram. However, Gast *et al.* [9], using the Asakura-Oosawa depletion potential (1), found a phase diagram containing a fluid-solid transition, in line with previous findings, but the solid-solid transition was missing altogether. In order to understand this discrepancy, we have used our theoretical scheme to obtain the phase behavior of this potential. In Fig. 4(a) we show that, for the lowest value of q used by Gast *et al.*, the solid-solid transition is still metastable with respect to the fluid-solid transition. For a lower value ($q=0.05$) the solid-solid transition appears as a stable transition [Fig. 4(b)]. Note that these results compare equally favorably with the simulation results of the real mixture as the other, more elaborate potentials. This basically indicates that all the physics is already contained in the linear term of the depletion potential.

The depletion potentials used are valid for small η_s , which are actually accurate for mixtures of spheres with very different sizes, but break down for large q . It is interesting to note that the full depletion potentials Eqs. (2) and (4) give

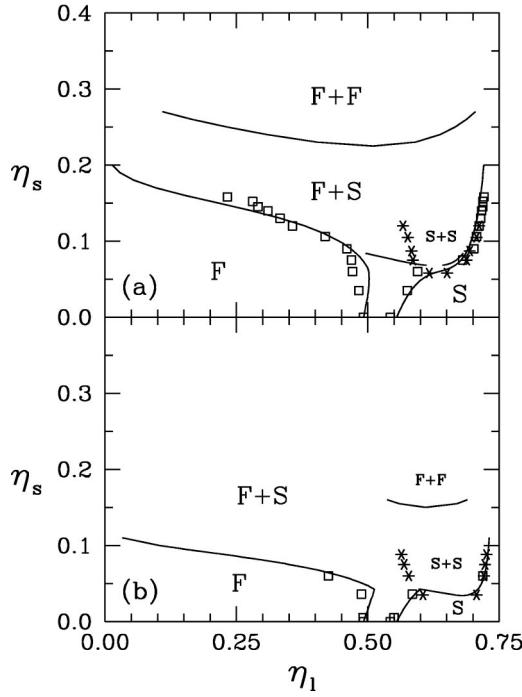


FIG. 4. Same as Fig. 2 but for the Asakura and Oosawa potential. Size ratios are $q=0.1$ (top) and $q=0.05$ (bottom).

rise to phase diagrams in complete agreement with those of Figs. 2–4 except for $q \geq 0.2$, where phase equilibria become totally unreasonable. This is apparent in Fig. 5, which shows an unphysical phase behavior, not observed in the simulations of the real mixture. This means that in the region where the small η_s expansion is no longer valid, the full depletion potential also ceases to make sense, and that departures from the simulation results for the real mixture are to be associated with an invalid potential rather than with a breakdown of perturbation theory, which for this range of parameters is still in reasonable agreement with simulation results.

However, a more fundamental analysis is necessary to understand the reason why the quantitative results for the fluid-fluid demixing transition are not satisfactory while our theory is able to predict very accurately the behavior of the solid phase, including the melting and solid-solid transitions. In fact, an important tendency to clustering is expected in the

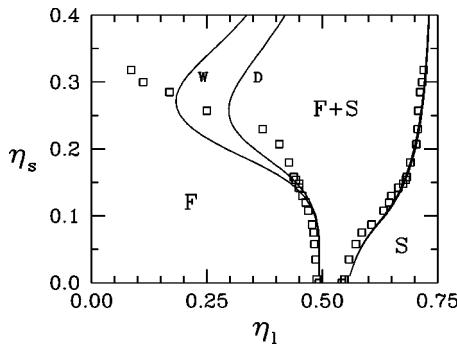


FIG. 5. Theoretically predicted phase diagram for binary HS mixtures, using the full Derjaguin (D) and wedge (W) approximations for the depletion potential. The size ratio is $q=0.2$. Squares indicate MC results for phase boundaries corresponding to the real HS mixture.

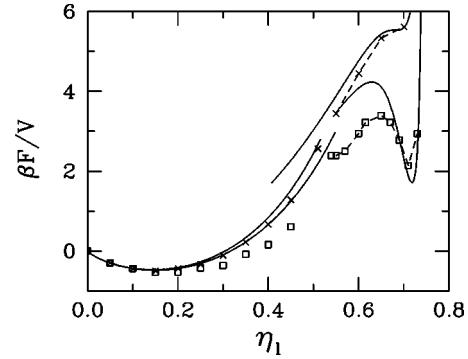


FIG. 6. Free energy $\beta F/V$ vs η_l for $q=0.1$ at $\eta_s=0.09$ and $\eta_s=0.13$ (top and bottom curves and symbols, respectively) for the third-order approximation for the depletion potential of Götzelmann *et al.* The volume V is expressed in units of σ_l^3 and $\beta=1/kT$. The curves and symbols for large η_l are obtained for the solid while those for low η_l correspond to the fluid. Solid lines are results from the present theory. Symbols are results from MC simulations. Dashed lines are guides to the eye.

low-density liquid phase at high η_s , which is induced by the depletion potential. For the values of q considered in this study, this potential presents a narrow and deep attractive well. In terms of an effective rdf of the liquid, this should cause the presence of a first peak significantly higher than that predicted by the Verlet-Weiss approximation. Within a first-order perturbation scheme, the consequence is a larger contribution from the attractive interaction in the low-density regime and, therefore, the appearance of a van der Waals loop in the free-energy branch at lower densities, which, in the end, causes a displacement of the fluid-fluid demixing transition in the same direction.

In the solid phase, however, the situation is different because the HS core of the intermolecular potential can stabilize a solid structure where the nearest-neighbor distance is large enough to prevent particles from feeling the attractive well due to their neighbors. Clustering in the solid phase pays a large entropy price due to the hard-core interaction and is expected to be less important than in the liquid phase. When η_l increases, the nearest-neighbor distance decreases and the large spheres feel the attractive depletion potential more strongly, so that there is an increasingly negative contribution to the free energy. In contrast, near close packing the repulsive hard-core contribution dominates the free energy. The final balance makes an elbow (or van der Waals loop) to develop in the solid free-energy branch if the depletion potential is strong enough, i.e., at sufficiently high η_s values, which originates the solid-solid transition.

Figure 6 shows this elbow for $q=0.1$ in comparison with simulation results. This demonstrates that perturbation theory is well justified in the case of the solid phase because the reference system is, to a large extent, determining the structure of the system. This fact, together with a very accurate approximation for the averaged two-body distribution function like the one we are using, explains the good agreement of our results with simulations as far as the solid phase and its transitions are concerned. Note that in the region of large η_s , the solid phase coexists with a liquid of very low density for which clustering effects, not considered explicitly in the theory, are expected to be important, as mentioned before.

However, these clustering effects do not have a significant impact on the phase diagram in this region since phase equilibria between the solid and the liquid are basically driven by the deep free-energy elbow of the solid, accurately rendered by our theory, and the ideal-gas chemical potential of a mixture of clusters. The coexistence density of the liquid is not very sensitive to the latter provided this is large and negative, a feature that is contained in our mean-field theory, which represents the mixture as a simple uniform gas of particles.

Once the solid-solid transition shows up, for q around 0.1, the topology of the phase diagram remains the same as q decreases down to $q=0$ [Figs. 2(b)–2(d)]. As q decreases, the depletion potential becomes deeper and more narrow. Thus the free-energy elbow becomes thinner and moves to higher densities, and so does the solid-solid transition. For sufficiently small q , the elbow gets extremely narrow and located practically at the packing fraction $\eta=\eta_{\text{cp}}/(1+q)^3$, where η_{cp} corresponds to close packing. This value determines the critical density of the solid-solid transition while the critical η_s is given by the minimum value necessary for the elbow to develop. As η_s increases, the expanded coexisting solid will ultimately meet the HS melting transition, giving rise to a fluid-solid-solid triple point.

It is interesting to note that the phase diagrams roughly scale with q . In other words, as q decreases, the coexistence lines corresponding to the fluid and expanded solid tend to flatten off, a signature of sticky-sphere behavior. For small q and η_s , the leading term of the depletion potential (hence the perturbation free energy) is proportional to η_s/q^3 . Then, for finite q , and provided η_s is sufficiently small, the depletion potential has no appreciable effects and the fluid-solid transition of the hard spheres is the only one appearing in a finite range above $\eta_s=0$. The topology of the phase diagram is that shown in Fig. 2(d), where $q=0.0001$. Note that the case $q=0.00001$ has been included in the same figure so that the scaling behavior can be grasped. It is also worth noting that the scaling seems to move the interesting zone of the diagram out of the region where the clustering effects should be important. In the limit $q=0$, the depth of the free-energy elbow is infinite, regardless of the value of η_s (except for the obvious case $\eta_s=0$) and located at η_{cp} . The system undergoes a phase separation into an infinitely dilute fluid and a close-packed solid. The sticky-sphere model is recovered.

IV. CONCLUSION

In conclusion, we have used a first-order perturbation theory to investigate the phase diagram of an asymmetric binary mixture of hard spheres, taken as an effective one-component system whose spherical molecules interact via a depletion potential. Several approximations for the depletion potential, derived by different authors, have been used. Our theory can explain the topology of the phase diagram and its evolution with size ratio, and the results obtained are also in excellent agreement with computer-simulation studies of the effective system. In addition, comparison has been made with the results of simulations performed on the real hard-sphere mixture; this provides some indirect assessment on the validity of both the different depletion-potential approximations and our theoretical approach. It is to be noted that our first-order perturbation theory, and that of Gast *et al.*, which includes higher-order terms, agree with these simulations even in the region where clustering is expected to be important. Other perturbation theories seem incapable of describing systems of particles interacting through very short-ranged potentials. Also interesting is the fact that the different potentials give practically the same phase diagram, and that the simple Asakura and Oosawa potential already contains all the features of the phase diagram: fluid-solid coexistence along with a solid-solid transition for $q<0.1$ and a metastable fluid-fluid transition. Our results indicate that a simple depletion potential, linear in η_s , may render the real mixture in an accurate fashion provided the size ratio is not very high.

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