

## Crystallization and phase separation in nonadditive binary hard-sphere mixtures

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We calculate for the first time the full phase diagram of an asymmetric *nonadditive* hard-sphere mixture. The nonadditivity strongly affects the crystallization and the fluid-fluid phase separation. The global topology of the phase diagram is controlled by an effective size ratio  $y_{\text{eff}}$ , while the fluid-solid coexistence scales with the depth of the effective potential well.

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Entropically driven phase transitions have received much attention lately because of their direct relevance to the observed phase-behavior of colloidal suspensions [1]. Theoretical work has focused on the asymmetric binary hard-sphere (HS) system, a deceptively simple mixture of large and small particles, which exhibits an interesting competition between demixing into dilute and concentrated suspensions of large particles, driven by the familiar osmotic depletion effect [2], and freezing into an ordered crystalline phase. Recent Monte Carlo (MC) simulations [3] of binary colloidal dispersions of spherical particles with additive diameters  $\sigma_1$  and  $\sigma_2$ , and size-ratio  $y = \sigma_2/\sigma_1 \leq 0.2$ , have convincingly demonstrated that the demixing transition conjectured earlier [4] is always preempted by a direct freezing of a low concentration disordered (“fluid”) phase into an fcc crystal of large particles. It was argued elsewhere [5] that a small degree of nonadditivity of the diameter  $\sigma_{12}$ , determining the distance of closest approach between large and small particles, might drive the demixing transition from metastable to stable. This view has been supported by recent MC simulations [6], which show that nonadditivity significantly lowers the packing fraction at the critical point of the fluid-fluid coexistence curve. However, to reach firm conclusions concerning the observability of a fluid-fluid demixing transition, the effect of nonadditivity on the freezing transition must also be considered explicitly, in order to map out a complete phase diagram. This is precisely the objective of this Rapid Communication, where the important influence of nonadditivity on the global phase behavior of highly asymmetric hard sphere mixtures is evaluated within a systematic statistical mechanical perturbation treatment. Even a small nonadditivity is shown to have a large effect on the interpretation of the phase behavior, and experiments on sterically or charge-stabilized binary “HS” colloids are shown to generically exhibit nonadditive behavior.

Consider a binary system of HS with distances of closest approach  $\sigma_{\alpha\beta}$  ( $1 \leq \alpha, \beta \leq 2$ ), such that  $\sigma_{11} = \sigma_1$ ,  $\sigma_{22} = \sigma_2$ , and

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})(1 + \Delta), \quad (1)$$

where the nonadditivity parameter  $\Delta$  can be positive or negative. The case  $\Delta = 0$  corresponds to additive HS, and has been widely studied with the usual techniques of the statistical mechanics of fluids. An extreme example of nonaddi-

tivity is provided by the case  $\sigma_{22} = 0$ ,  $\Delta > 0$ , which is the familiar Asakura-Oosawa model [2] of colloid-polymer mixtures, allowing for full interpenetrability of polymer coils. This system is predicted to exhibit phase separation into dilute and concentrated colloid fluid phases for large enough  $\Delta$  [7,8], in good agreement with experimental findings [9]. The present work is concerned with the case of small positive nonadditivity for HS mixtures with small size-ratios which would lead to a metastable demixing transition in the additive limit,  $\Delta = 0$ .  $\Delta > 0$  will obviously favor demixing since phases involving a majority of particles of the same species will allow a more efficient packing [10].

To examine the possibility of a fluid-fluid phase separation for  $\Delta > 0$ , it seems natural to develop a perturbation theory expansion in powers of  $\Delta$  around a reference mixture of identical composition, involving additive HS. The free energy per unit volume  $f_0 = F_0/V$ , of the latter is rather accurately given by the semi-empirical equation of state proposed by Mansoori *et al.* [11], which improves on the compressibility equation of state derived from the analytic solution of the Percus-Yevick (PY) equations [12]. Note that neither predicts a spinodal instability for any size-ratio or composition, as characterized by a vanishing determinant of the stability matrix  $M = |\partial^2 f_0 / \partial n_\alpha \partial n_\beta|$ , where  $n_\alpha = N_\alpha/V$  is the number density of  $\alpha$  spheres. However for fixed packing fraction, they predict that  $M$  approaches zero as  $y^3$  [12], suggesting that for larger and larger size-asymmetry, smaller and smaller perturbations to the purely additive case can drive the stability matrix negative. The additive case is in a sense “marginal” to phase-separation, which explains why the very existence of such a separation is so sensitive to the particular approximations used [4].

A direct application of standard thermodynamic perturbation theory [13] to the unlike pair potential:  $v_{12}^{(\lambda)}(r) = v_{12}^{(0)}(r/(1 + \lambda\Delta))$ , where  $\lambda = 0$  and  $1$  correspond, respectively, to the additive reference system with diameter  $\sigma_{12}^{(0)}$ , and to the nonadditive mixture of interest, leads to the first order correction to the free energy,

$$\beta(F - F_0)/V = 4\pi\Delta n_1 n_2 \sigma_{12}^{(0)3} g_{12}^{(0)}(\sigma_{12}^{(0)}). \quad (2)$$

In Eq. (2),  $g_{12}^{(0)}(\sigma_{12}^{(0)})$  is the contact value of the unlike pair distribution function of the reference mixture taken from the analytic solution of the PY equation for an additive binary HS mixture [12]. The fluid-fluid spinodal curves resulting from this two-component perturbation theory using both the

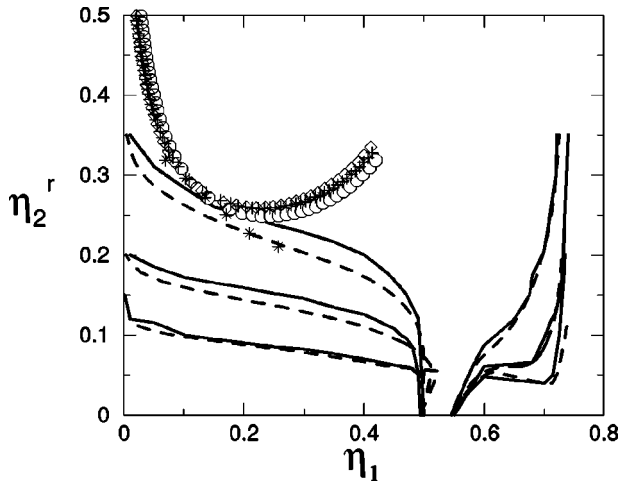


FIG. 1. Upper curves are fluid-fluid spinodals for  $y=0.2$ ,  $\Delta=0.033$  as obtained from the four theories described in the text: Mansoori reference ( $\circ$ ), PY reference ( $\diamond$ ), Barbooy-Gelbart ( $+$ ), and BPGG ( $*$ ). The lower three sets of curves compare the fluid-solid binodals calculated by first order perturbation theory in the potential of Eq. (3) (dashed lines) with MC results [3] (solid lines) for the additive case,  $\Delta=0$ . From top to bottom,  $y=0.2$ ,  $0.1$ , and  $0.05$  respectively.

Mansoori [11] and PY [12] reference  $F_0$ 's are compared in Fig. 1 to an approximate series expansion due to Barbooy and Gelbart [14] for a size-ratio  $y=0.2$  and  $\Delta=0.033$ . Note that the results are plotted for a semigrand ensemble: the binary mixture is in osmotic equilibrium with a reservoir of small spheres which fixes their chemical potential  $\mu_2$ ; the thermodynamic variables controlling the phase behavior are the packing fractions,  $\eta_1 = \pi n_1 \sigma_1^3 / 6$ , of the large spheres in the mixture and  $\eta_2^r$  of small spheres in the reservoir (or equivalently  $\mu_2$ ). In sharp contrast to the additive case where different theories yield dissimilar results [3], all three approaches yield similar results for the spinodal curves. Moreover, they are consistent with results from numerical solutions of the Ballone-Pastore-Galli-Gazzillo (BPGG) integral equation [15], at least for low values of  $\eta_1$ . As expected, the small correction due to the nonadditivity triggers a phase-separation which is absent in the two additive reference systems ( $\Delta=0$ ). The demixing transition, which is marginal for additive HS's [4], is strongly enhanced by a modest degree of nonadditivity. Moreover, increasing  $\Delta$  shifts the demixing transition to lower and lower packing fraction  $\eta_2^r$ , of small spheres, as shown in Fig. 2.

The above two-component perturbation scheme cannot be adapted to investigate the freezing of nonadditive HS mixtures, mainly because the crystal phase of the additive reference system is poorly understood for small size-ratios  $y$ . HS alloys form substitutionally disordered crystals for  $y \geq 0.85$  [16], and interesting superlattice structures for  $y \leq 0.6$  [17], but the structure for smaller values of  $y$  (say  $y \leq 0.3$ ) is not well understood, although it has been conjectured that the large spheres might form an FCC lattice, permeated by a fluid of small spheres, at least for sufficiently small  $y$  [18]. To avoid these difficulties, one may resort to an effective one-component description, by integrating out the degrees of freedom of the small spheres for any given configuration of large spheres. This procedure leads to effective interaction

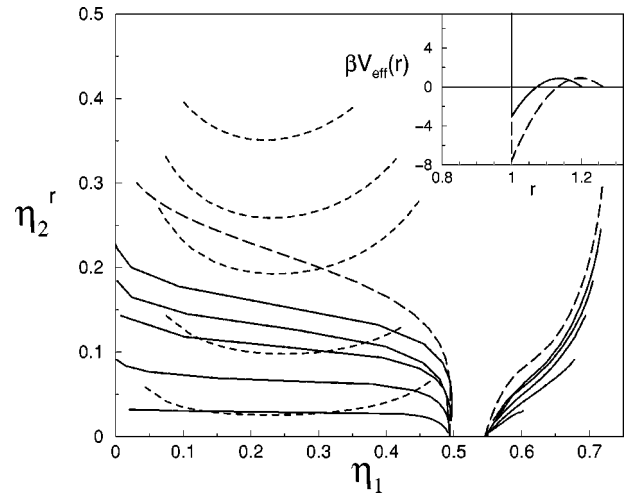


FIG. 2. Fluid-fluid spinodals (dashed lines) and fluid-solid binodals (solid lines) for  $y=0.2$ , and  $\Delta=0.02, 0.033, 0.05, 0.1$ , and  $0.25$  (from top to bottom). The long-dashed curve is the fluid-solid binodal for  $\Delta=0$ . Inset: effective potentials of Eq. (3) for  $y=0.2$ ,  $\eta_2^r=0.3$ ,  $\Delta=0$  (solid line) and  $\Delta=0.05$  (dashed line).

potentials between the large spheres which are determined by the free energy (or grand potential) of the inhomogeneous fluid of small spheres in the "external field" of the larger particles. The *basic philosophy* behind effective potentials in complex fluids is that the (considerable) initial effort spent deriving accurate effective potentials is recouped when they are used as input into the well developed machinery of liquid state theory [13]. In the case of colloid-polymer mixtures, this approach leads to the Asakura-Oosawa effective pair potential between large spheres [19], and for additive HS mixtures the effective pair potential has recently been extended to include excluded volume correlations between small spheres [20,3]. The procedure used in these references may be generalized to derive the following effective pair potential between large spheres in a nonadditive HS mixture,

$$\beta V_{\text{eff}}(r) = \infty; \quad r \leq \sigma_1$$

$$\beta V_{\text{eff}}(r) = \frac{-3\eta_2^r(1+y_{\text{eff}})}{2y^3} \{h(r)^2 + \eta_2^r[4h(r)^2 - 3yh(r)]\} + (\eta_2^r)^2[10h(r)^2 - 12yh(r)];$$

$$\sigma_1 \leq r \leq \sigma_1(1+y_{\text{eff}}), \quad (3)$$

where the effective size-ratio is

$$y_{\text{eff}} = y + \Delta + \Delta y, \quad (4)$$

while the function  $h(r) = (1+y_{\text{eff}}) - r/\sigma_1$ . The term linear in  $\eta_2^r$  is the purely attractive Derjaguin form of the Asakura-Oosawa potential, with the effective size-ratio  $y_{\text{eff}}$ , while the higher order terms describe the partially repulsive effects of the correlation-induced layering of the small spheres around the large spheres. As shown in the inset of Fig. 2, increasing  $\Delta$  at fixed  $\eta_2^r$  deepens the attractive well, while the correlation-induced repulsive barrier remains roughly the same.

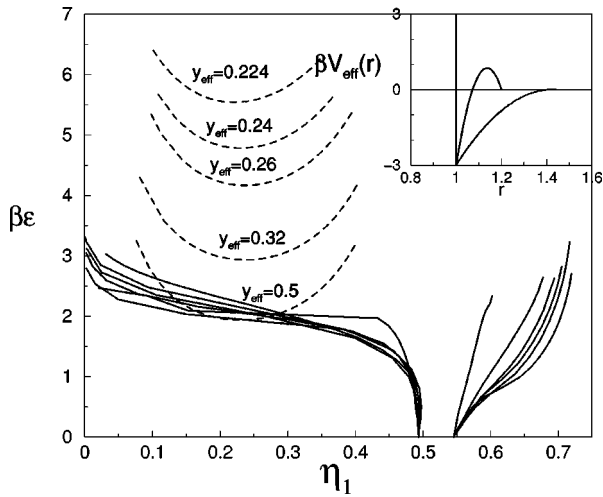


FIG. 3. Same as Fig. 2 but with the  $y$  axis rescaled with respect to the well-depth at contact of Eq. (3). Inset: two typical effective potentials from Eq. (3) for  $y_{\text{eff}}=0.2$ , and  $y_{\text{eff}}=0.44$ ; both result in very similar liquidus lines.

The effective interaction for  $r > \sigma_1$  is treated as a perturbation of the one-component HS reference system, and standard first order perturbation theory [13,7] is applied to calculate the free energy and determine the fluid-solid phase coexistence. The predictions of this effective one-component perturbation theory are compared in Fig. 1 to MC data for the additive ( $\Delta=0$ ) case (which in turn compares well with full two-component MC simulations [3]); the agreement is seen to be good, thus lending confidence to the extension of the theory to the non-additive case, for which no MC data are available. Interestingly this success is not mirrored for the fluid-fluid transition: the one-component perturbation theory predicts a critical point at much higher values of  $\eta_1$  than was found in the simulations, demonstrating that care must be taken when applying ideas culled from the field of simple fluids to the effective potentials arising from complex fluids. On the other hand, the two-component perturbation theory embodied in Eq. (2) turns out to be much more accurate and has been used throughout to determine the demixing of nonadditive HS's into two fluid phases.

Results for  $0.02 \leq \Delta \leq 0.25$  are shown in Fig. 2. Both the fluid-fluid spinodal and the liquidus line of the freezing transition are seen to shift to lower  $\eta_2^r$  as  $\Delta$  increases, so that the fluid-fluid coexistence curve remains metastable up to  $\Delta \approx 0.2$ , at which stage the critical point becomes stable. The two-component perturbation theory cannot be trusted for significantly larger values of  $\Delta$ , because of its first order nature. On the other hand, nonadditivity is expected to remain rather small for sterically or electrostatically stabilized colloids, so that the present calculations imply that it may be unlikely to observe fluid-fluid phase coexistence in asymmetric colloidal mixtures.

However, the calculations lead to another unexpected prediction. If the phase diagrams in Fig. 2 are rescaled, by choosing the reduced well depth at contact  $\beta\epsilon = \beta V_{\text{eff}}(\sigma_1)$ , rather than  $\eta_2^r$ , as the thermodynamic variable along the  $y$  axis, the fluid-solid liquidus curves for all values of  $\Delta$  fall practically on top of each other. This ‘‘quasiuniversal’’ behavior is shown in Fig. 3: the fluid-solid liquidus line scales

with well-depth at contact, and is largely independent of the shape or range (characterized by  $y_{\text{eff}}$ ) of the effective pair potential between the larger spheres. This behavior contrasts sharply with the fluid-fluid coexistence curves, which are very sensitive to the range and shape of the effective potential. Note that the fluid-fluid demixing transition becomes stable for  $y_{\text{eff}} \geq 0.4$ , which is comparable to the results of direct simulations of the Asakura-Oosawa model for colloid-polymer mixtures [21].

The possibility of phase-separation in binary hard-sphere mixtures inspired a series of experiments on hard-sphere-like colloids [22]. The hard-sphere repulsion is achieved by steric stabilization, with a repulsive outer brush of co-polymer, or else the colloids are stabilized by repulsive electrostatic interactions, with enough salt added to obtain a very short screening length. Interactions between charge-stabilized binary colloids are well described by the DLVO potential [23,24]. For sterically stabilized colloids, the interaction between two spheres can be estimated by combining the interaction between two flat brush-covered surfaces, which is well described by the Alexander-de Gennes theory [23], with the Derjaguin approximation, which results in:  $V_{22}(r - \sigma_{22}) = y V_{11}(r - \sigma_{11})$ , and  $V_{12}(r - \sigma_{12}) = [2y/(1+y)] V_{11}(r - \sigma_{11})$ , where  $V_{\alpha\beta}(r - \sigma_{\alpha\beta})$  is the interaction potential between the brushes of species  $\alpha$  and  $\beta$ . The repulsive interaction is smaller between smaller particles because the brush surface overlap area is smaller as a function of distance  $r$ . The three effective hard-sphere diameters can be estimated by the diameter at which the interaction is a few times  $k_B T$ , and then used to determine the nonadditivity. For both sterically and electrostatically stabilized binary colloidal mixtures this results in:

$$\Delta = \frac{l}{\sigma_{12}^{(0)}} \ln \left( \frac{2\sqrt{y}}{1+y} \right) + O \left( \frac{l}{\sigma_{12}^{(0)}} \right)^2, \quad (5)$$

where  $l$  is the decay length of the brush [23], or the Debye screening length of the DLVO interaction. To first order, the nonadditivity depends neither on the prefactors in the inter-

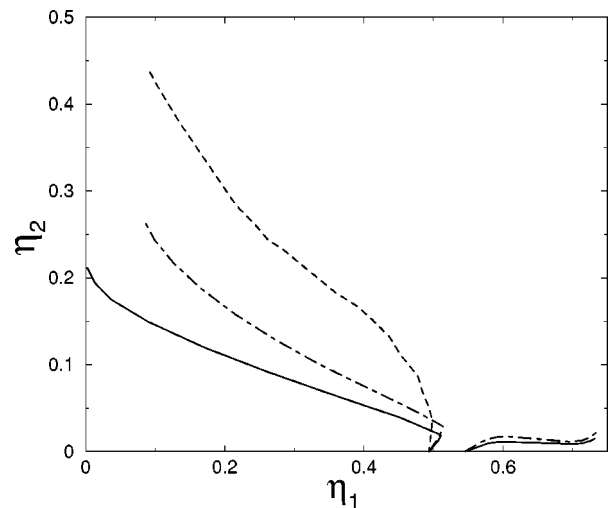


FIG. 4. Fluid-solid binodals for  $y=0.1075$ ,  $\Delta=0$  (solid lines) and  $\Delta=-0.01$  (dash-dotted lines) plotted for absolute  $\eta_2$  (not  $\eta_2^r$ ) to compare to the liquidus line from Imhof and Dhont [22] for the same  $y$  (dashed line).

actions, nor on exactly how many times  $k_B T$  is chosen as the hard-sphere criterion; only the “softness” of the potential enters. Since the logarithmic factor in Eq. (5) is negative, sterically or electrostatically stabilized colloidal mixtures will manifest *negative* nonadditivity. For example, the popular model colloids made of polymethylmethacrylate (PMMA) cores are stabilized by a poly-12-hydroxyterephthalic acid (PHS) brush, typically 10–12 nm wide, with  $l \approx 3-4$  nm [23], a number confirmed by direct measurements with a surface-force apparatus [25]. Thus a mixture with the larger species at 400 nm and the smaller at 40 nm ( $y=0.1$ ) will have a negative nonadditivity of about  $\Delta = -0.01$ ; i.e., the cross-diameter  $\sigma_{12}$  is 1% less than the additive cross-diameter  $\sigma_{12}^{(0)}$ .

Figure 4 demonstrates that even a small amount of nega-

tive nonadditivity has a relatively large effect on the phase diagram, raising the liquidus line to higher effective values of  $\eta_2$ . No fluid-fluid demixing is expected for  $\Delta < 0$ .

In conclusion then, we have demonstrated that nonadditivity has an important effect on the phase-diagram of asymmetric binary hard-sphere mixtures, affecting both the fluid-fluid and the fluid-solid lines. The fluid-solid liquidus lines show a near-universal behavior, and experimental hard-sphere-like colloidal dispersions are expected never to separate into two fluid phases.

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