

## Demixing can occur in binary hard-sphere mixtures with negative nonadditivity

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A binary fluid mixture of nonadditive hard spheres characterized by a size ratio  $\gamma = \sigma_2/\sigma_1 < 1$  and a nonadditivity parameter  $\Delta = 2\sigma_{12}/(\sigma_1 + \sigma_2) - 1$  is considered in infinitely many dimensions. From the equation of state in the second virial approximation (which is exact in the limit  $d \rightarrow \infty$ ) a demixing transition with a critical consolute point at a packing fraction scaling as  $\eta \sim d2^{-d}$  is found, even for slightly negative nonadditivity, if  $\Delta > -\frac{1}{8}(\ln \gamma)^2$ . Arguments concerning the stability of the demixing with respect to freezing are provided.

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The crystallization of a hard-sphere fluid, observed in computer simulations [1] and at that time controversial, is a clear and well-established example of an entropy-driven phase transition. Yet, up until now it has defied a rigorous statistical mechanical proof. Other phase transitions governed by entropy, in particular the phase separation in binary hard-core mixtures, have only been proven [2] for a simple two-dimensional lattice model of two types of particles. In the absence of an exactly solvable model in three dimensions, which could provide insight into the detailed mechanisms leading to phase separation in athermal systems such as hard-core mixtures, different strategies have been adopted to address this problem; for instance, to consider a geometry that leads to a nontrivial volume-driven phase separation, as in the case of a mixture of parallel hard cubes [3], or to explore the situation in higher spatial dimensions [4].

Due to the interest (both theoretical and in practical applications) of phase separation, the demixing problem in *additive* hard-sphere mixtures has received a lot of attention in the literature. An analysis of the solution of the Percus-Yevick equation for binary additive hard-sphere mixtures [5] led to the conclusion that no phase separation into two fluid phases existed in these systems. The same conclusion is reached if one considers the most popular equation of state proposed for such mixtures, namely the Boublík-Mansoori-Carnahan-Starling-Leland (BMCSL) [6] equation of state. For a long time the belief was that this was a true physical feature. Nevertheless, this belief started to be seriously questioned after Biben and Hansen [7] obtained fluid-fluid segregation in additive hard-sphere mixtures out of the solution of the Ornstein-Zernike equation with the Rogers-Young closure and subsequent work has concentrated on attempting to clarify the issue. Coussaert and Baus [8] have proposed an equation of state with improved virial behavior for a binary additive hard-sphere mixture that predicts a fluid-fluid transition at very high pressures (metastable with respect to a fluid-solid one). On the other hand, Regnaut *et al.* [9] have examined the connection between empirical expressions for

the contact values of the pair distribution functions and the existence of fluid-fluid separation in mixtures of additive hard spheres. Further, in the case of highly asymmetric binary additive hard-sphere mixtures, the depletion effect has been invoked as the physical mechanism behind demixing (see for instance Ref. [10] and the bibliography therein). Finally, demixing in mixtures of additive hard spheres has been examined recently [11] using the low density expansion of the pressure by adding successively one more exact virial coefficient (up to the sixth virial coefficient). In this latter work it was found that already within the second virial coefficient approximation the fluid separates into two phases of different composition with a lower consolute critical point.

In contrast to the above results, which have the drawback of having been derived under various approximations and are therefore open to question and controversy, nonadditive hard-core systems with *positive* nonadditivity are certainly known to exhibit fluid-fluid demixing, although again this has not been rigorously proved in general. The celebrated Widom-Rowlinson model [12] represents a prototype system that allows the detailed study of such a phase transition, an aspect that continues to be of interest in the recent literature [13]. Provided fluid-fluid segregation really occurs in additive hard-sphere mixtures, where size asymmetry would be the source of the transition, it is not unreasonable to expect that, given a certain degree of (high) size asymmetry, demixing may also be present in the case of hard-sphere mixtures with small *negative* nonadditivity. This feature, however, seems to have hardly received any attention [14]. The purpose of this paper is to address this problem and provide evidence in favor of the statement posed in the title of the paper. To do so, we will not work in three-dimensional space, but rather consider the limit of infinitely many dimensions in which our result will be exact.

Although there had been a few earlier papers [15,16] dealing with hard spheres in dimensions greater than three, it was after the pioneer work of Frisch *et al.* [17], in which they showed that the classical hard-sphere fluid in infinitely many dimensions was amenable to a full analytical solution, that studies of high-dimensional hard-sphere systems became common over the years [4,18–23]. The fact that features such as the freezing transition are present in all dimensionalities (except for  $d=1$ ) and the parallel between high spatial dimensions and limiting high density situations that seems to exist in fluids (with the added bonus of greater mathematical

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simplicity as one increases the number of dimensions) suggest that one can gain insight into the thermodynamic behavior of, say, three-dimensional systems by looking at a similar problem in higher dimensions. As a matter of fact, the very elegant work of Carmesin *et al.* [21] has exploited this approach to illustrate phase separation in a hard-sphere mixture with positive nonadditivity in infinite spatial dimensionality. We now consider the more general case also for  $d \rightarrow \infty$  in which the nonadditivity may take negative values.

Let us consider a binary mixture of nonadditive hard spheres of diameters  $\sigma_1$  and  $\sigma_2$  in  $d$  dimensions. The hard core of the interaction between a sphere of species 1 and a sphere of species 2 is  $\sigma_{12} \equiv \frac{1}{2}(\sigma_1 + \sigma_2)(1 + \Delta)$ , where the parameter  $\Delta$  characterizes the degree of nonadditivity of the interactions. Further assume (something that will become exact in the limit  $d \rightarrow \infty$  [21]) that the equation of state of the mixture is described by the second virial coefficient only, namely

$$p = \rho k_B T [1 + B_2(x_1)\rho], \quad (1)$$

where  $p$  is the pressure,  $\rho$  is the number density,  $k_B$  is Boltzmann's constant,  $T$  is the temperature,

$$B_2(x_1) = v_d 2^{d-1} (x_1^2 \sigma_1^d + x_2^2 \sigma_2^d + 2x_1 x_2 \sigma_{12}^d) \quad (2)$$

is the second virial coefficient,  $x_1$  and  $x_2 = 1 - x_1$  are the mole fractions, and  $v_d = (\pi/4)^{d/2} / \Gamma(1 + d/2)$  is the volume of a  $d$ -dimensional sphere of unit diameter. The Gibbs free energy per particle is (in units of  $k_B T$ )

$$g = x_1 \ln(x_1 \rho \Lambda_1^d) + x_2 \ln(x_2 \rho \Lambda_2^d) + 2B_2(x_1)\rho, \quad (3)$$

where  $\Lambda_i$  ( $i=1,2$ ) are the thermal de Broglie wavelengths. Given a size ratio  $\gamma \equiv \sigma_2/\sigma_1 < 1$ , a value of  $\Delta$ , and a dimensionality  $d$ , the consolute critical point  $(x_{1c}, p_c)$  is the solution to  $(\partial^2 g / \partial x_1^2)_p = (\partial^3 g / \partial x_1^3)_p = 0$ , provided of course it exists. Then, from Eq. (1) one can get the critical density  $\rho_c$ .

We now introduce the scaled quantities

$$\tilde{p} \equiv 2^{d-1} v_d d^{-2} p \sigma_1^d / k_B T, \quad y \equiv d^{-1} B_2 \rho. \quad (4)$$

Consequently, Eqs. (1) and (3) can be rewritten as

$$\tilde{p} = y(y + d^{-1}) / \tilde{B}_2, \quad (5)$$

$$g = \sum_{i=1}^2 x_i \ln(x_i \lambda_i) + \ln(A_d y / \tilde{B}_2) + 2dy, \quad (6)$$

where  $\tilde{B}_2 \equiv B_2 / 2^{d-1} v_d \sigma_1^d$ ,  $\lambda_i \equiv (\Lambda_i / \sigma_1)^d$ , and  $A_d \equiv d / 2^{d-1} v_d$ . Next we take the limit  $d \rightarrow \infty$  and assume that the volume ratio  $\tilde{\gamma} \equiv \gamma^d$  is kept fixed and that there is a (slight) nonadditivity  $\Delta = d^{-2} \tilde{\Delta}$  such that the scaled nonadditivity parameter  $\tilde{\Delta}$  is also kept fixed in this limit. Thus, the second virial coefficient can be approximated by  $\tilde{B}_2 = \tilde{B}_2^{(0)} + \tilde{B}_2^{(1)} d^{-1} + O(d^{-2})$ , where  $\tilde{B}_2^{(0)} = (x_1 + x_2 \tilde{\gamma}^{1/2})^2$  and  $\tilde{B}_2^{(1)} = x_1 x_2 \tilde{\gamma}^{1/2} K$ , with  $K \equiv \frac{1}{4} (\ln \tilde{\gamma})^2 + 2\tilde{\Delta}$ . Let us remark that in order to find a consolute critical point, it is essential to keep the term of order  $d^{-1}$  if  $\tilde{\Delta} \leq 0$ . The equation of state (5) can then be inverted to yield  $y = y^{(0)} + y^{(1)} d^{-1} + O(d^{-2})$ , with  $y^{(0)} = \sqrt{\tilde{p} \tilde{B}_2^{(0)}}$  and  $y^{(1)}$

$= -\frac{1}{2} (1 - y^{(0)}) \tilde{B}_2^{(1)} / \tilde{B}_2^{(0)}$ . In turn, the Gibbs free energy (6) becomes  $g = g^{(0)} d + g^{(1)} + O(d^{-1})$ , with  $g^{(0)} = 2y^{(0)}$ ,  $g^{(1)} = \sum_i x_i \ln(x_i \lambda_i) + \ln(A_d y^{(0)} / \tilde{B}_2^{(0)}) + 2y^{(1)}$ , while the chemical potentials  $\mu_1 = g + x_2 (\partial g / \partial x_1)_p$  and  $\mu_2 = g - x_1 (\partial g / \partial x_1)_p$  are given by  $\mu_i = \mu_i^{(0)} d + \mu_i^{(1)} + O(d^{-1})$ , where  $\mu_1^{(0)} = 2\tilde{p}^{1/2}$ ,  $\mu_1^{(1)} = \ln(A_d x_1 \lambda_1 \sqrt{\tilde{p} / \tilde{B}_2^{(0)}}) - 1 / \sqrt{\tilde{B}_2^{(0)}} + (x_2 / x_1) (\tilde{\gamma} \tilde{p})^{1/2} \tilde{B}_2^{(1)} / \tilde{B}_2^{(0)}$ , and  $\mu_2$  is obtained from  $\mu_1$  by the changes  $x_1 \leftrightarrow x_2$ ,  $\lambda_1 \rightarrow \lambda_2 / \tilde{\gamma}$ ,  $\tilde{\gamma} \rightarrow 1 / \tilde{\gamma}$ ,  $\tilde{p} \rightarrow \tilde{p} \tilde{\gamma}$ ,  $\tilde{B}_2 \rightarrow \tilde{B}_2 / \tilde{\gamma}$ .

The coordinates of the critical point are readily found to be

$$x_{1c} = \frac{\tilde{\gamma}^{3/4}}{1 + \tilde{\gamma}^{3/4}}, \quad \tilde{p}_c = \frac{(1 + \tilde{\gamma}^{1/4})^4}{4\tilde{\gamma}K^2}. \quad (7)$$

Note that  $x_{1c}$  is independent of  $\tilde{\Delta}$ . The coexistence curve, which has to be obtained numerically, follows from the conditions  $\mu_i^{(1)}(x_A, \tilde{p}) = \mu_i^{(1)}(x_B, \tilde{p})$  ( $i=1,2$ ) where  $x_1 = x_A$  and  $x_1 = x_B$  are the mole fractions of the coexisting phases. Once the critical consolute point has been identified in the pressure vs concentration plane, we can obtain the critical density. The dominant behavior of  $\tilde{B}_2$  at the critical point is  $\tilde{B}_2^{(0)}(x_{1c}) = \tilde{\gamma} / (1 - \tilde{\gamma}^{1/4} + \tilde{\gamma}^{1/2})^2$ , while  $y_c^{(0)} = (1 + \tilde{\gamma}^{1/4})^2 / 2(1 - \tilde{\gamma}^{1/4} + \tilde{\gamma}^{1/2})K$ . Hence, the critical density readily follows after substitution in the scaling relation given in Eq. (4). For our purposes it is also convenient to consider the packing fraction defined as  $\eta = v_d \rho \sigma_1^d (x_1 + x_2 \tilde{\gamma})$  and its scaled version  $\tilde{\eta} \equiv d^{-1} 2^d \eta$  [24]. At the critical point, this latter takes the nice expression

$$\tilde{\eta}_c = \frac{(\tilde{\gamma}^{1/8} + \tilde{\gamma}^{-1/8})^2}{K}. \quad (8)$$

Figure 1 shows  $x_{1c}$ ,  $\tilde{p}_c$ , and  $\tilde{\eta}_c$  as functions of  $\tilde{\gamma}$  and in the two latter cases for  $\tilde{\Delta} = -0.1$  (negative nonadditivity),  $\tilde{\Delta} = 0$  (additive mixture), and  $\tilde{\Delta} = 0.1$  (positive nonadditivity). The previous results clearly indicate that a demixing transition is possible not only for additive or positively nonadditive mixtures but even for negative nonadditivities. The only requirement is  $K > 0$ , i.e.,  $\tilde{\Delta} > -\frac{1}{8} (\ln \tilde{\gamma})^2$  or, equivalently,  $\Delta > -\frac{1}{8} (\ln \gamma)^2$ . The curve representing the threshold situation  $\tilde{\Delta} = -\frac{1}{8} (\ln \tilde{\gamma})^2$  is plotted in Fig. 2, where we have also displayed  $\tilde{\Delta}$ , as obtained from Eq. (8), as a function of  $\tilde{\gamma}$  for three different values of the critical packing fraction:  $\tilde{\eta}_c = 1$ ,  $\tilde{\eta}_c = 1.5$ , and  $\tilde{\eta}_c = 2$ . These choices for  $\tilde{\eta}_c$  are meant to be illustrative and have been taken after the following considerations.

One may reasonably wonder whether the demixing we have obtained for negative nonadditivity will occur for packing fractions within the stable fluid regime and where the equation of state is well represented by the second virial approximation. A natural way to look into this issue would be to compare with the close-packing value  $\tilde{\eta}_{cp}$ . Unfortunately,  $\tilde{\eta}_{cp}$  is not known in the case of mixtures. Nevertheless, some insight about it can be gained by examining the parallel case of a one-component fluid in infinitely many dimensions. In such a case, there exist known upper bounds for  $\tilde{\eta}_{cp}$  [22]. Further, another (lower) estimate can be given

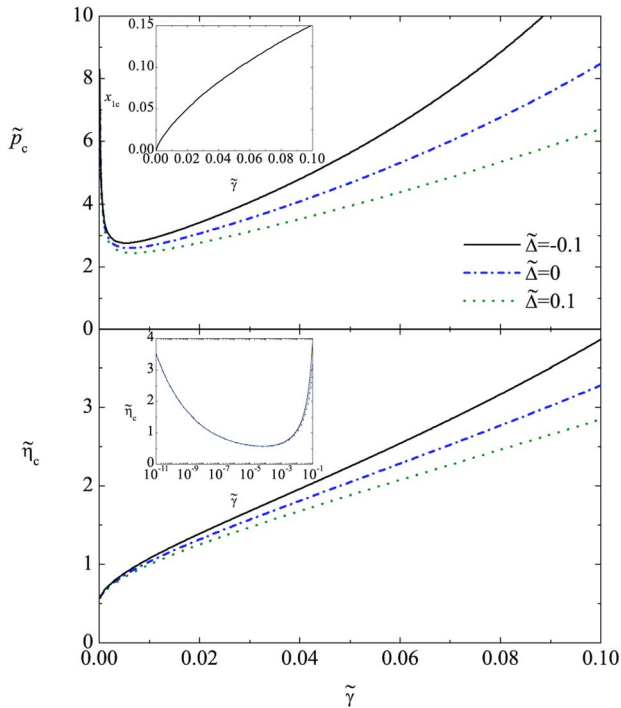


FIG. 1. (Color online) Plot of  $x_{1c}$  (inset, upper panel),  $\tilde{p}_c$  (upper panel), and  $\tilde{\eta}_c$  (lower panel) as functions of  $\tilde{\gamma}$ . The (scaled) critical pressure and packing fraction are displayed for three different values of the (scaled) nonadditivity parameter:  $\tilde{\Delta} = -0.1$  (solid lines),  $\tilde{\Delta} = 0$  (dash-dotted lines), and  $\tilde{\Delta} = 0.1$  (dotted lines). Note the non-monotonic dependence of  $\tilde{p}_c$  and  $\tilde{\eta}_c$  on  $\tilde{\gamma}$  (for the latter case, see inset in the lower panel).

by taking the contributions of the second and third virial coefficients to be of a similar order of magnitude. While this is of course not conclusive, all these estimates for  $\tilde{\eta}_{cp}$  may be shown to diverge as  $d \rightarrow \infty$ , suggesting that the fluid-fluid phase separation may indeed take place. Provided the (scaled) packing fraction at freezing  $\tilde{\eta}_f$  is different from zero, the demixing transition may be stable and not preempted by a fluid-solid transition. Again  $\tilde{\eta}_f$  is unknown but we may once more refer to the one-component case. For this system, Colot and Baus [19] have conjectured that  $(\eta_f/\eta_{cp})^{1/d}$  becomes independent of  $d$  for high  $d$ . Further, from the analysis of the results in  $d=3,4,5$  [16,20], and  $d=7$  [23] one finds that  $\tilde{\eta}_f \approx 1.3$ . Since at freezing or melting the Helmholtz free energies of the fluid and the solid should be of the same order of magnitude, by considering the former given by the second virial approximation and the latter as obtained from free volume theory with the estimate  $(\eta_f/\eta_{cp})^{1/d} \approx 0.8$ , we obtain the rough estimate  $\tilde{\eta}_f \approx 2.3$ . Irrespective of the numbers, the point is that these results seem to confirm that  $\tilde{\eta}_f$  is different from zero and finite. Therefore, even if the range of values of negative  $\tilde{\Delta}$  in which stable demixing occurs is limited and restricted to highly asymmetric mixtures, as indicated in Fig. 2, the important issue is that it is certainly there. So the question of whether demixing can occur in binary mixtures of hard spheres with negative nonadditivity can be given a positive answer.

While the high dimensionality limit has allowed us to address the problem in a mathematically simple and clear-cut

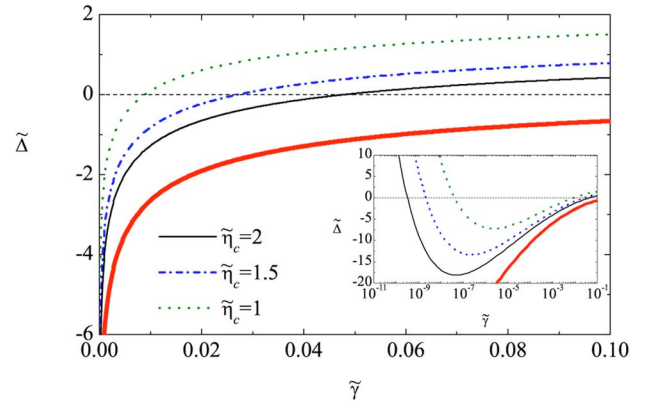


FIG. 2. (Color online) Plot of  $\tilde{\Delta}$  vs  $\tilde{\gamma}$  for different values of the critical packing fraction:  $\tilde{\eta}_c = 2$  (thin solid line),  $\tilde{\eta}_c = 1.5$  (dash-dotted line), and  $\tilde{\eta}_c = 1$  (dotted line). The lowest thick solid line corresponds to the threshold condition  $\tilde{\Delta} = -\frac{1}{8}(\ln \tilde{\gamma})^2$ . A demixing transition with the scaling properties of the text is only possible for mixtures with nonadditivities and size ratios represented by points above the thick curve. On the other hand, a transition with a (scaled) critical packing fraction smaller than a given value of  $\tilde{\eta}_c$  is only possible for points above the corresponding curve. The threshold curve goes to minus infinity as  $\tilde{\gamma} \rightarrow 0$  but the other curves have a minimum that depends on the choice of  $\tilde{\eta}_c$  (see inset). This implies that for *extremely* asymmetric mixtures ( $\tilde{\gamma} \rightarrow 0$ ) demixing at a given finite value of  $\tilde{\eta}_c$  becomes possible only if the nonadditivity is positive and sufficiently large.

way, the possibility of demixing with negative nonadditivity is not an artifact of that limit. Demixing is known to occur for positive nonadditive binary mixtures of hard spheres in three dimensions and compelling evidence in the additive case exists, at least in the metastable fluid region. Even though in a three-dimensional mixture the equation of state is certainly more complicated than Eq. (1) and the demixing transition reported here for negative nonadditivity is possibly metastable with respect to the freezing transition, the main effects at work (namely the competition between depletion due to size asymmetry and heterocoordination due to negative nonadditivity) are also present. In fact, it is interesting to point out that Roth *et al.* [14], using the approximation of an effective one-component fluid with pair interactions to describe a binary mixture of nonadditive hard spheres and employing an empirical rule based on the effective second virial coefficient, have also suggested that demixing is possible for small negative nonadditivity and high size asymmetry. Our exact results lend support to this suggestion based on approximate calculations and confirm the fact that the limit  $d \rightarrow \infty$  allows one to get a caricature or toy model to highlight features already present in real systems.

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- [24] Note that, while the scaling implied in  $\tilde{\gamma}$  is the same as that of Ref. [21], the one of the packing fraction is different ( $\eta_c \sim 2^{-d}d$  in our case in contrast to  $\eta_c \sim 2^{-d}$  in theirs) due to the different scaling of the nonadditivity parameter  $\Delta$  ( $\Delta \sim d^{-2}$  here and  $\Delta \sim d^{-1}$  in Ref. [21]). As mentioned, our scaling for  $\Delta$  is necessary to deal with negative nonadditivity. But of course, for positive nonadditivity, our results are consistent with those of Ref. [21].