Demixing can occur in binary hard-sphere mixtures with negative non-additivity

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

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The crystallization of a hard-sphere fluid, first observed in computer simulation \cite{1} and at that time controversial, is a clear and presently 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, has only been proven \cite{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 non trivial volume-driven phase separation, as in the case of a mixture of parallel hard cubes \cite{3}. Or else, to explore the situation in higher spatial dimensions \cite{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 \cite{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) \cite{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 \cite{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. Cousseau and Baus \cite{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. \cite{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. \cite{10} and the bibliography therein). Finally, demixing in mixtures of additive hard spheres has been examined recently \cite{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, non-additive hard-core systems with positive non-additivity are certainly known to exhibit fluid-fluid demixing, although again this has not been rigorously proved in general. The celebrated Widom–Rowlinson model \cite{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 \cite{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 non-additivity. This feature, however, seems to have hardly received any attention \cite{14}. The purpose of this Communication 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 \cite{15,16} dealing with hard spheres in dimensions greater than
Consequently, Eqs. (1) and (3) can be rewritten as

\[ p = \rho k_B T [1 + B_2(x_1) \rho], \tag{1} \]

where \( p \) is the pressure, \( \rho \) is the number density, \( k_B \) is Boltzmann’s constant, \( T \) is the temperature, and

\[ B_2(x_1) = v_2 d^{-1} (x_1^2 \sigma_1^d + x_2^2 \sigma_2^d + 2 x_1 x_2 \sigma_1^d \sigma_2^d) \tag{2} \]

is the second virial coefficient, \( x_1 \) and \( x_2 = 1 - x_1 \) being the mole fractions and \( v_2 = (\pi/4)^{d/2}/(1 + d/2) \) being the volume of a d-dimensional sphere of unit diameter. The Gibbs free energy per particle is (in units of \( k_B T \))

\[ g = x_1 \ln (x_1 \rho \Lambda_1^d) + x_2 \ln (x_2 \rho \Lambda_2^d) + 2 B_2(x_1) \rho, \tag{3} \]

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 \((x_{1c}, \rho_c)\) is the solution to \((\partial^2 g/\partial x_1^2)_p = (\partial^2 g/\partial x_2^2)_p = 0\), provided of course it exists. Then, from Eq. (1) one can get the critical density \( \rho_c \).

We now introduce the scaled quantities

\[ \tilde{p} \equiv d^{-1} v_d d^{-1} \rho d^{-1} \Lambda_1^d / k_B T, \quad y \equiv d^{-1} B_2 \rho. \tag{4} \]

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

\[ \tilde{p} = y (y + d^{-1}) / B_2, \tag{5} \]

\[ g = \sum_{i=1}^{2} x_i \ln (x_i \lambda_i) + \ln (A_d y / B_2) + 2 dy, \tag{6} \]

where \( \tilde{B}_2 \equiv B_2 / 2 d^{-1} v_d d^{-1} \), \( \lambda_i \equiv (\Lambda_i / \sigma_i)^d \), and \( A_d \equiv d / 2 d^{-1} v_d \). Next we take the limit \( d \to \infty \) and assume that the volume ratio \( \tilde{\gamma} \equiv \gamma^d \) is kept fixed and that there is a (slight) non-additivity \( \Delta = d^{-2} \tilde{\Delta} \) such that the scaled non-additivity parameter \( \tilde{\Delta} \) is also kept fixed in this limit. Thus, the second virial coefficient can be approximated by

\[ \tilde{B}_2 \approx \tilde{B}_2^{(0)} + \tilde{B}_2^{(1)} d^{-1} + O(d^{-2}), \]

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 \( y^{(1)} = -1/2 \left( 1 - y^{(0)} \tilde{B}_2^{(1)} / \tilde{B}_2^{(0)} \right) \).

In turn, the Gibbs free energy (6) becomes \( g = g^{(0)} d + g^{(1)} + O(d^{-1}) \), with \( g^{(0)} = 2 \tilde{y}^{(0)} \), \( g^{(1)} = \sum_i x_i \ln (x_i \lambda_i) + \ln \left( A_d \tilde{y}^{(0)} / \tilde{B}_2^{(0)} \right) + 2 \tilde{y}^{(1)} \), 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

\[ \rho^{(1)} = 2 \tilde{p}^{1/2}, \quad \mu^{(1)} = \ln \left( A_d \tilde{y}^{(0)} / \tilde{p} \tilde{B}_2^{(0)} \right) - 1 / \tilde{B}_2^{(0)} + \left( x_2 / x_1 \right) (\tilde{p}^{1/2} / \tilde{B}_2^{(0)}) \tilde{B}_2^{(1)} / \tilde{B}_2^{(0)} \]

and \( \mu_2 \) is obtained from \( \mu_1 \) by the changes \( x_1 \leftrightarrow x_2 \), \( \lambda_1 \rightarrow \lambda_2 / \tilde{\gamma} \), \( \tilde{\gamma} \rightarrow 1 / \tilde{\gamma} \), \( \tilde{p} \rightarrow \tilde{p} \gamma \), \( \tilde{B}_2 \rightarrow \tilde{B}_2 / \tilde{\gamma} \).

The coordinates of the critical point are readily found to be

\[ x_{1c} = \gamma^{3/4} / (1 + \gamma^{3/4}), \quad \tilde{\rho}_c = \left( 1 + \gamma^{1/4} \right)^4 / 4\gamma K^2. \tag{7} \]

Note that \( x_{1c} \) is independent of \( \tilde{\Delta} \). The coexistence curve, which has to be obtained numerically, follows from the conditions \( \rho^{(1)} / \tilde{p} = \mu^{(1)} / \tilde{B}_2 \) \((i = 1, 2) \), where \( x_1 = x_A \) and \( x_2 = x_B \) are the mole fractions of the coexisting phases. Once the consolute critical point has been identified in the pressure/concentration plane, we can obtain the critical density. The dominant behavior of \( \tilde{B}_2 \) at the critical point is \( \tilde{B}_2^{(0)}(x_{1c}) = \gamma / (1 - \gamma^{1/4} + \gamma^{1/2})^2 \), while \( y^{(0)} = (1 + \gamma^{1/4})^2 / (2 (1 - \gamma^{1/4} + \gamma^{1/2}) K) \). Hence, the critical density readily follows after substitution in the scaling relation given in Eq. (1). For our purposes it is also convenient to consider the packing fraction defined as \( \eta = v_d \rho d^{-1} \Lambda_1^d \) and its scaled version \( \tilde{\eta} \equiv d^{-2} \eta \) [23]. At the critical point, this latter takes the nice expression

\[ \tilde{\eta}_c = (\gamma^{1/8} + \gamma^{-1/8})^2 / K. \tag{8} \]

Figure 1 shows \( x_{1c}, \tilde{\rho}_c, \) and \( \tilde{\eta}_c \) as functions of \( \tilde{\gamma} \) and in the two latter cases for \( \tilde{\Delta} = -0.1 \) (negative non-additivity), \( \tilde{\Delta} = 0 \) (additive mixture) and \( \tilde{\Delta} = 0.1 \) (positive non-additivity). The previous results clearly indicate that a demixing transition is possible not only for additive or positively non-additive mixtures but even
for negative non-additivities. The only requirement is $K > 0$, i.e. $\Delta > -\frac{1}{8} (\ln \gamma)^2$ or, equivalently, $\Delta > -\frac{1}{8} (\ln \gamma)^2$. The curve representing the threshold situation $\Delta = -\frac{1}{8} (\ln \gamma)^2$ is plotted in Fig. 2, where we have also displayed $\Delta$, as obtained from Eq. [2], as a function of $\eta_c$ 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 non-additivity 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 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 $d \to \infty$, 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 recur to the one-component case. For this system, Colot and Baus [19] have conjectured that $(\tilde{\eta}_f/\tilde{\eta}_{cp})^{1/d}$ becomes independent of $d$ for high $d$. Further, from the analysis of the results in $d = 3, 4, 5, [18, 20]$, and $d = 7$ [22] 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 $(\tilde{\eta}_f/\tilde{\eta}_{cp})^{1/d} \approx 0.8$, 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 $\Delta$ 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 non-additivity 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 way, the possibility of demixing with negative non-additivity can be given a positive answer.
non-additivity is not an artifact of that limit. Demixing is known to occur for positive non-additive 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 non-additivity is possibly metastable with respect to the freezing transition, the main effects at work (namely the competition between depletion due to size asymmetry and hetero-coordination due to negative non-additivity) 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 non-additive hard spheres and employing an empirical rule based on the effective second virial coefficient, have also suggested that demixing is possible for small negative non-additivity and high size asymmetry. Our exact results lend support to this suggestion based on approximate calculations and confirm the fact that the limit $d \to \infty$ allows one to get a caricature or toy model to highlight features already present in real systems.

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Note that, while the scaling implied in $\bar{\gamma}$ is the same as that of Ref. [21], the one of the packing fraction is different ($\eta_c \sim 2^{-d}$ in our case in contrast to $\eta_c \sim 2^{-d}$ in theirs) due to the different scaling of the non-additivity parameter $\Delta$ ($\Delta \sim d^{-2}$ here and $\Delta \sim d^{-3}$ in Ref. [21]). As mentioned, our scaling for $\Delta$ is necessary to deal with negative non-additivity. But of course, for positive non-additivity, our results are consistent with those of Ref. [21].