On the effective one-component description of highly asymmetric hard-sphere binary fluid mixtures

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The phase diagram of a binary fluid mixture of highly asymmetric additive hard spheres is investigated. Demixing is analyzed from the exact low-density expansions of the thermodynamic properties of the mixture and compared with the fluid-fluid separation based on the effective one-component description. Differences in the results obtained from both approaches, which have been claimed to be equivalent, are pointed out and their possible origin is discussed. It is argued that to deal with these differences new theoretical approximations should be devised.

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It is well known that, due to the widely different time and length scales involved, it is a very difficult task to describe a soft matter complex fluid composed of mesoscopic (colloidal) particles and microscopic (small) particles, i.e. a colloidal suspension. Therefore people have struggled for years trying to devise strategies that may render a tractable description. On the theoretical side, a rather successful and often employed approach in the colloids literature is that of coarse graining. In this technique the idea is to integrate out the irrelevant degrees of freedom (the small particles) to end up with a one-component system of colloidal particles described by effective interactions [1]. One of the most celebrated effective interactions results from the depletion mechanism first described by Asakura and Oosawa [2]. Suppose that two colloidal hard spheres are immersed in an ideal fluid of small hard spheres. When the separation of the surfaces of two large spheres is less than the diameter of the small ones, the depletion of the latter from the gap between the colloids leads to an unbalanced osmotic pressure which, in turn, results in an effective attraction between the two large spheres. Although the Asakura-Oosawa depletion pair potential is concerned only with the limit of extreme dilution, the theory of the depletion mechanism has recently been reexamined by also including the interactions between the small spheres [3,4]. In several of the recent studies the depletion mechanism has been invoked as the possible driving force for demixing, i.e. a phase transition whereby a binary fluid mixture of hard spheres separates into two fluid phases of different composition.

The aim of this paper is to shed some more light on the usefulness or limitations of the depletion pair potential, i.e. the consideration of an effective one-component fluid of large spheres with effective pair interactions for describing the phase behavior of a binary fluid mixture of highly asymmetric additive hard spheres [5]. Such an issue has recently been addressed by simulations [6,7,8,9] but the analysis unfortunately provides no definitive answer due to limitations in the presently available simulation algorithms.

Recently [10] we have analyzed the demixing transition of a binary fluid mixture of \( N = N_1 + N_2 \) additive hard spheres of diameters \( \sigma_1 \) and \( \sigma_2 \) (\( \sigma_1 > \sigma_2 \)). For a fixed diameter ratio \( \gamma = \sigma_2/\sigma_1 \), the thermodynamic properties of the mixture were described in terms of the number density \( \rho = N/V \), with \( V \) the volume, the partial number fraction of the big spheres \( x = N_1/N \), and the total packing fraction \( \eta = \eta_1 + \eta_2 \), where \( \eta_1 = \pi \rho \sigma_1^3 x/6 \) and \( \eta_2 = \pi \rho \sigma_2^3 (1-x) \gamma^3/6 \) are the packing fractions of the large and the small spheres. Demixing was studied by starting from the exact low-density expansions of the thermodynamic properties, using as input analytical expressions [11,12] and numerical computations [13,14,15,16,17,18] for the virial coefficients so far reported in the literature (up to the sixth). For all the size asymmetries considered we found that, by successively incorporating in the density expansions a new exact virial coefficient, the critical consolute point moves to higher values of the pressure and of the total packing fraction as shown in Fig. 1. It is also seen in this figure that the rate of convergence is slow and so definitive conclusions on the location of the critical consolute point cannot yet be reached with the available data on virial coefficients.

We have also compared these findings with the fluid-fluid separation resulting from different empirical proposals for the equation of state [13,20,21], that attempt to reproduce the virial behavior and/or to comply with consistency conditions of the contact values of the radial distribution functions. We have realized that for historical reasons all these “rescaled” equations of state yield the exact second and third virial coefficients but inherit the singularity of the Percus-Yevick theory. We have shown that this apparently innocuous singularity arbitrarily introduces, as compared to the exact low-density expansion of the pressure, additional dependencies on \( x \) through the fourth, fifth, and so on virial coefficients. Such dependencies make the location of the critical consolute point to vary enormously from one equation of state to another, so that the predictions stemming from each of them are indeed unreliable.

The demixing transition of a binary mixture of additive
hard spheres may be analyzed using different thermodynamic planes. In order to compare to well documented results in the effective one-component fluid, we first consider the \((\eta_1 - \eta_2)\) plane. In Fig. 2 we present the binodals resulting from the exact low-density expansions up to the sixth virial coefficient for two size asymmetries, namely \(\gamma = 0.2\) and \(\gamma = 0.1\), and up to the fifth virial coefficient for \(\gamma = 0.05\). Note that the density region spanned by each binodal cannot go beyond the point where the total packing fraction occupied by the spheres reaches for the dense phase the highest possible value. Since these values are not known, we have drawn all the curves up to the limiting (unphysical) value \(\eta = 1\). A comparison between these binodals and parallel ones derived using the depletion mechanism [5] indicates the following. For \(\gamma = 0.2\), the low-density expansion predicts demixing, whereas there is no fluid-fluid separation in the effective one-component fluid. The qualitative behavior of the binodals for \(\gamma = 0.1\) and \(\gamma = 0.05\) is, on the other hand, rather similar in both approaches. However, there are two main differences: 1) the values of \(\eta_2\) for the mixture are much lower than the corresponding ones in the effective one-component fluid; 2) the critical consolute points already lie outside the range where the binodals are predicted in the effective one-component fluid.

Figure 3 is yet another presentation of the binodals, this time in the \((\eta_1 - p)\) plane, with \(p\) the pressure. These binodals follow from the low-density expansions by keeping the same number of exact virial coefficients as in Fig. 2. Since no values of the pressure for the coexisting phases have been reported in the effective one-component fluid in [5], a direct comparison between both approaches is not possible in this case. Nevertheless, the following comments are in order. It is known that a one-component fluid with pairwise interactions consisting of a repulsive part and a short-range attraction can only produce in the \((\eta_1 - p)\) plane a van der Waals-like fluid-fluid separation ending in an upper critical point, the concavity of the binodals pointing downwards. Moreover, it is well established that, by strongly reducing the range of the attractions with respect to that of the repulsions, the usual phase diagram with two stable transitions, namely fluid-fluid and fluid-solid, changes and the fluid-fluid transition becomes metastable with respect to the fluid-solid transition [22]. By a further reduction of the range of the attractions, a stable isostructural solid-
solid transition develops at high densities in the phase diagram \([23, 24]\). The phase behavior found in Ref. \([6]\) follows indeed this trend. Note that although the zero-body and one-body terms (the volume terms) in the effective one-component description play no role in determining the phase equilibria, they are however responsible for inverting the concavity of the binodals from downwards to upwards, yielding the same concavity as the one found in the true binary mixture. The importance of the volume terms in the determination of the complete phase diagram should therefore not be ignored \([1]\).

On the other hand, the resulting phase diagrams found in Ref. \([3]\) also indicate that, for the depletion pair potential used in this reference, the small repulsive barrier that follows the attractive potential close to the surface of the large sphere does not qualitatively modify the phase diagram that would result by only considering a purely short-range attractive potential. The predictions for the phase diagram in the effective one-component fluid \([3]\) for \(\gamma = 0.1\) (a metastable fluid-fluid transition) and for \(\gamma = 0.05\) (a metastable fluid-fluid transition and a stable solid-solid transition) are indeed at grips with the foregoing remarks.

It should be clear that due to the fact that only a few exact virial coefficients are available and that the radius of convergence of the virial series in the case of mixtures is not known, definite conclusions derived from the low-density expansions cannot be drawn. Nevertheless, the observed trends lead to the following considerations. As shown in Fig. 1, as one increases the number of terms in the low-density expansions, both the critical pressure and the critical total packing fraction grow. It is not clear whether this feature will change by including more exact virial coefficients (when available) in the density expansions, but all the evidence so far makes it unlikely. In any event, provided the trend obtained with the low-density expansions is a true feature, two possible scenarios arise. One may envisage the convergence of the critical constants to a thermodynamic state with either a physical or an unphysical critical total packing fraction. Indeed, the terms physical and unphysical depend on the resulting solid phase at high densities. For example, if the freezing transition corresponds to the partial freezing of the large spheres, i.e. a face-centered cubic lattice formed by the large spheres while the small spheres remain disordered \([14]\), the close packing fraction of the large spheres \(\eta_1^{\text{CP}} \approx 0.74\) defines the boundary between physical and unphysical. In the first scenario the demixing transition would be thermodynamically metastable with respect to the freezing transition as found in previous studies, while in the second no demixing would be present at all. At this stage we have no way to decide which of the two scenarios is correct since, by incorporating up to the fifth (sixth) virial coefficient in the exact low-density expansions for \(\gamma = 0.05\) (0.1), the critical packing fraction of the big spheres \(\eta_1^*\) is \(\eta_1^* = 0.595(0.557)\). Concerning this point, a related analysis carried out with the Boublík-Mansoori- Carnahan-Starling-Leland (BMCSL) equation of state \([25]\) (which predicts no demixing) is illustrative. This is shown in Fig. 1. The striking feature to be noted is the excellent agreement of the results obtained with the exact low-density expansion (c.f. Fig. 1) and those obtained with the truncated BMCSL equation of state. By including additional virial coefficients of the BMCSL equation of state it is seen that \(\eta_c \simeq \eta_1^*\) exceeds the close-packing fraction of the large spheres.

In order to understand the differences between the phase diagrams presented in Fig. 2 using the exact low-density expansions and the effective one-component description, the following considerations should be pointed out. For \(\gamma = 0.2\) both approaches would be equivalent whenever the critical packing fraction of the big spheres resulting from the low-density expansions converges to an unphysical value. As indicated above, for \(\gamma = 0.05\) and \(\gamma = 0.1\) the critical consolute points obtained with a reduced number of exact virial coefficients already lie outside the range where the effective one-component description locates the binodals. In these cases the effective one-component description would only provide a qualitative approximation of the true binary mixture if \(\eta_1^*\) converges to a physical value. Otherwise (convergence to an unphysical value) the predictions of both approaches would be completely at odds with each other in this basic issue. All these possibilities can indeed only be tested by including more exact virial coefficients in the density expansions. As a possible source for the differences found between the exact density expansions and the effective one-component description we suggest that it may be due to the fact that, in order to determine in the latter the phase diagram and to perform the direct simulations \([3]\), the Carnahan-Starling equation of state.
is used for describing both the big and the small hard spheres. Note that the Percus-Yevick-type singularity of the Carnahan-Starling equation of state may induce for each component different (through $\eta_1$ and $\eta_2$) spurious $x$-dependences similar to those discussed in Ref. [10] in connection with equations of state derived from "rescaled" virial expansions. These dependencies would in turn lead to unreliable predictions on the location of the demixing transition.

Up to here and due to the involved approximations, none of the arguments and results that we have discussed lead to a neat conclusion concerning the claimed equivalence of the effective one-component description vis a vis the true binary mixture description of highly asymmetric hard spheres. Therefore, new theoretical approaches to deal with this problem should be sought. In this respect, systematic and controlled approximations in the fluid regime, may profitably be undertaken. Of course these approximations will in turn lead to unreliable predictions on the location of the demixing transition.

We may stress that the present paper may also serve to stimulate efforts towards additional virial coefficients of highly asymmetric binary fluid mixtures of additive hard spheres, we hope that the present paper may also serve to stimulate efforts in this direction.

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