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Rescaled density expansions and demixing in hard-sphere binary mixtures

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The demixing transition of a binary fluid mixture of additive hard spheres is analyzed for different size asymmetries by starting from the exact low-density expansion of the pressure. Already within the second virial approximation the fluid separates into two phases of different composition with a lower consolute critical point. By successively incorporating the third, fourth, and fifth virial coefficients, the critical consolute point moves to higher values of the pressure and to lower values of the partial number fraction of the large spheres. When the exact low-density expansion of the pressure is rescaled to higher densities as in the Percus-Yevick theory, by adding more exact virial coefficients a different qualitative movement of the critical consolute point in the phase diagram is found. It is argued that the Percus-Yevick factor appearing in many empirical equations of state for the mixture has a deep influence on the location of the critical consolute point, so that the resulting phase diagram for a prescribed equation has to be taken with caution. © 2004 American Institute of Physics. [DOI: 10.1063/1.1791611]

Demixing is a common phase transition in fluid mixtures usually originated on the asymmetry of the interactions between the different components in the mixture. In the case of binary additive hard-sphere mixtures, the existence of demixing has been studied theoretically since decades, and the issue has been at times controversial. The importance of this problem resides in the fact that if fluid-fluid separation occurs, it would represent a neat example of an entropy-driven phase transition, i.e., a phase separation based only on the size asymmetry of the spheres. The solution of the Ornstein-Zernike (OZ) equation with the Percus-Yevick (PY) closure for additive hard-sphere mixtures by Lebowitz¹ and the ensuing analysis of the thermodynamic properties of a binary mixture by Lebowitz and Rowlinson² played a major role in the discussion and in many of the later theoretical developments. The great advantage of the PY theory is that it yields analytic expressions for the equation of state (taking both the virial and the compressibility routes) as well as for the contact values of the radial distribution functions. Its main drawbacks are the fact that it predicts a singularity in the pressure when the total volume fraction occupied by the spheres is equal to one (which is physically unattainable) and the thermodynamic consistency problem, i.e., the fact that the virial and the compressibility routes lead to different expressions for the equation of state. In any case, the immediate conclusion that follows from this theory is that it predicts no separation into two fluid phases. The same conclusion is reached if one considers the most popular (and reasonably accurate when compared to simulation data) equation of state proposed for hard-sphere mixtures, namely, the Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) equation,³ which can be obtained by an empirical interpolation of the

virial and the compressibility equations of the PY theory. However, the fluid-fluid segregation found by Biben and Hansen⁴ using the OZ equation with the Rogers-Young closure for highly asymmetric spheres indicated otherwise and renewed interest in demixing.

One can analyze theoretically the demixing transition in hard-sphere binary mixtures taking different routes. Of particular concern to us here is the approach based on the determination of an equation of state for the mixture beyond the PY theory. Since no exact result is available, various possibilities arise, including the solution of the OZ equation with different closures. However, this would most likely produce no analytical results. That is the reason behind the many different empirical equations of state that have been proposed in the literature. Apart from aiming at providing a reasonably accurate account of the available simulation data, they attempt to reproduce virial behavior and/or to comply with consistency conditions of the contact values of the radial distribution functions (for a recent review of these consistency conditions see Ref. 5 and references therein). In any event, all of them yield the exact second and third virial coefficients but at the same time inherit the singularity of the PY theory.

Coussaert and Baus⁶ have recently proposed an equation of state for a binary hard-sphere mixture with improved virial behavior that predicts a fluid-fluid transition at very high pressures (metastable with respect to freezing). On a different vein, Regnaut *et al.*⁷ have examined the connection between empirical expressions for the contact values of the radial distribution functions (which amounts to stating the corresponding equation of state for the mixture) and demixing. In this paper the demixing transition is analyzed by starting from the exact low-density expansion of the pressure. Our findings are then compared with the fluid-fluid separation resulting from different empirical proposals for the equation of state. It is found that qualitative differences appear which confirm that demixing in binary additive hard-

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sphere mixtures is still an open question which deserves further investigation.

We consider a binary fluid mixture of $N=N_1+N_2$ additive hard spheres of diameters σ_1 and σ_2 ($\sigma_1>\sigma_2$). The thermodynamic properties of the mixture can be described in terms of the number density $\rho\equiv N/V$, with V the volume, the partial number fraction of the big spheres $x\equiv N_1/N$, and the parameter $\gamma\equiv\sigma_2/\sigma_1$ which measures the size asymmetry. For particles of equal mass, the Helmholtz free-energy per particle $f\equiv f(\rho,x,\gamma)$ reads

$$\beta f = \ln(\rho\Lambda^3) - 1 + x \ln x + (1-x)\ln(1-x) + \sum_{n=1}^{\infty} \frac{1}{n} B_{n+1}(x,\gamma)\rho^n, \quad (1)$$

where $\beta\equiv 1/k_B T$, with T the absolute temperature and k_B Boltzmann's constant, plays only the role of a scale factor, Λ is the thermal de Broglie wavelength of the particles, and $B_{n+1}(x,\gamma)$ are the virial coefficients of the mixture. The pressure $p\equiv p(\rho,x,\gamma)$ is found from the thermodynamic relation $p = \rho^2(\partial f/\partial \rho)$ yielding,

$$\beta p = \rho \left[1 + \sum_{n=1}^{\infty} B_{n+1}(x,\gamma)\rho^n \right]. \quad (2)$$

By a Legendre transformation we have, moreover, eliminated from Eq. (2) the number density in favor of the pressure and analyzed the phase separation using the Gibbs free-energy per particle $g\equiv g(p,x,\gamma)=f+p/\rho$.

For fixed γ , the lower critical consolute point, p_c and x_c , is found from the convexity conditions,

$$\left[\frac{\partial^2 g}{\partial x^2} \right]_{p_c, x_c} = 0, \quad \left[\frac{\partial^3 g}{\partial x^3} \right]_{p_c, x_c} = 0. \quad (3)$$

Since $g=x\mu_1+(1-x)\mu_2$, where $\mu_1\equiv\mu_1(p,x,\gamma)$ and $\mu_2\equiv\mu_2(p,x,\gamma)$ are the chemical potentials of the components, and from the Gibbs-Duhem relation $x(\partial\mu_1/\partial x)+(1-x)\times(\partial\mu_2/\partial x)=0$, by also fixing the pressure ($p>p_c$), the partial number fractions of the big spheres at coexistence, x' and x'' , are obtained from the coexistence conditions,

$$\left[\frac{\partial g}{\partial x} \right]_{x'} = \left[\frac{\partial g}{\partial x} \right]_{x''}, \quad (4)$$

$$\left[g - x \frac{\partial g}{\partial x} \right]_{x'} = \left[g - x \frac{\partial g}{\partial x} \right]_{x''},$$

expressing the equality of the chemical potentials in both phases.

We have truncated the density expansion in Eq. (2) at fifth order since analytical expressions are known^{8,9} for $B_2(x,\gamma)$ and $B_3(x,\gamma)$, while $B_4(x,\gamma)$ and $B_5(x,\gamma)$ have been evaluated numerically.¹⁰⁻¹³ Demixing has been investigated for small γ values, say $\gamma=0.05, 0.1, 0.2, 0.3$, and 0.4 . For $\gamma=0.1$ we have also included a recent numerical evaluation¹⁴ of $B_6(x,\gamma)$.

We have first kept the density expansion up to second order, where the Gibbs free energy can be obtained analytically, and found that demixing occurs within this simple approximation. In Fig. 1 we plot the resulting phase diagram

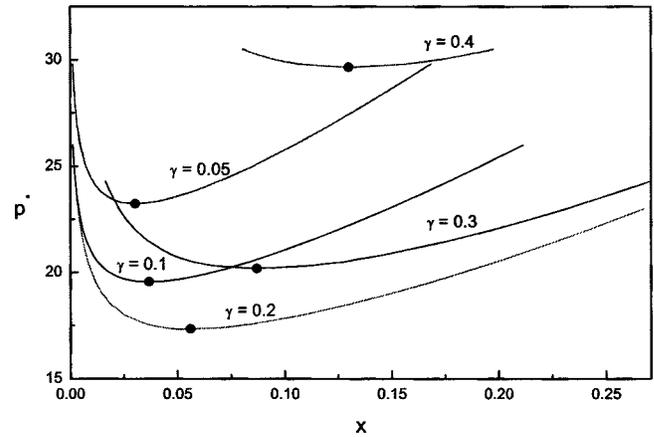


FIG. 1. Phase diagram in the (x,p^*) plane, with $p^*=\beta p\sigma_1^3$, of a binary additive hard-sphere mixture for different size asymmetries as obtained from the second virial approximation. The full dots denote the critical consolute points while the lines correspond to the coexistence curves.

for different γ values. We first note that the coexistence curves are restricted to a small region in the phase diagram since, for each γ , the pressure may only be increased until the total volume fraction occupied by the spheres, $\eta = \pi[x+(1-x)\gamma^3]\rho\sigma_1^3/6$, reaches for the dense phase the highest possible value. Since these highest volume fractions are not known, all the curves have been drawn up to the limiting (unphysical) value $\eta=1$. It is seen that by decreasing the size asymmetry of the spheres the critical pressure first decreases and the coexistence region widens. After the critical pressure reaches a minimum ($\gamma\approx 0.2$) the trend is reversed. In contrast, the critical composition x_c always increases with γ . Note that when going for $\gamma=0.3$ to $\gamma=0.4$ the critical volume fraction η_c changes from 0.505 to 0.819, i.e., the coexistence region has shrunk substantially and this explains why by further increasing γ demixing disappears. We point out that this unexpected qualitative behavior is also encountered by keeping the virial expansion up to k th order ($k=3, 4, 5$) and similar to the phase diagram found in Ref. 6.

An important feature for all the reported size asymmetries is that by successively incorporating the third, fourth, and fifth (sixth) virial coefficients, the critical pressure p_c increases whereas the critical partial number fraction x_c decreases, as shown in Table I.

The last finding seems to be in contradiction with the results by Coussaert and Baus who rescaled the density expansion in Eq. (2) by assuming that the behavior of the pressure for high densities is the same as the one found in the PY theory, i.e.,

$$\beta p = \frac{\rho}{(1-\eta)^3} \left[1 + \sum_{n=1}^k C_{n+1}(x,\gamma)\rho^n \right], \quad (5)$$

where the upper limit k in the sum indicates that Eq. (5) guarantees, through $C_{n+1}(x,\gamma)$, that βp has $k+1$ exact virial coefficients at low densities. Coussaert and Baus found that, when going from $k=3$ to $k=4$, the critical consolute point moves to lower values of p_c and to higher values of x_c .

TABLE I. Critical constants p_c^* , x_c , and η_c for different γ values as obtained from the low-density expansion of the pressure by keeping $n-1$ exact virial coefficients (indicated as B_n).

γ	B_2			B_3			B_4			B_5			B_6		
	p_c^*	x_c	η_c												
0.05	23.23	0.0304	0.276	50.84	0.0294	0.428	95.18	0.0254	0.530	154.4	0.0223	0.598			
0.1	19.55	0.0368	0.274	38.68	0.0365	0.394	67.16	0.0333	0.476	102.6	0.0308	0.534	144.1	0.0289	0.576
0.2	17.33	0.0561	0.339	28.48	0.0525	0.381	44.60	0.0498	0.432	64.00	0.0489	0.476			
0.3	20.18	0.0869	0.505	27.58	0.0769	0.447	39.56	0.0727	0.463	54.00	0.0724	0.492			
0.4	29.65	0.1300	0.819	33.40	0.1134	0.580	43.56	0.1066	0.548	56.46	0.1054	0.554			

Since the PY factor, $1/(1-\eta)^3$, strongly increases the pressure with respect to the pressure at low densities, the amplitude of the changes induced by adding one more exact virial coefficient in Eq. (5) led the authors to conclude that *the movement of the critical consolute point casts some doubt on the convergence of the procedure*. Indeed, for a given k in Eq. (5) the PY factor yields $B_n(x, \gamma) \neq 0$ ($n \geq k+2$), which are otherwise zero in the exact density expansion up to $(k+1)$ th order. Since the virial coefficients $B_n(x, \gamma)$ ($n \geq k+2$) in Eq. (5) depend on x through the exact virial coefficients $B_n(x, \gamma)$ ($n \leq k+1$), it can be concluded that the *different* additional dependences on x for $k=3$ and $k=4$ are responsible for shifting the critical consolute point to lower (higher) values of p_c (x_c). Using a recent numerical evaluation of the sixth virial coefficient¹⁴ for $\gamma=0.1$, we have confirmed the lack of convergence of this procedure and found that the critical consolute point moves from $p_c^* = 5377$ and $x_c = 0.0008$ ($k=3$) to $p_c^* = 2565$ and $x_c = 0.0088$ ($k=4$) and to $p_c^* = 1572$ and $x_c^* = 0.0020$ ($k=5$).

By the same argument, it is important to emphasize that the PY factor appearing in a great variety of empirical equations of state for a binary hard-sphere fluid mixture, arbitrarily introduces, as compared to the exact density expansion, additional x dependences through the virial coefficients $B_n(x, \gamma)$ ($n \geq 4$) if, as a matter of fact, the empirical equations only preserve the first two exact virial coefficients. The additional x dependences are also linked to the particular form of the empirical equation of state. This would explain why very similar equations of state do predict no demixing or demixing, and why, whenever it exists, the location of the critical consolute point strongly depends on the proposed empirical equation. In order to illustrate this point, we have analyzed four proposals for the equation of state that can be cast in the form of Eq. (5) with either $k=3$ or $k=4$ and which predict demixing.¹⁵ They are the proposals by Hamad¹⁶ (which we will label as H-K and H-CS depending

on whether the Kolafa or the Carnahan-Starling equation for the monocomponent fluid is used as input) and the two extended Carnahan-Starling equations (eCS-I and eCS-II) of Santos *et al.*¹⁷ All these equations have been introduced as alternatives to the BMCSL equation of state. It turns out that these four equations lead to the first two exact virial coefficients but differ in the predictions for $B_n(x, \gamma)$ ($n \geq 4$). Nevertheless, they all give good agreement with the available simulation results for the compressibility factor.¹⁸⁻²¹ The scatter in the values for the critical constants shown in Table II is so evident that there is no indication as to whether one should prefer one equation over the others, if any. For example, in the proposals by Hamad p_c^* is always an increasing function of γ . In the cases of the eCS-I and eCS-II, p_c^* does not follow this trend and can be up to two orders of magnitude higher. Moreover, the eCS-II does not predict demixing for $\gamma \geq 0.2$.

In conclusion, we want to stress our main result, namely, that the location of the critical consolute point of a binary hard-sphere fluid mixture, and hence the determination of the complete phase diagram (including the stability of demixing relative to freezing) have to be taken with caution when using empirical rescaled density expansions behaving in a PY-type manner. A deeper assessment is precluded at this stage and must await the determination of yet higher virial coefficients.

After this paper was originally submitted, and due to a doubt that arose from the numerical value of the sixth virial coefficient as reported in Ref. 14, we became aware through private correspondence with A. J. Masters of a complementary paper by Vlasov and Masters.²² There, the authors provide the most recent numerical values of the virial coefficients (up to the sixth) for various values of γ . For $\gamma=0.1$, they also compute the seventh virial coefficient and the critical consolute points considering different levels of truncation

TABLE II. The same as in Table I as obtained from the equations of state proposed by Hamad (Ref. 16) (H-K and H-CS) and the two extended Carnahan-Starling equations (eCS-I and eCS-II) of Santos *et al.* (Ref. 17).

γ	H-K			H-CS			eCS-I			eCS-II		
	p_c^*	x_c	η_c									
0.05	27.68	0.1120	0.589	29.68	0.1001	0.595	3599	0.0093	0.822	1096	0.0004	0.204
0.1	38.05	0.1114	0.624	42.97	0.0968	0.636	1307	0.0203	0.757	832.0	0.0008	0.290
0.2	74.77	0.0244	0.389	77.98	0.0197	0.366	653.4	0.0537	0.725
0.3	121.5	0.0263	0.471	148.1	0.0211	0.478	581.9	0.0998	0.738
0.4	337.3	0.0263	0.620	751.2	0.0179	0.681	663.4	0.1532	0.766

of the density expansion. Their critical constants are in good agreement with the data in Table I.

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