Virial Approach to Hard-Sphere Demixing

Tamara Coussaert and Marc Baus

Faculté des Sciences, Case Postale 231, Université Libre de Bruxelles, Campus Plaine, B-1050 Bruxelles, Belgium

(Received 27 June 1997)

We propose a perturbative modification of the Carnahan-Starling equation of state for a binary hard-sphere mixture which brings its virial coefficients into better agreement with recent numerical findings. The resulting analytic equation of state predicts a demixing transition whose spinodals and binodals are in qualitative agreement with recent numerical and experimental findings. [S0031-9007(97)03986-0]

PACS numbers: 64.75.+g, 05.70.Ce, 82.60.Lf

Demixing transitions whereby a multicomponent equilibrium fluid separates into phases of different composition are ubiquitous in nature [1]. It is generally believed that a necessary condition for the occurrence of demixing is a sufficiently large asymmetry between the parameters characterizing the like- and unlike-particle interactions. In the case of hard-sphere (HS) mixtures there can be no asymmetry between the energy scales involved since HS interactions are governed solely by the geometric characteristics of the different species. In the particular case of additive HS there is also no geometric asymmetry because the contact distance σ_{ij} between species i and j is related to the diameter σ_i of species i by the additivity relation, $\sigma_{ij}=(\sigma_i+\sigma_j)/2$, and hence, $2\sigma_{ij}-\sigma_{ii}-\sigma_{jj}=0$. It is thus very much the question whether the only remaining asymmetry, namely, the size asymmetry, $\sigma_i-\sigma_j$, is sufficient to drive, by a purely entropic mechanism, a demixing transition in fluid mixtures of additive HS. It came thus as no surprise when the analytic results obtained within the Percus-Yevick (PY) closure of the Ornstein-Zernike (OZ) equations indicated the absence of demixing in (additive) HS mixtures with any number of components [2]. Recently, numerical evidence has been found that more elaborate closures of the OZ equations do, however, predict demixing in a very asymmetric binary HS mixture [3]. Experiments performed on colloidal systems which are thought to approximate HS mixtures rather well seem to support this finding although it appears difficult to disentangle the demixing transition from a close-by freezing transition [4]. A theoretical study focusing from the start on very asymmetric binary HS mixtures does lend further support to the presence of a spinodal instability in such systems [5]. A similar situation is found in the study of (HS-)colloid and (coil-)polymer mixtures [6]. In analogy with the colloid-polymer studies, the physical mechanism behind the HS-demixing transition is usually also traced back to an osmotic depletion effect [7]. The underlying assumption being that the depletion force is attractive although recent studies indicate that this is not always the case [8]. We would like therefore to draw attention here to another recent finding indicating that the fifth virial coefficient of a binary HS mixture becomes negative in the region of strong size asymmetry [9]. All current equations of state of HS mixtures [2,5] do, however, miss this qualitatively new feature. Although the relation between the depletion mechanism and a negative fifth virial coefficient is not obvious, we note that both point towards many-body interactions with a strong dependence on the size asymmetry. In what follows we will present an alternative approach to HS demixing which focuses mainly on this virial aspect.

We consider a mixture of N_i (additive) hard spheres of diameter σ_i enclosed in a volume V at the equilibrium temperature T. The thermodynamic properties of this mixture can be described in terms of either the partial number densities $\rho_i=N_i/V$, or the total density $\rho=\sum_i\rho_i$ and the partial number fractions $x_i=N_i/N$, with $\sum_i x_i=1$ and $N=\sum_i N_i$ being the total number of spheres. We first focus our attention on the equation of state or compressibility factor, $Z=\beta p/\rho$, p being the pressure, $\beta=1/k_BT$, and k_B is Boltzmann's constant. The virial coefficients of the mixture, B_n, are defined by $Z=\sum_{n=1}^{\infty}B_n\rho^{n-1}$ (see, e.g., [10]). From simulations [11] of binary mixtures ($i=1,2$) of weak to moderate size asymmetry, say $\gamma>0.3$ where $\gamma=\sigma_2/\sigma_1\leq 1$ measures the size asymmetry, it is known that Z is well approximated by the Carnahan-Starling (CS) expression, say Z_{CS} (see [12]). In order to take advantage of this fact we will write in a perturbative fashion, $Z=Z_{\mathrm{CS}}+\Delta Z$ with $\Delta Z=\sum_n(B_n-B_n^{\mathrm{CS}})\rho^{n-1}$, where B_n^{CS} denotes the CS approximation of B_n, i.e., $Z_{\mathrm{CS}}=\sum_n B_n^{\mathrm{CS}}\rho^{n-1}$, whereas the closed-form expression of Z_{CS} reads [10,12]

$$Z_{\mathrm{CS}}=\frac{1}{(1-\xi_3)}+\xi_0\,\frac{3\bar{\xi}_1\bar{\xi}_2}{(1-\xi_3)^2}+\xi_0^2\,\frac{\bar{\xi}_2^3(3-\xi_3)}{(1-\xi_3)^3}\,, \tag{1}$$

where we have used the standard variables, $\xi_k=\frac{\pi}{6}\sum_i\rho_i\sigma_i^k$, and also $\bar{\xi}_k=\sum_i x_i\sigma_i^k=\xi_k/\xi_0$ with $k=0,1,2,3$. For the mixture, only B_1,B_2,B_3 are known explicitly, namely [13],

$$\bar{B}_1=\bar{\xi}_0,\qquad \bar{B}_2=\bar{\xi}_0\bar{\xi}_3+3\bar{\xi}_1\bar{\xi}_2\,,$$

$$\bar{B}_3=\bar{\xi}_0\bar{\xi}_3^2+6\bar{\xi}_1\bar{\xi}_2\bar{\xi}_3+3\bar{\xi}_2^3\,, \tag{2}$$

where $B_n=\bar{B}_n(\frac{\pi}{6})^{n-1}$, while B_4 and B_5 have recently been computed numerically in [9]. From (1) it follows

0031-9007/97/79(10)/1881(4)$10.00

that $\Delta B_n = B_n - B_n^{\mathrm{CS}}$ vanishes for $n = 1, 2, 3$ and hence $\Delta Z = \rho^3 \Delta B_4 + \rho^4 \Delta B_5 + \cdots$, where the ellipses denote terms which at present are unknown for the mixture. As a first perturbative improvement of Z_{CS} we propose to approximate Z by $\overline{Z}$ with

$$\overline{Z} = Z_{\mathrm{CS}} + \xi_0^3 \Delta \overline{B}_4 + \xi_0^4 \Delta \overline{B}_5 \,, \tag{3}$$

although it is not known whether the virial expansion of $\Delta Z = Z - Z_{\mathrm{CS}}$ really converges. To obtain $\Delta \overline{B}_4 = \overline{B}_4 - \overline{B}_4^{\mathrm{CS}}$ and $\Delta \overline{B}_5 = \overline{B}_5 - \overline{B}_5^{\mathrm{CS}}$ we use

$$\begin{aligned} \overline{B}_4^{\mathrm{CS}} &= \overline{\xi}_0 \overline{\xi}_3^3 + 9 \overline{\xi}_1 \overline{\xi}_2 \overline{\xi}_3^2 + 8 \overline{\xi}_2^3 \overline{\xi}_3 \,, \\ \overline{B}_5^{\mathrm{CS}} &= \overline{\xi}_0 \overline{\xi}_3^4 + 12 \overline{\xi}_1 \overline{\xi}_2 \overline{\xi}_3^3 + 15 \overline{\xi}_2^3 \overline{\xi}_3^2 \,, \end{aligned} \tag{4}$$

as follows from (1), whereas for $\overline{B}_4, \overline{B}_5$ we use the exact decomposition [10],

$$\overline{B}_n = \sum_{k=0}^{n} x_1^k x_2^{n-k} \overline{B}_n^{(k)}(\sigma_1, \sigma_2) \,, \tag{5}$$

of $\overline{B}_n$ into the $(n+1)$ partial virial coefficients of the binary mixture $\overline{B}_n^{(k)}(\sigma_1, \sigma_2)$ or their dimensionless counterparts $b_n^{(k)}(\gamma)$, with $\overline{B}_n^{(k)}(\sigma_1, \sigma_2) = \sigma_1^{3(n-1)} b_n^{(k)}(\gamma)$ and $\gamma = \sigma_2/\sigma_1$, and fit the $b_4^{(k)}(\gamma)$ and $b_5^{(k)}(\gamma)$ functions to the numerical data of [9] by using simple polynomial expressions in γ. Before doing so we observe that the symmetry relation, $\overline{B}_n^{(k)}(\sigma_1, \sigma_2) = \overline{B}_n^{(n-k)}(\sigma_2, \sigma_1)$ or $b_n^{(k)}(\gamma) = \gamma^{3(n-1)} b_n^{(n-k)}(\frac{1}{\gamma})$ with, in particular, $b_{2k}^{(k)}(\gamma) = \gamma^{3(2k-1)} \times b_{2k}^{(k)}(\frac{1}{\gamma})$ when $n = 2k$ implies that not all the functions $b_n^{(k)}(\gamma)$ are independent. In this way we obtain explicit analytic expressions [14] for $\overline{B}_4$ and $\overline{B}_5$ valid for any $0 \le x_1 = 1 - x_2 \le 1$ and $0 \le \gamma \le 1$. It is found that $\overline{B}_4$ is fairly close to $\overline{B}_4^{\mathrm{CS}}$ with $(B_4 - B_4^{\mathrm{CS}})/\sigma_1^9$ always positive and never exceeding its one-component value. On the contrary, $\overline{B}_5$ has a negative well [9] which is missing in $\overline{B}_5^{\mathrm{CS}} \ge 0$ leading to negative values for $(B_5 - B_5^{\mathrm{CS}})/\sigma_1^{12}$ when $0 < \gamma \lesssim 0.5$ and $0 < x_1 \lesssim 0.6$ (see Fig. 1). Because of the presence of this negative well in $\overline{B}_5$, the correction $\xi_0^3 \Delta \overline{B}_4 + \xi_0^4 \Delta \overline{B}_5$ to Z_{CS} in (3) exhibits a similar negative well which can be viewed then as resulting from a density dependent effective attraction, not between the real HS but between HS described by the CS approximation. We also observe that as $\gamma \rightarrow 1$, $\overline{Z}$ of (3) tends to $\overline{Z}^{\gamma=1} = Z_{\mathrm{CS}}^{\gamma=1}(\eta) + 0.362\eta^3 + 0.237\eta^4$ with $\eta = \frac{\pi}{6}\rho\sigma_1^3$, the packing fraction of the one-component system ($\sigma_1 = \sigma_2$). Our pressure for the one-component system exceeds thus slightly the CS pressure for large η, a result in agreement with the available computer simulations (see [10,11]). In the opposite limit, $\gamma \rightarrow 0$, whereby the small spheres reduce to point particles ($\sigma_2 \rightarrow 0$) $\overline{Z}$ reduces to the expected result [10], $\overline{Z}^{\gamma=0} = x_1 Z_1 + x_2/(1 - \eta_1)$, where $\eta_1 = \frac{\pi}{6}\rho_1\sigma_1^3$ and $Z_1 = \overline{Z}^{\gamma=1}(\eta_1)$ is the compressibility factor of a one-component system of large spheres (σ_1). Next we consider the Helmholtz free energy per particle, f, which we denote in this approximation as $\overline{f}$, with $\beta\overline{f} = \beta f_{\mathrm{CS}} + \frac{\xi_0^3}{3}\Delta\overline{B}_4 + \frac{\xi_0^4}{4}\Delta\overline{B}_5$, where f_{CS} represents the analytic expression obtained for f from Z_{CS}. From the zeros of the determinant of the matrix, $\frac{\partial^2(\rho\overline{f})}{\partial\rho_i\partial\rho_j}$, we find that the mixture presents a spinodal instability (see Fig. 2) not unlike

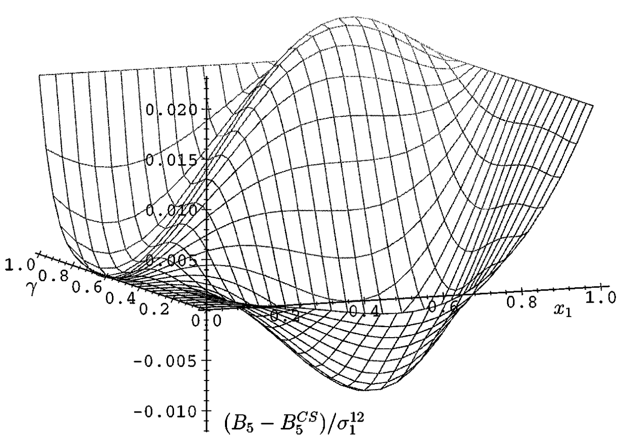

FIG. 1. The dimensionless deviation, $(B_5 - B_5^{\mathrm{CS}})/\sigma_1^{12}$, of the fifth virial coefficient B_5 from its CS approximation [12] for a binary HS mixture of size ratio, $\gamma = \sigma_2/\sigma_1$, and number fraction (concentration) of large spheres, x_1. The values of B_5 have been obtained [14] from a polynomial interpolation of the numerical results of [9]. It is seen that B_5 is everywhere close to B_5^{CS} but becomes negative in the region $0 < \gamma \lesssim 0.5$ and $0 < x_1 \lesssim 0.6$, while B_5^{CS} is always positive. When, as proposed here, the CS theory is corrected perturbatively, the negative well in $(B_5 - B_5^{\mathrm{CS}})/\sigma_1^{12}$ can be viewed as providing an effective attraction which drives the HS fluid mixture into a two-phase state.

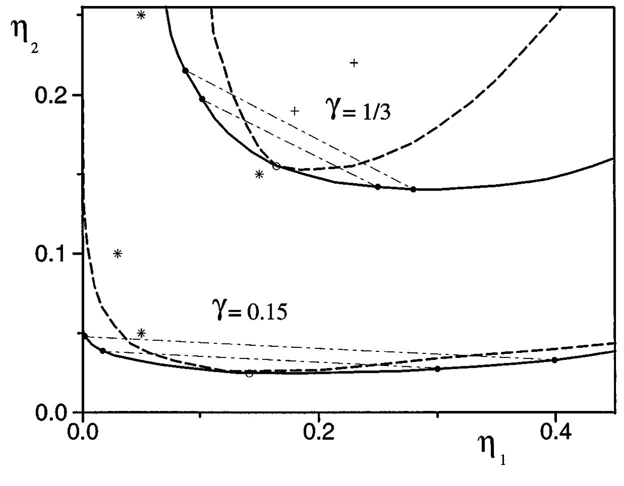

FIG. 2. Spinodals (broken lines) and binodals (full lines) of the demixing transition of a binary HS mixture in the η_1-η_2 plane, with $\eta_i = \frac{\pi}{6}\sigma_i^3\rho_i$ being the packing fraction of species i ($i = 1, 2$). In this representation the tie lines (dot-dashed lines) between the coexisting fluid phases (full dots) are oblique (for clarity only a few tie-lines are shown). The critical (consolute) point is indicated by an open dot. The lower curves correspond to a size ratio, $\gamma = \sigma_2/\sigma_1$, of $\gamma = 0.15$ and the upper curves to $\gamma = 1/3$. For the case $\gamma = 1/3$, the experiments of Dinsmore *et al.* (see [4]) clearly indicate that the fluid mixture is stable (unstable) for the systems represented by $*$ $(+)$, in agreement with our theoretical spinodal.

the one found in [3–5]. To find the corresponding binodals we can perform either a double-tangent construction on the Gibbs free energy per particle $\bar{g}$ ($\beta\bar{g} = \beta\bar{f} + \bar{Z}$) versus x_1 at constant p and T (or for HS at constant βp) or else solve the coexistence conditions of equality of the pressures and chemical potentials ($\bar{\mu}_i = \frac{\partial(\rho\bar{f})}{\partial\rho_i}$) between the coexisting phases (see Fig. 2). As already mentioned above, the demixing transition is not the only phase transition governing the HS mixture for small γ. It is generally believed [3–5] that there also is a close-by freezing transition of the fluid mixture into a solid alloy whose structure is not known with precision but which could consist of a crystal of large spheres permeated by a fluid of small spheres. Such a partial freezing or sublattice melting transition is typical of superionic conductors for which the size asymmetry between the positive and negative ions is also known to be crucial [15]. Here we have studied this transition for an HS mixture within the GELA ("generalized effective liquid approximation") of [16]. The corresponding phase diagram is shown in Fig. 3. It is seen that for pressures exceeding that of the lower consolute point of the demixing transition both demixing and partial freezing can occur depending on whether the small spheres constitute the majority or minority phase. When γ increases the demixing transition eventually becomes metastable, while for $\gamma \gtrsim 0.5$ other solid phases come into competition with the fluid mixture [17].

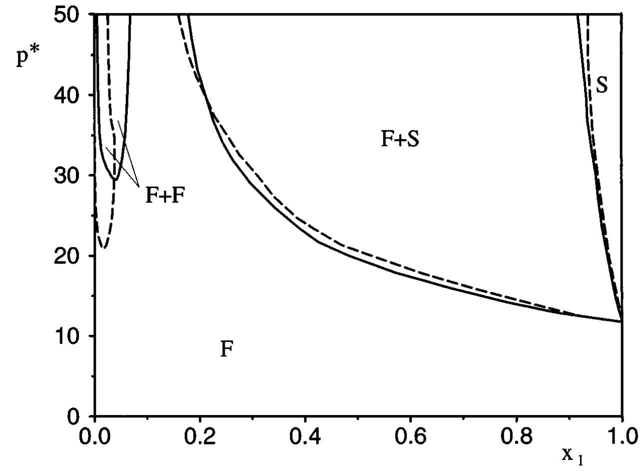

FIG. 3. The pressure-composition phase diagram of a binary HS mixture of size ratio $\gamma = 0.15$ (broken lines) and $\gamma = 0.30$ (full lines). Here $p^* = \beta p \sigma_1^3$ is the reduced pressure, $\gamma = \sigma_2/\sigma_1$, while σ_1 and x_1 correspond to the diameter and number fraction of the large spheres. The phases considered are the fluid mixture (F) of composition x_1 ($x_2 = 1 - x_1$) and a "solid" alloy (S) of composition x_1 in which the large spheres form a face centered cubic structure while the small spheres remain fluid. The latter phase has been assumed to compete with the demixing transition for reduced pressures p^* of the order of the critical value p_c^* of the lower critical consolute point (we find $p_c^* \simeq 29$ for $\gamma = 0.30$ and $p_c^* \simeq 22$ for $\gamma = 0.15$). For larger pressures one expects solid alloys of a different structure [17] to compete with the fluid mixture.

In conclusion, we have shown that the possibility of demixing in binary mixtures of additive hard spheres can be traced back to the occurrence in these systems of a negative fifth virial coefficient for small size ratios and small to moderate concentrations of large spheres. A simple modification (3) of the CS equation of state (1) has been proposed and shown to lead to results in agreement with those obtained from other sources [3–5].

M. B. acknowledges financial support from the Fonds National de la Recherche Scientifique.

[1] J. S. Rowlinson and F. L. Swinton, *Liquids and Liquid Mixtures* (Butterworth, London, 1982).

[2] J. L. Lebowitz, Phys. Rev. **133**, A895 (1964); J. L. Lebowitz and J. S. Rowlinson, J. Chem. Phys. **41**, 133 (1964); A. Vrij, J. Chem. Phys. **69**, 1742 (1978).

[3] T. Biben and J. P. Hansen, Phys. Rev. Lett. **66**, 2215 (1991); J. Phys. Condens. Matter **3**, F65 (1991); Y. Rosenfeld, Phys. Rev. Lett. **72**, 3831 (1994); J. Phys. Chem. **99**, 2857 (1995).

[4] A. D. Dinsmore, A. G. Yodh, and D. J. Pine, Phys. Rev. E **52**, 4045 (1995); A. Imhof and J. K. G. Dhont, Phys. Rev. Lett. **75**, 1662 (1995); U. Steiner, A. Meller, and J. Stavans, Phys. Rev. Lett. **74**, 4750 (1995); P. D. Kaplan, J. L. Rouke, A. G. Yodh, and D. J. Pine, Phys. Rev. Lett. **72**, 582 (1994); J. S. van Duijneveldt, A. W. Heinen, and H. N. W. Lekkerkerker, Europhys. Lett. **21**, 369 (1993); S. Sanyal, N. Easwar, S. Ramaswamy, and A. K. Sood, Europhys. Lett. **18**, 107 (1992).

[5] H. N. W. Lekkerkerker and A. Stroobants, Physica (Amsterdam) **195A**, 387 (1993).

[6] W. C. K. Poon and P. N. Pusey, in *Observation, Prediction and Simulation of Phase Transitions in Complex Fluids,* edited by M. Baus, L. F. Rull, and J. P. Ryckaert (Kluwer Academic Publishers, Dordrecht, 1995), p. 3, and references therein.

[7] S. Asakura and F. Oosawa, J. Chem. Phys. **22**, 1225 (1954); A. Vrij, Pure Appl. Chem. **48**, 471 (1976).

[8] T. Biben, P. Bladon, and D. Frenkel, J. Phys. Condens. Matter **8**, 10 799 (1996); Y. Mao, M. E. Cates, and H. N. W. Lekkerkerker, Physica (Amsterdam) **222A**, 10 (1995); P. Attard, J. Chem. Phys. **91**, 3083 (1989).

[9] F. Saija, G. Fiumara, and P. V. Giaquinta, Mol. Phys. **87**, 991 (1996); **89**, 1181 (1996).

[10] T. Boublik and I. Nezbeda, Collect. Czech. Chem. Commun. **51**, 2301 (1986).

[11] P. H. Fries and J. P. Hansen, Mol. Phys. **48**, 891 (1983); G. Jackson, J. S. Rowlinson, and F. van Swol, J. Phys. Chem. **91**, 4907 (1987); D. H. L. Yau, K. Y. Chan, and D. Henderson, Mol. Phys. **88**, 1237 (1996).

[12] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969); T. Boublik, J. Chem. Phys. **53**, 471 (1970); G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Jr. Leland, J. Chem. Phys. **54**, 1523 (1971). (Note that in the case of the mixture the CS expression is often referred to as the BMCSL expression, but for notational convenience we continue to use here the one-component abbreviation CS also for the mixture.)

[13] Note that numerically $\overline{\xi}_0 = x_1 + x_2$ is equal to 1 but its presence in (2) is nevertheless useful when it comes to counting powers of x_i as needed for (5).

[14] T. Coussaert and M. Baus (to be published).

[15] See, e.g., W. Dietrich, P. Fulde, and I. Peschel, Adv. Phys. **29**, 527 (1980); H. Xu and M. Baus, J. Phys. C **20**, L373 (1987), and references therein.

[16] J. F. Lutsko and M. Baus, Phys. Rev. A **41**, 6647 (1990); see also H. Xu and C. Barentin, J. Phys. Condens. Matter **7**, L13 (1995).

[17] See, e.g., J. L. Barrat, M. Baus, and J. P. Hansen, Phys. Rev. Lett. **56**, 1063 (1986); H. Xu and M. Baus, J. Phys. Condens. Matter **4**, L663 (1992), and references therein.