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On the critical non-additivity driving segregation of asymmetric binary hard sphere fluids

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A previously proposed version of thermodynamic perturbation theory, appropriate for singular pair interactions between particles, is applied to binary mixtures of hard spheres with non-additive diameters. The critical non-additivity Δ_C required to drive fluid–fluid phase separation is determined as a function of the ratio $\xi \leq 1$ of the diameters of the two species. $\Delta_C(\xi)$ is found to decrease with ξ and to go through a minimum for $\xi \simeq 0.015$ before increasing sharply as $\xi \to 0$, irrespective of the total packing-fraction η of the mixture. These results are the basis of an estimate of the range of size ratios for which a binary mixture of *additive* hard spheres exhibit a fluid–fluid miscibility gap. This range is conjectured to be $0.01 \lesssim \xi \lesssim 0.1$.

Keywords: perturbation theory; simple liquids; binary mixture; hard sphere; phase separation

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1. Introduction

Miscibility gaps are a very common occurrence in multi-component fluids or solids. In simple, molecular fluids, demixing of species of comparable size is generally of enthalpic origin, associated with preferential cohesive forces. In complex fluids, on the other hand, in particular in colloidal dispersions, where species may differ considerably in size, segregation is often entropy-driven, as illustrated by the familiar depletion mechanism in colloid–polymer mixtures [1,2]. The simplest model system exhibiting entropy-driven phase separation is a binary mixture of hard spheres. If the two species of spheres have non-additive diameters, i.e. if the distance of closest approach between the centres of opposite species is larger than the sum of the radii of the two species, a modest deviation from additivity leads to demixing into two fluid phases of different composition [3]. Thus non-additivity, which is the rule, rather than the exception, in most colloidal systems, is a common cause of entropic phase separation. However even perfectly additive binary hard-sphere mixtures are now believed to phase separately, provided the ratio ξ of the radii of small and large spheres is sufficiently small and the partial packing fractions are sufficiently large [4–9]. Fluid–fluid phase separation has been shown to be pre-empted by the coexistence of a low density fluid and a high density solid of very different compositions, so that fluid–fluid coexistence is thermodynamically only metastable [8]. However, due to slow crystal nucleation kinetics, fluid–fluid coexistence may in fact be observable in appropriate colloidal mixtures where the unavoidable polydispersity of the small and large species will slow down the nucleation even further.

The two mechanisms responsible for fluid–fluid phase separation in hard-sphere systems are thus non-additivity and size asymmetry, or a combination of both. For perfectly additive mixtures, the size ratio ξ necessary to drive phase separation has been estimated to be of the order of 0.1 or less [8], while for larger ratios ($0.1 \lesssim \xi \leq 1$), a critical degree of non-additivity Δ_C (defined in Section 2) is required to induce fluid–fluid demixing. The simulations in [8] were mostly based on an effective one-component representation of the additive binary mixture, using an effective depletion potential between the large spheres, but the results were tested against explicit two-component simulations over a range of physical conditions, and good agreement was found. Very recently additional results for effective depletion potentials have been published [10]. In [3] it was shown that Δ_C decreases with ξ, and is expected to go to zero (additivity) as the size ratio approaches $\xi \simeq 0.1$. However in the limit $\xi \to 0$, the additive system reduces to a mixture of hard spheres and point particles (ideal gas). Such a system is not expected to phase separately because there is no entropic 'incentive', in the form of an increase of the volume accessible to the point particles. This intuitive statement is confirmed by a simple free volume calculation similar to that of Lekkerkerker *et al.* [11]

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for the Asakura–Oosawa (AO) model of colloid–polymer mixtures. These authors calculated fluid–solid and fluid–fluid–solid phase diagrams for several values of the non-additivity parameter Δ relative to the hard-sphere diameter σ. A thermodynamically stable fluid–fluid phase separation occurs for $\Delta \gtrsim 0.32$ in reasonable agreement with later experimental findings of the appearance of a fluid–fluid–solid triple point in the phase diagram of colloid–polymer mixtures characterised by $\Delta \simeq 0.25$ [12]. An elementary extension of their calculation (sketched in Appendix 2) shows that, within free volume theory, the critical non-additivity required to drive a (metastable) fluid–fluid phase separation of hard spheres and point particles (i.e. the AO model) is $\Delta_C \simeq 0.17$. This observation raises the question whether fluid–fluid demixing predicted to occur for additive hard spheres below a size ratio $\xi \simeq 0.1$ terminates at a lower value of ξ, say $\xi = \xi_l$, below which a positive value of the non-additivity parameter Δ is required to drive phase separation, as expected from the $\xi = 0$ limit. In other words, is the fluid–fluid miscibility gap for additive hard spheres restricted to a limited range of size ratios $0 < \xi_l \leq \xi \leq \xi_u \simeq 0.1$?

In the present paper we address this problem by calculating the critical non-additivity required to induce fluid–fluid segregation as a function of ξ over the full range $[0, 1]$. We apply a recently developed thermodynamic perturbation theory adapted to singular interactions [13,14] to calculate the free energy of the non-additive binary hard-sphere fluid as a function of packing fraction and concentration. The predictions for the onset of spinodal instability presented in the following sections indeed suggest that a non-zero non-additivity ($\Delta_C > 0$) is required to trigger fluid–fluid demixing for extremely asymmetric mixtures ($0 \leq \xi \leq \xi_l \simeq 0.01$) as well as for size ratios $\xi \geq \xi_u \simeq 0.1$.

2. Model and theory

We consider binary mixtures of hard spheres of diameters σ_A and σ_B ($>\sigma_A$). The three pair distances of closest approach are

$$\begin{aligned} \sigma_{AA} &= \sigma_A, \\ \sigma_{BB} &= \sigma_B, \\ \sigma_{AB} &= \frac{1}{2}(\sigma_A + \sigma_B)(1 + \Delta), \end{aligned} \tag{1}$$

where Δ (≥ 0) is the dimensionless non-additivity parameter. The hard-sphere pair 'potentials' are

$$v_{\alpha\beta}(r) = \begin{cases} \infty, & r < \sigma_{\alpha\beta}, \\ 0, & r > \sigma_{\alpha\beta}; \quad \alpha, \beta = \text{A or B}. \end{cases} \tag{2}$$

$\Delta = 0$ corresponds to the familiar and widely studied additive binary hard-sphere mixture. The reduced thermodynamic properties of this athermal system depend only on the partial packing fractions $\eta_\alpha = \pi\rho_\alpha\sigma_\alpha^3/6$ ($\alpha = \text{A, B}$), where $\rho_\alpha = N_\alpha/V$ is the number density, or number of spheres per unit volume, or equivalently on the total packing fraction $\eta = \eta_A + \eta_B$ and the concentration $x = x_A = N_A/(N_A + N_B)$ of species A ($x_B = 1 - x_A$). The solution of the Percus–Yevick (PY) integral equation theory for the partial pair distribution function $g_{\alpha\beta}(r)$ provides analytic expressions for the equation of state (e.o.s.) and the Helmholtz free energy F [15] which predict accurate results, compared to available simulation data, for low and moderate packing fractions (say $\eta \lesssim 0.3$), at least for size ratios

$$\xi = \sigma_A/\sigma_B, \tag{3}$$

which are not too small. For higher packing fractions ($0.3 \lesssim \eta \lesssim 0.5$), very accurate thermodynamic properties are provided by the semi-empirical e.o.s. of Boublik [16] and Mansoori *et al.* [17] (BMCSL). The corresponding expression for the reduced excess Helmholtz free energy per particle ($N = N_A + N_B$) reads [17]

$$\begin{aligned} f^{\text{ex}} = \frac{\beta F^{\text{ex}}}{N} = \\ -\frac{3}{2}(1 - y_1 + y_2 + y_3) + (3y_2 + 2y_3)/(1 - \eta) \\ +\frac{3}{2}(1 - y_1 - y_2 - \frac{1}{3}y_3)/(1 - \eta)^2 + (y_3 - 1)\ln(1 - \eta), \end{aligned} \tag{4}$$

where

$$\begin{aligned} y_1 &= \delta\frac{(\sigma_A + \sigma_B)}{(\sigma_A\sigma_B)^{1/2}}, \\ y_2 &= \delta\frac{(\sigma_A\sigma_B)^{1/2}}{\eta}\left(\frac{\eta_A}{\sigma_A} + \frac{\eta_B}{\sigma_B}\right), \\ y_3 &= \frac{(x_A\sigma_A^2 + x_B\sigma_B^2)^3}{(x_A\sigma_A^3 + x_B\sigma_B^3)^2} \end{aligned}$$

and

$$\delta = (\sigma_A\sigma_B)^{1/2}(\sigma_A - \sigma_B)^2\frac{x_A x_B}{x_A\sigma_A^3 + x_B\sigma_B^3}.$$

The BMCSL e.o.s. has been tested by computer simulations of binary hard-sphere mixtures, except for small size ratios ξ where simulations experience ergodicity problems [18,19]. The validity of the free-energy function (4) is thus not established for $\xi \lesssim 0.2$, when the partial packing fractions η_A and η_B are comparable.

Both PY [20] and BMCSL theories predict that additive binary hard-sphere fluids are miscible for all

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size ratios ξ and packing fractions η, in contradiction with later findings, based on self-consistent integral equations [4,5,9], free volume theory [6], density functional theory [7], and simulations [8] which predict a fluid–fluid miscibility gap for sufficiently small size ratios ($\xi < 0.2$) and high packing fractions, i.e. under conditions where the former two theories have not been validated. Since fluid–fluid phase separation appears to be marginal, small inaccuracies in the free energy may be sufficient to suppress segregation. On the other hand it has been shown that a modest degree of non-additivity ($0 < \Delta \ll 1$) is sufficient to drive fluid–fluid demixing, even for fairly symmetric mixtures [3]. For a systematic exploration of the dependence of critical non-additivity as a function of size ratio, over the full range $0 \leq \xi \leq 1$, we have calculated the free energy of a fluid of non-additive hard spheres, using additive hard spheres with the same diameters σ_A and σ_B as a reference system, and the recently developed Mayer f-function thermodynamic perturbation theory [13,14]. Dividing the pair potential between particles into a reference part and a perturbation,

$$v_{\alpha\beta}(r) = v^{(0)}_{\alpha\beta}(r) + w_{\alpha\beta}(r), \tag{5}$$

the standard thermodynamic perturbation theory of Zwanzig amounts to a cumulant expansion of the Helmholtz free energy in 'powers' of the dimensionless perturbations $w_{\alpha\beta}(r)/k_BT$ [21,22]. In the case of non-additive hard spheres characterised by the pair interactions defined in Equations (1) and (2), the perturbation part, which acts only between opposite pairs, is singular

$$w_{AB}(r) = \begin{cases} 0, & r < \frac{1}{2}(\sigma_A + \sigma_B), \\ \infty, & \frac{1}{2}(\sigma_A + \sigma_B) < r < \sigma_{AB}, \\ 0, & r > \sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)(1 + \Delta), \end{cases} \tag{6}$$

which lead to divergent corrections to the free energy. This can be circumvented by an expansion in powers of the Mayer f-function, rather than w_{AB}, namely

$$f_{AB}(r) = \begin{cases} 0, & r < \frac{1}{2}(\sigma_A + \sigma_B), \\ -1, & \frac{1}{2}(\sigma_A + \sigma_B) < r < \sigma_{AB}, \\ 0, & r > \sigma_{AB}. \end{cases} \tag{7}$$

Details of the corresponding expansion of free energy are given in [14]. To first order

$$f = \frac{F}{Nk_BT} = f^{id} + f_0^{ex} + f_1, \tag{8}$$

where f^{id} is the ideal contributions, given within an irrelevant density and concentration independent term, by

$$f^{id} = x_A \ln \eta_A + x_B \ln \eta_B. \tag{9}$$

f_0^{ex} is the excess free energy of the additive reference system, given by Equation (4) within BMCSL theory, while the first-order perturbation is

$$f_1 = -4\pi x_A x_B \rho \int_0^\infty g^{(0)}_{AB}(r) f_{AB}(r) r^2 \, dr, \tag{10}$$

where $g^{(0)}_{AB}(r)$ is the A–B partial pair distribution function of the reference fluid, i.e. of the *additive* binary hard-sphere mixture. The latter can be taken from the analytical solution of the PY equations [15], as given by Kahl and Pastore over the whole range of distances r [23]. Since PY theory becomes unreliable at high packing fractions and for small size ratios ξ, we have used its semi-empirical extension proposed by Grundke and Henderson [24] and subsequent improvements [25]. Details are given in Appendix 1.

The explicit expression for the second-order correction f_2 to the free energy is given in [14]; it involves, in particular, a fluctuation term, which would require a knowledge of the three- and four-body distribution functions of the reference system, and is hence rather intractable. However it was shown in the same paper that the first-order expansion (8) gives very accurate results (compared to simulation data) in the case where $\xi = 1$ and $\Delta = 0.2$, as well as for a one-component hard-sphere fluid, when the diameter is swollen from σ to $\sigma(1 + \Delta)$, with $\Delta \lesssim 0.1$. All calculations reported below were hence based on the first-order expression (8). From our previous experience, we expect convergence of the perturbation theory to be satisfactory, as long as $\Delta < \xi$.

3. Thermodynamic stability of binary mixtures

The conditions of thermodynamic stability of binary mixtures against phase separation are well documented [26,27]. Let $f(x, v)$ be the reduced Helmholtz free energy per particle of an athermal system, an intensive thermodynamic function of the intensive variables $x \equiv x_A$ and $v = 1/\rho$ (total volume per particle). If the binary mixture were incompressible, the condition of thermodynamic stability against concentration fluctuations would reduce to

$$\left(\frac{\partial^2 f(x, v)}{\partial x^2}\right)_v > 0. \tag{11}$$

For a compressible mixture however, the condition of stability against combined concentration and density fluctuations, generalising Equation (11) is [26,27]

$$\left(\frac{\partial^2 f}{\partial v^2}\right)_x \left(\frac{\partial^2 f}{\partial x^2}\right)_v - \left(\frac{\partial^2 f}{\partial v \partial x}\right)^2 > 0, \tag{12}$$

which is easily shown to be equivalent to the more familiar condition for the reduced Gibbs free energy (or free enthalpy) $g(x, P) = f + Pv/k_B T$, namely

$$\left(\frac{\partial^2 g(x,P)}{\partial x^2}\right)_P > 0, \tag{13}$$

where P is the overall pressure of the mixture.

The spinodal associated with fluid–fluid phase separation is determined by turning the inequality (12) into an equality. Switching from the variables x, v to x, $\eta(x, v)$, the equation for the spinodal reads

$$\eta\left(\frac{\partial^2 f}{\partial x^2}\right)_\eta \left(\frac{\partial^2 f}{\partial \eta^2}\right)_x + 2\left(\frac{\partial^2 f}{\partial x^2}\right)_\eta \left(\frac{\partial f}{\partial \eta}\right)_x + 2\eta\Sigma(x)\left(\frac{\partial^2 f}{\partial x \partial \eta}\right)\left(\frac{\partial f}{\partial \eta}\right)_x - \eta\left(\frac{\partial^2 f}{\partial x \partial \eta}\right)^2 - \eta\Sigma^2(x)\left(\frac{\partial f}{\partial \eta}\right)_x^2 = 0, \tag{14}$$

where $\Sigma(x) = (\sigma_A^3 - \sigma_B^3)/(x_A\sigma_A^3 + x_B\sigma_B^3)$.

For the non-additive hard-sphere mixture considered here, the (approximate) free energy function, to be substituted into Equation (14), is given by Equations (4) and (8)–(10). The derivatives of f^{id} and f_0^{ex} are taken analytically, while those of f_1 are calculated numerically. For given values of ξ, η, and Δ, the left-hand side of Equation (14) is calculated for all $x \in [0, 1]$. Δ is then gradually increased (from an initial value of 0) until the stability condition is violated. This determines the critical non-additivity parameter Δ_C required to drive fluid–fluid phase separation. The results of these calculations are presented in the following section.

4. Results and conjectures

We have carried out the calculations laid out in Section 3 for many values of the size ratio ξ, covering the full interval $0 < \xi \leq 1$. The key output is the variation of the critical non-additivity Δ_C with ξ. A similar calculation was carried out in [3], but was based on a very different approximation for the Helmholtz free energy of a binary mixture of non-additive hard spheres. In that paper f was derived from a truncated Barboy–Gelbart expansion of the e.o.s. in powers of the variables $y_\alpha = \rho_\alpha/(1-\eta)$ [28]. The latter reduces to the PY compressibility e.o.s. in the limit of additive hard spheres ($\Delta \to 0$), which is not a particularly good approximation at high packing fractions ($\eta \gtrsim 0.4$), and for small size ratios ξ.

Results for Δ_C as a function of ξ, for a total packing fraction $\eta = 0.5$, from the present calculations based on three different approximations for $g_{AB}^{(0)}(r)$, are compared in Figure 1 to the data from [3]. The general trend is seen to be always the same with Δ_C decreasing sharply with ξ, for $\xi \lesssim 0.5$, in all cases. The results based on the present thermodynamic perturbation theory are sensitive to the reference system (additive hard-sphere mixture) pair distribution function $g_{AB}^{(0)}(r)$: there are significant differences between the $\Delta_C(\xi)$ data obtained with the PY and Grundke–Henderson (GH) pair distribution functions; the GH results are seen to be insensitive to the choice of contact value $g_{AB}^{(0)}\big(r = (\sigma_A + \sigma_B)/2\big)$ [24,25]. None of the theories predicts that $\Delta_C \to 0$ as $\xi \to \xi_u \simeq 0.1$ as expected [5–9]. Note however that Δ_C is systematically very small ($\Delta_C \lesssim 0.01$) in the vicinity of $\xi \simeq 0.1$; in particular $\Delta_C \lesssim 0.1\,\xi$, thus validating first-order thermodynamic perturbation theory as used in the present paper. Another important observation is that $\Delta_C(\xi)$, as calculated within the latter approach using the GH reference pair distribution function, goes in fact through a minimum around $\xi = 0.015$. The Δ_C versus ξ curve for several packing fractions are plotted in Figure 2, while an enlargement restricted to the range $\xi \leq 0.1$ is shown in Figure 3. Figure 2 shows that for a given ξ, Δ_C decreases with increasing η, in other words a larger degree of non-additivity is required to drive phase separation at lower packing fractions. Figure 3 shows the behaviour for $\xi \leq 0.15$ and $0.35 \leq \eta \leq 0.5$. All $\Delta_C(\xi)$ curves go through a minimum for $\xi \simeq 0.015$, before increasing sharply as ξ decreases further towards zero. At the minimum Δ_C is roughly equal to $\xi/2$, but upon decreasing ξ further, $\Delta_C(\xi)$ rapidly

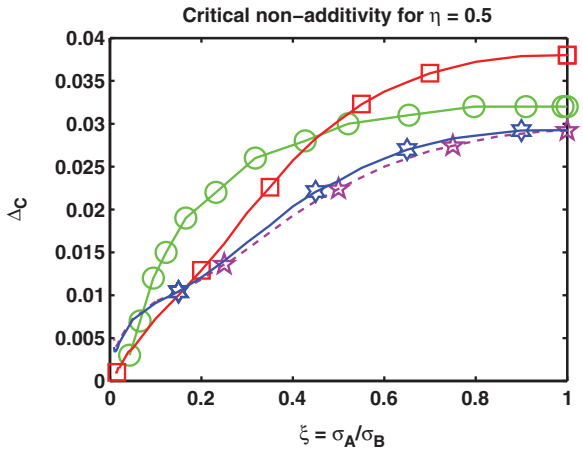

Figure 1. Critical non-additivity, Δ_C, versus size ratio ξ obtained using different approximations; circles: data from [3]; squares: results from first-order perturbation theory, using $g_{AB}(r)$ from [23]; hexagrams: results from first-order perturbation theory, using $g_{AB}(r)$ from [24]; pentagrams: results from first-order perturbation theory, using $g_{AB}(r)$ from [24] with improvement from [25].

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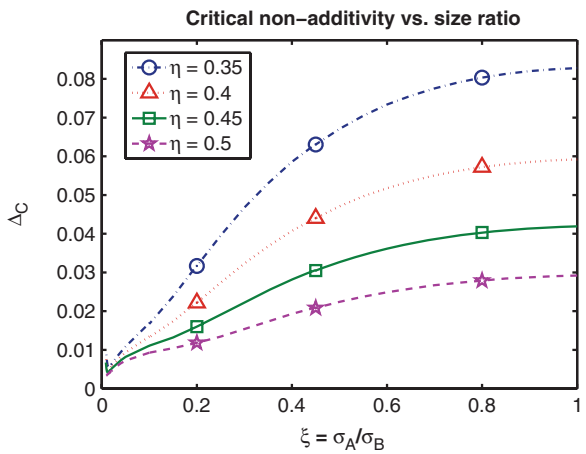

Figure 2. Critical non-additivity Δ_C versus size ratio ξ for several values of the total packing fraction η, calculated using the GH reference system pair distribution functions.

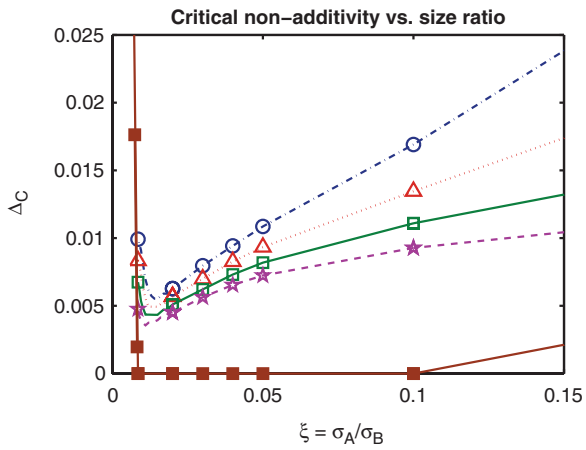

Figure 3. Enlargement of the curves in Figure 2 for small size ratios $\xi < 0.15$. The curve with the full squares is the curve for $\eta = 0.45$ (open squares) shifted downward, such that $\Delta_C(\xi = 0.1) = 0$.

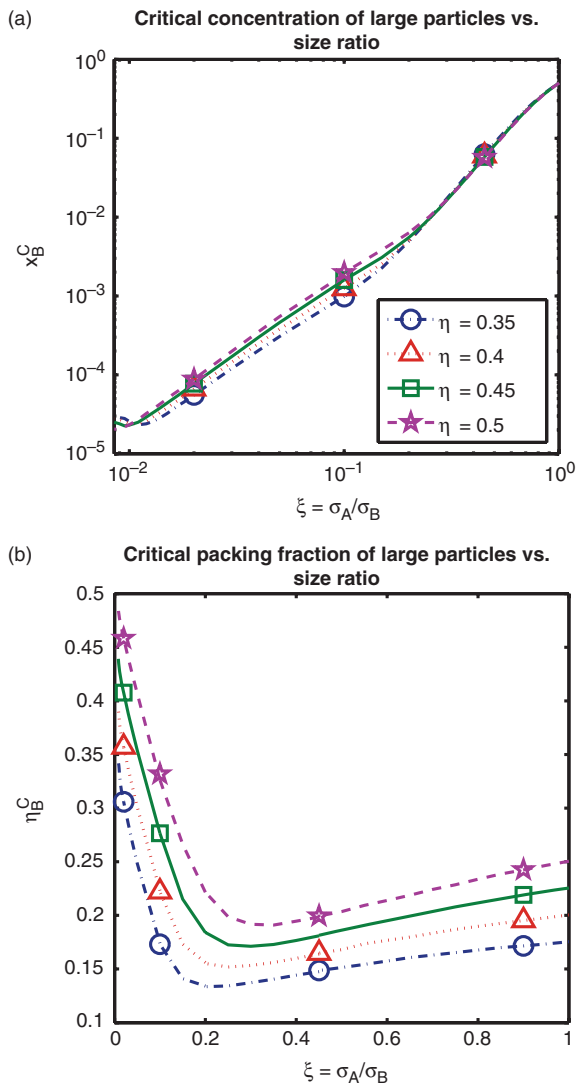

Figure 4. (a) Critical concentration x_B^C of large spheres versus size ratio ξ for several values of the total packing fraction η. (b) Corresponding critical packing fractions η_B^C versus ξ.

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becomes comparable to or larger than ξ, such that the first-order expression (8) of the free energy can no longer be expected to be valid. The break-down of the truncated thermodynamic perturbation theory is illustrated by the appearance of an unphysical maximum in $\Delta_C(\xi)$ for $\xi < 0.01$, whereas Δ_C is expected to grow as $\xi \to 0$. The value of Δ_C for $\xi = 0$ (i.e. a mixture of hard spheres and point particles) can be easily estimated by adapting the free volume theory of [4] and [11] to this special case as sketched in Appendix 2. The theory predicts $\Delta_C \simeq 0.17$ for the onset of fluid–fluid phase separation when $\xi = 0$ (Asakura–Oosawa model). We thus expect Δ_C to increase from its minimum value $\simeq 0.005$ to $\Delta_C \simeq 0.17$ in the narrow interval between $\xi \simeq 0.015$ and $\xi = 0$.

The variation of the critical concentration x_B^C and of the packing fraction η_B^C of the large spheres with size ratio ξ are plotted in Figures 4(a) and (b) for several values of the total packing fraction η. x_B^C is seen to drop sharply with ξ by nearly 4 orders of magnitude between $\xi = 1$ and $\xi = 0.01$, and to depend little on η. The variation of η_B^C with ξ is

non-monotonic. η_B^C first decreases slowly with ξ, goes through an η-dependent minimum around $\xi \simeq 0.25$, before increasing sharply to its limiting value $\eta_B^C(\xi = 0) = \eta$ (the contribution of the point particles to the total packing fraction is zero).

Since $\Delta_C > 0$ for all ξ, the present theory fails to predict the phase separation of additive hard-sphere mixtures for $\xi \lesssim 0.1$. This failure may of course be traced back to the use of the BMCSL free energy (4) for the reference system of additive hard spheres, which predicts full miscibility for all compositions and size ratios. However the very small values of Δ_C predicted to drive phase separation hint that BMCSL theory barely 'misses' the expected demixing transition, due to a small error in the free energy for small size ratios ξ. A heuristic procedure to compensate for this small inaccuracy of the BMCSL free energy is to shift the $\Delta_C(\xi)$ curves downwards, such that $\Delta_C = 0$ for $\xi = 0.1$ and $\eta = 0.45$, as predicted by the MC simulations of [8]. The tentative 'corrected' $\Delta_C(\xi)$ curve for $\eta = 0.45$ is shown in Figure 3, where negative values of $\Delta_C(\xi)$ are replaced by $\Delta_C = 0$. This speculative construction suggests that Δ_C takes on non-vanishing positive values for $\xi \lesssim 0.01$, i.e. a miscibility gap in a dense ($\eta \gtrsim 0.45$) binary mixture of additive hard spheres is only expected over a narrow range of size ratios $0.01 \lesssim \xi \lesssim 0.1$.

5. Conclusions

The key speculative prediction of the present paper is that highly asymmetric binary mixtures of additive hard spheres undergo a fluid–fluid phase separation for size ratios ξ in the range $0.01 \lesssim \xi \lesssim 0.1$ and for sufficiently high packing fractions. We have reached this conclusion, or rather conjecture, by an indirect approach, starting from binary mixtures of hard spheres with non-additive diameters, as defined in Equations (6) or (7), and using a version of thermodynamic perturbation theory adapted to singular (hard core) perturbations [13,14]. A modest degree of non-additivity ($\Delta < 0.1$) will drive phase separation for any size ratio ξ. As already shown in [3], using a different theoretical approach, the critical non-additivity parameter Δ_C required to drive fluid–fluid phase separation at a given value of the total packing fraction η, decreases with decreasing ξ, but never goes to zero (which would correspond to an additive hard-sphere mixture) because the free energy of the additive reference system is always a convex function of the thermodynamic variables. However Δ_C is found to go through a positive minimum as a function of ξ, reaching very small values of the order of 0.005, suggesting that the BMCSL free energy barely misses the thermodynamic instability associated with demixing. Since advanced integral equation theories [4,5,9], free volume theory [6] and MC simulations [8] all predict phase separation for sufficiently small ξ, we have shifted our predicted $\Delta_C(\xi)$ curves downward, such that $\Delta_C = 0$ for $\xi = 0.1$ and $\eta \simeq 0.45$ in agreement with the MC results of [8].

The second key finding of our work is that $\Delta_C(\xi)$ goes through an η-dependent minimum for $\xi \simeq 0.015$, before increasing sharply as $\xi \to 0$, where Δ_C is expected to reach its limiting value $\Delta_C(\xi = 0) \simeq 0.17$ predicted by free volume theory [11] (Appendix 2). The heuristic downward shift of the $\Delta_C(\xi)$ curves (by an amount $\delta(\Delta_C) \simeq -0.01$) then leads to $\Delta_C(\xi) = 0$ for $\xi \simeq 0.01$ at the lower end. Thermodynamic perturbation theory combined with the heuristic shift of the $\Delta_C(\xi)$ curve hence leads to the conjecture that fluid–fluid phase separation is restricted to the limited range of size ratios $0.01 \lesssim \xi \lesssim 0.1$. The shifted $\Delta_C(\xi)$ function takes negative values in that interval, raising the intriguing possibility that highly asymmetric binary hard-sphere systems might demix, even for (slightly) negative values of the non-additivity parameter Δ, which always favour miscibility. This tendency is hence compensated by a stronger tendency towards segregation induced by a large size asymmetry.

The present calculations do not consider binary hard-sphere solid phases, and the possibility of the coexistence of fluid and solid phases of different compositions. Fluid–solid phase separation has been shown to pre-empt fluid–fluid segregation, which is hence a metastable phase transition [8]. However, as mentioned earlier in this paper, the fluid–fluid phase separation might be observable, provided the crystal nucleation kinetics is sufficiently low. Possible candidates for the observation of fluid–fluid demixing are binary dispersions of sterically stabilised colloidal particles ($\sigma \simeq 10$–100 nm) and nanoparticles or micelles ($\sigma \simeq 1$–5 nm).

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Appendix 1. The pair distribution function of the reference system

For the pair distribution function $g_{\mathrm{AB}}^{(0)}(r)$ of the reference system, i.e. of a binary mixture of additive hard spheres, we have used either the piece-wise analytical PY solution [15,23] or the semi-empirical improvement due to Grundke and Henderson [24], namely

$$g_{\mathrm{AB}}^{(0)}(r|\eta, x_{\mathrm{A}}, \sigma_{\mathrm{A}}, \sigma_{\mathrm{B}}) = \Theta(r-\sigma_{\mathrm{AB}}) \times \left(g_{\mathrm{PY}}(r|\eta, x_{\mathrm{A}}, \sigma'_{\mathrm{A}}, \sigma'_{\mathrm{B}}) + \frac{A\sigma_{\mathrm{AB}}}{r}\exp[-b(r-\sigma_{\mathrm{AB}})] \times \cos\left(b(r-\sigma_{\mathrm{AB}})\right)\right). \tag{15}$$

The Heaviside step function Θ ensures that the pair distribution function vanishes inside the core ($r<\sigma_{\mathrm{AB}}$). The rescaled radii $\sigma'_A = \sigma_{\mathrm{A}}(1-\eta/16)^{1/3}$ and $\sigma'_B = \sigma_{\mathrm{B}}(1-\eta/16)^{1/3}$ shift the phase of the oscillating pair distribution function slightly compared to the PY solution. The prefactor A of the second term on the r.h.s. of Equation (15) allows one to adjust the contact value of $g_{\mathrm{PY}}(r)$ which is too low:

$$A = g_{\mathrm{AB}}^{(0)}(\sigma_{\mathrm{AB}}|\eta, x_{\mathrm{A}}, \sigma_{\mathrm{A}}, \sigma_{\mathrm{B}}) - g_{\mathrm{PY}}(\sigma_{\mathrm{AB}}|\eta, x_{\mathrm{A}}, \sigma'_{\mathrm{A}}, \sigma'_{\mathrm{B}}), \tag{16}$$

where $g_{\mathrm{AB}}^{(0)}(\sigma_{\mathrm{AB}}|\eta, x_{\mathrm{A}}, \sigma_{\mathrm{A}}, \sigma_{\mathrm{B}})$ is determined by the BMCSL equation of state [16,17] or by a further improvement which is expected to be more accurate for small size ratios ξ [25]. The inverse length b in the second term of the r.h.s. of Equation (15) is determined as explained in the GH paper [24], using the exact relation:

$$\begin{aligned}\frac{k_{\mathrm{B}}T}{\rho_{\mathrm{A}}}\frac{\partial\rho_{\mathrm{A}}}{\partial\mu_{\mathrm{B}}} &= 4\pi\rho_{\mathrm{B}}\int_0^\infty \left[g_{\mathrm{AB}}^{(0)}(r|\eta, x_{\mathrm{A}}, \sigma_{\mathrm{A}}, \sigma_{\mathrm{B}}) - 1\right]r^2\,\mathrm{d}r \\ &= 4\pi\rho_{\mathrm{B}}\int_0^\infty \left[g_{\mathrm{PY}}(r|\eta, x_{\mathrm{A}}, \sigma'_{\mathrm{A}}, \sigma'_{\mathrm{B}}) - 1\right]r^2\,\mathrm{d}r \\ &\quad + 2\pi A\rho_{\mathrm{B}}\sigma_{\mathrm{AB}}^2/b,\end{aligned} \tag{17}$$

where the l.h.s. is calculated from the BMCSL free-energy function.

Appendix 2. Free volume calculation of Δ_{C} in the $\xi = 0$ limit

Lekkerkerker *et al.* [11] used free volume theory to calculate the full phase diagram of the AO model for mixtures of hard-sphere colloids and ideal polymers. This model is a limiting case of a binary mixture of non-additive hard spheres considered in the present paper, when $\xi = \sigma_{\mathrm{A}}/\sigma_{\mathrm{B}} = 0$. They found coexistence between a low density fluid phase and a high density crystal phase with different compositions, for $\Delta \lesssim 0.32$. For larger non-additivities a fluid–fluid–solid triple point and a fluid–fluid critical point appear. We have adapted their calculation to determine the critical non-additivity parameter Δ_{C} beyond which a metastable fluid–fluid phase separation appears. The colloidal B particles of diameter σ_{B} are not affected by the presence the point A particles, and hence their contribution to the reduced free energy per particle $f = F/Nk_{\mathrm{B}}T$ is accurately given by the Carnahan–Starling free energy, which is the one-component version of the BMCSL free energy (4), namely (including the ideal contribution):

$$f_{\mathrm{C}} = F_{\mathrm{B}}(N_{\mathrm{C}}, V)/Nk_{\mathrm{B}}T = x_{\mathrm{B}}\left[\ln(\eta) + \frac{\eta(4-3\eta)}{(1-\eta)^2}\right], \tag{18}$$

where $\eta \equiv \eta_{\mathrm{B}} = N_{\mathrm{B}}\pi\sigma_{\mathrm{B}}^3/6V$.

The point A particles are excluded from a sphere of diameters $\sigma_B + \Delta$ centred on each of the B particles. The *mean* volume $V' < V$ accessible to the point particles can be calculated using Widom's insertion theorem [29] with the result [4,11]:

$$\begin{aligned} V' &= \alpha V \\ \alpha &= (1-\eta)\exp(-A\gamma - B\gamma^2 - C\gamma^3), \end{aligned} \tag{19}$$

where $\gamma = \eta/(1-\eta)$; $A = 3\Delta + 3\Delta^2 + \Delta^3$, $B = 9/2\Delta^2 + 3\Delta^3$, and $C = 3\Delta^3$.

Since the A particles do not mutually interact their contribution to the free energy is purely ideal, i.e. (with $\rho'_A = N_A/V'$)

$$f_A = x_A \ln(\rho'_A) = x_A \ln(\rho_A/\alpha). \tag{20}$$

If $f = f_A + f_B$ is substituted into Equation (13) we find that spinodal instability first appears when $\Delta = \Delta_C \simeq 0.17$, in the fluid range $\eta \leq 0.5$.

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