

Demixing in a single-peak distributed polydisperse mixture of hard spheres

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Abstract. – An analytic derivation of the spinodal of a polydisperse mixture is presented. It holds for fluids whose excess free energy can be accurately described by a function of a few moments of the size distribution. It is shown that one such mixture of hard spheres in the Percus-Yevick approximation never demixes, despite its size distribution. In the Boublík-Mansoori-Carnahan-Starling-Leland approximation, though, it demixes for a sufficiently wide log-normal size distribution. The importance of this result is twofold: first, this distribution is unimodal, and yet it phase separates; and second, log-normal size distributions appear in many experimental contexts. The same phenomenon is shown to occur for the fluid of parallel hard cubes.

Our knowledge of the phase behavior of mixtures has increased a lot in the last decade. Generally speaking, above a certain concentration binary mixtures phase separate due to the so-called depletion effect [1]. This mechanism has an entropic origin: mixtures phase separate when this produces a sufficient gain in free volume to increase the entropy of the system. More intuitively, depletion is an effective attraction arising from the unbalanced pressure resulting when two solute particles are so close together that no solvent particle fits in between them. Either way we look upon it, in real colloids this mechanism is supplemented by energetic attractions or repulsions that enhance or inhibit the transition. In order to ascertain to which extent depletion is the basic mechanism of demixing, considerable effort has been focused on additive hard particle mixtures, which are free of energetic interactions.

Binary hard spheres (HS), the simplest hard-particle mixture, have proven very controversial in settling the question on the entropic nature of demixing. More than thirty years ago Lebowitz and Rowlinson [2] showed that according to the Percus-Yevick (PY) solution of the Ornstein-Zernike equation binary HS never demix; a few years later Vrij [3] extended this result

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to p -component HS mixtures in the same approximation. However, the PY approximation has a well-known thermodynamic inconsistency, as it yields two different equations of state, none of which being very accurate at large densities. It is also well known that a linear interpolation of both produces a rather accurate equation of state; in the case of mixtures, the latter is known as the BMCSL equation of state [4,5]. In spite of its higher accuracy, the authors showed that it predicts the stability of any binary mixture.

The BMCSL equation of state is heuristic in its construction, so this led Biben and Hansen [6] to consider the more accurate Rogers-Young closure approximation. In this way they found signs of a spinodal instability for diameter ratios of the HS smaller than 0.2. Several authors [7,8] subsequently confirmed that other approximate schemes yield the same instability, although for diameter ratios strongly dependent on the approximation. It was hence believed that phase separation does occur in sufficiently asymmetric binary mixtures of HS, an idea further supported by the demixing found in binary mixtures of parallel hard cubes (PHC) both in computer simulations on a lattice [9] and from fundamental measure theory [10] in continuum space.

Presently a different scheme is being accepted to describe demixing of very asymmetric binary mixtures of hard particles [11]: phase separation occurs between a small-particle-rich fluid and a large-particle-rich crystal [12-18], and this coupling with the translational degrees of freedom strongly enhances demixing. It may even cause, for very large asymmetry, the appearance of an isostructural solid-solid transition [15-17] as that found for narrow and deep attractive potentials—the reason being that depletion induces one such potential between the large particles [15-17,19].

But colloids are hardly mono or bidisperse. By their very nature, colloidal particles are usually different from each other, and the preparation process of a colloidal suspension gives rise to a size distribution of particles in the colloid. Hence colloids are best modeled as polydisperse systems. Polydispersity has received increasing attention in the past years [20-28] because it causes strong qualitative effects on the phase behavior of the monodisperse counterpart. Termination of the freezing transition of a HS fluid [22,23], regularization of adhesive potentials [27,17], or appearance of a vapor-liquid transition in adhesive HS [28] are but a few examples.

Phase equilibrium in polydisperse systems is more complicated than in monodisperse systems: equilibrium equations between coexisting phases become functional equations when polydispersity is present [20,21]. Much of the effort has indeed concentrated in taking advantage of extra symmetries (as the dependence of the excess free energy on the moments of the distribution [25,26]), in mapping the polydisperse system into a simpler one (*e.g.* a binary mixture [23]), or in treating polydispersity as a perturbation of a reference fluid [24], with the purpose of reducing equilibrium to a few algebraic equations. Specifically, by means of a moment-based formalism Warren [29] has shown that while a binary fluid of HS in the BMCSL approximation never demixes, it does so if enough polydispersity is introduced and the diameter ratio of the two “main” species is sufficiently small. This unexpected result proves that the effect of polydispersity can be more subtle and nontrivial than one can tell *a priori*.

In this letter I will push this result much further. Though polydisperse, Warren’s system has two clearly differentiated species. I will show that for demixing to occur this is not necessary if the size distribution decays sufficiently slowly. Again using a moment-based formalism (equivalent to Warren’s but based on different grounds) to obtain a spinodal of an arbitrary mixture (with several species, polydisperse, or both), I will prove that BCSML polydisperse HS with a *log-normal* size distribution (*i.e.* the logarithm of the diameters follows a normal distribution) phase separate provided the standard deviation of the distribution is above a threshold. This result is surprising because one such distribution is unimodal. It is thus clear that the long-size tail plays a crucial role in inducing demixing, but although slowly decaying,

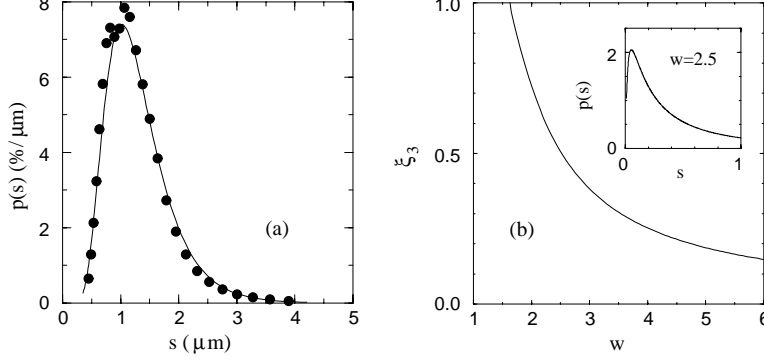


Fig. 1. – (a) Distribution, $p(s)$ (in percentage per μm), of diameters, s (in μm), for a suspension of *mullite* ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), a ceramic powder used in structural ceramic applications. Bullets are the experimental data; the line is a fit of a log-normal distribution of mean $\bar{x} = 1.57 \mu\text{m}$ and standard deviation $w = 0.43\bar{x}$. (Experimental data courtesy of R. Moreno, Instituto de Cerámica y Vidrio, CSIC, Madrid, Spain.) (b) Volume fraction, ξ_3 , as a function of the standard deviation of the log-normal size distribution, w , at which a spinodal instability appears. Inset: size distribution for the particular value $w = 2.5$.

this tail decays faster than any power law. In addition, it is important to stress that, contrary to what one might believe, log-normal distributions are very common in many polydisperse systems: ultrafine metal particles, paint and rubber pigments, photographic emulsions, dust particles, aerosols, cloud droplets, or suspensions of ceramic powders (see [30] and references therein; see also fig. 1(a)), are a few examples. Therefore this effect should be experimentally accessible, provided any of these systems can be prepared with sufficiently large size dispersion.

In what follows I will briefly describe the formalism to obtain the spinodal in the case that the excess free energy of a mixture depends on a few moments of the size distribution. Then I will apply this formalism to polydisperse HS and PHC in scaled particle approximation (equivalent to PY in the case of HS), and I will finally prove the above-mentioned result.

Suppose we have a multicomponent hard particle mixture, whose free energy per unit volume is $f \equiv \beta F/V = f^{\text{id}} + f^{\text{ex}}$, with $f^{\text{id}} = \sum_i \rho_i [\ln \mathcal{V}_i \rho_i - 1]$, \mathcal{V}_i the thermal volume of species i , β the reciprocal temperature (in units of the Boltzmann constant), and ρ_i the number density of species i . Let us further assume that $f^{\text{ex}} = \phi(\xi)$, ξ denoting the set of moments $\{\xi_0, \xi_1, \dots, \xi_p\}$, where $\xi_k = \sum_i \sigma_i^k \rho_i$ (σ_i is the diameter of species i). Stability of the mixture requires f to be a convex function in all of its variables. As in any hard particle system f depends on temperature through an additive term (the free energy of the ideal gas) and hence it is always convex with respect to this variable. The study of stability is thus restricted to the set of densities of the species involved. If we define the matrix

$$M_{ij} \equiv \frac{\partial^2 f}{\partial \rho_i \partial \rho_j} = \frac{1}{\rho_i} \delta_{ij} + \frac{\partial^2 \phi}{\partial \rho_i \partial \rho_j}, \quad (1)$$

then stability requires it to be positive definite. As it is so for low densities (ideal mixtures are always stable) the spinodal is usually described as the set of points in the densities space where $\det M = 0$ [2, 31]. This condition is equivalent to M having a zero eigenvalue, *i.e.* $M \cdot \mathbf{u} = 0$ for some vector $\mathbf{u} \neq 0$. Let us define for convenience a new vector \mathbf{e} as $u_i = \rho_i e_i$; then $M \cdot \mathbf{u} = 0$

means

$$e_i = - \sum_j \frac{\partial^2 \phi}{\partial \rho_i \partial \rho_j} \rho_j e_j. \quad (2)$$

For a polydisperse mixture, if $\rho(s) = \rho p(s)$, where ρ is the total number density of particles and $p(s)$ is the size probability distribution (in terms of a dimensionless diameter s , for instance), $f^{\text{id}} = \int ds \rho(s) [\ln \mathcal{V}(s) \rho(s) - 1]$ [20], $\xi_k = \int ds s^k \rho(s)$, but f^{ex} is still assumed to be of the form $f^{\text{ex}} = \phi(\xi)$. The stability condition is now the positive definiteness of the integral operator whose kernel is defined by

$$\mathcal{M}(s, t) \equiv \frac{\delta^2 f}{\delta \rho(s) \delta \rho(t)} = \frac{1}{\rho(s)} \delta(s-t) + \frac{\delta^2 \phi}{\delta \rho(s) \delta \rho(t)}. \quad (3)$$

While the determinant condition has no direct equivalent for an integral operator, the zero-eigenvalue one is a straightforward extension of (2):

$$e(s) = - \int dt \frac{\delta^2 \phi}{\delta \rho(s) \delta \rho(t)} \rho(t) e(t). \quad (4)$$

But we can simplify this equation by using

$$\frac{\delta^2 \phi}{\delta \rho(s) \delta \rho(t)} = \sum_{k,l=0}^p \frac{\partial^2 \phi}{\partial \xi_k \partial \xi_l} s^k t^l, \quad (5)$$

which transforms eq. (4) into

$$e(s) = - \sum_{k,l=0}^p \Phi_{kl} s^k \alpha_l, \quad \Phi_{kl} \equiv \frac{\partial^2 \phi}{\partial \xi_k \partial \xi_l}, \quad (6)$$

where $\alpha_l = \int ds s^l \rho(s) e(s)$. Substitution of eq. (6) into the latter definition yields⁽¹⁾

$$\alpha_n = - \sum_{k,l=0}^p \xi_{n+k} \Phi_{kl} \alpha_l. \quad (7)$$

For this equation to have nonzero solutions for α , we must have $\det \mathbf{Q} = 0$, with

$$\mathbf{Q}_{mn} \equiv \delta_{mn} + \sum_{k=0}^p \xi_{m+k} \Phi_{kn}, \quad m, n = 0, \dots, p. \quad (8)$$

For convenience we introduce the variables $y_k \equiv \xi_k / (1 - \xi_3)$ and define two new matrices, \mathbf{Y} and $\mathbf{\Omega}$, by $\mathbf{Y}_{mn} \equiv y_{m+n}$ and $\mathbf{\Omega} \equiv (1 - \xi_3) \mathbf{\Phi}_{mn}$. Then the condition reads $\mathcal{D} \equiv \det (\mathbb{I} + \mathbf{Y} \cdot \mathbf{\Omega}) = 0$, with \mathbb{I} the identity matrix.

Many scaled-particle theories can be written [10, 32, 33]

$$\phi = -\xi_0 \ln(1 - \xi_3) + A \frac{\xi_1 \xi_2}{1 - \xi_3} + B \frac{\xi_2^3}{(1 - \xi_3)^2}. \quad (9)$$

(Notice that if ϕ and ξ_k are all multiplied by the same constant the product $\mathbf{Y} \cdot \mathbf{\Omega}$ remains invariant, so we will assume these variables defined up to a constant.) For this particular

⁽¹⁾ This result can also be obtained, by the same procedure, from eq. (2), and so is valid for both multicomponent and polydisperse mixtures (or a combination of both).

choice of ϕ we will have

$$\Omega = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & A & Ay_2 \\ 0 & A & 6By_2 & Ay_1 + 6By_2^2 \\ 1 & Ay_2 & Ay_1 + 6By_2^2 & y_0 + 2Ay_1y_2 + 6By_3^3 \end{pmatrix}. \quad (10)$$

It is then straightforward to check that

$$\mathcal{D} = \frac{[1 + (1 - A)\xi_3]^2 + (6B - A^2)\xi_2\xi_4}{(1 - \xi_3)^4}, \quad (11)$$

where we have replaced the y 's in terms of the ξ 's. We are now ready to discuss specific cases.

Percus-Yevick HS correspond to choosing $A = 3$, $B = 3/2$ (definitions of ϕ and ξ_k carry an extra $\pi/6$ factor); then $\mathcal{D} = (1 + 2\xi_3)^2/(1 - \xi_3)^4$, the result obtained by Lebowitz and Rowlinson [2] for the binary mixture and later generalised by Vrij [3] for a multicomponent mixture. The validity of this result has now been extended for a polydisperse mixture (see footnote ⁽¹⁾).

Scaled-particle free energy for PHC is given by [10, 32] $A = 3$, $B = 1$. Then

$$\mathcal{D} = [(1 + 2\xi_3)^2 - 3\xi_2\xi_4]/(1 - \xi_3)^4. \quad (12)$$

By a suitable choice of ξ_2 and ξ_4 we can make $\mathcal{D} = 0$. If we consider a binary mixture we recover the result of ref. [10]. By defining $m_k \equiv \xi_k/\xi_3$, the mixture of PHC in this approximation will be stable provided $K(\xi_3) > m_2m_4$, where $K(\xi_3) \equiv (1 + 2\xi_3)^2/(3\xi_3^2)$. The function $K(x)$ diverges at $x = 0$ and it monotonically decreases to 3 as ξ_3 approaches 1. Then $m_2m_4 > 3$ is the condition to find demixing, and the larger the product m_2m_4 the smaller the value of ξ_3 at which it appears.

Schulz distribution is a common choice in studying polydispersity [20]. If the mean is set to 1, it can be written as

$$p(s) = w^{-2}\Gamma(w^{-2})(w^{-2}s)^{w^{-2}-1}e^{-w^{-2}s}, \quad (13)$$

with $0 < w < 1$ the standard deviation. Its moments are $\xi_n = \rho \prod_{k=0}^{n-1} (1 + kw^2)$ for $n \geq 1$, so $m_2m_4 = (1 + 3w^2)/(1 + 2w^2) < 4/3$. Therefore there is no demixing for such a distribution. It is easy to check that there is no demixing either for a uniform distribution in any interval of diameters. However if we consider a log-normal distribution with mean 1 and standard deviation $0 < w < \infty$,

$$p(s) = \frac{1 + w^2}{\sqrt{2\pi \ln(1 + w^2)}} \exp \left[-\frac{\ln^2[(1 + w^2)^{3/2}s]}{2 \ln(1 + w^2)} \right], \quad (14)$$

whose moments are given by $\xi_n = \rho(1 + w^2)^{n(n-1)/2}$, then $m_2m_4 = 1 + w^2$, which, by increasing w , can be made arbitrarily large. There is thus demixing for a log-normal distribution provided $w > \sqrt{2}$.

The latter result rises the question whether the same occurs for BMCSL HS. In this case the free energy is given by [20]

$$\phi = \left(\frac{\xi_2^3}{\xi_3^2} - \xi_0 \right) \ln(1 - \xi_3) + \frac{3\xi_1\xi_2}{1 - \xi_3} + \frac{\xi_2^3}{\xi_3(1 - \xi_3)^2}, \quad (15)$$

where, as in PY, ϕ and ξ_k are defined with an extra $\pi/6$ factor. The resulting expression for \mathcal{D} with the moments replaced by those of a log-normal distribution is a complicated formula relating the volume fraction, ξ_3 , and the standard deviation, w ; nevertheless, the spinodal can be numerically determined (fig. 1(b)). It can be seen that the threshold standard deviation for demixing is $w \approx 1.6$. The inset shows the size distribution for a value of w for which the spinodal occurs at liquid densities, in order to illustrate the long tail at large particle sizes. Comparing with fig. 1(a) and with the figures of ref. [30] we can see that standard experimental samples are still far from reaching the spinodal.

Before concluding I want to make two remarks concerning the observability of this demixing in real systems.

One question is how much can we trust the results obtained with the BMCSL approximation, considering for instance that, according to it, a binary mixture of hard spheres is always stable, while simulations show that a (metastable) fluid-fluid spinodal exists for sufficient asymmetry of the components [16]. We are then forced to conclude two things: (a) the predicted fluid-fluid demixing is very sensitive to the equation of state we use, and (b) the BMCSL approximation overestimates the stability of a mixture. Therefore, if the conclusion of this letter is regarded as qualitative rather than as an accurate prediction, we can infer that log-normally distributed polydisperse hard-sphere mixtures must be unstable in a region of the phase diagram which at least contains that obtained from the BMCSL approximation. So the phenomenon occurs in spite that the true spinodal will most likely not coincide with the one shown in fig. 1(b).

The second question concerns freezing. Again if we take the example of a binary mixture we can see that a fluid-solid demixing largely preempts the fluid-fluid one [15-17], and if this were also the case for our polydisperse fluid it would imply that the demixing reported here would just be metastable. This conclusion seems supported by a recent work of Sear [34] in which the author suggests that if the size distribution is sufficiently long-tailed (*e.g.*, the log-normal) the biggest particles will freeze in several highly packed solid phases *regardless the density of the mixture*. This singular phase behaviour is known to occur in adhesive fluids [17], and the reason for this connection is the similarity between the depletion potential experienced by the biggest spheres and the adhesive one [34]. However, polydispersity makes things more complex. Only very big particles will experience this effect (how big is not precised in ref. [34]), but big particles contribute very little to the first moments of the distribution; in other words, the coexisting fluid (now deficient in those biggest particles) may be described by almost the same moments, and thus still be unstable above a certain density. So again the demixing here reported may be observable after the biggest particles have precipitated forming crystals.

In summary, I have introduced a simple formalism to compute the spinodal of fluids whose excess free energy can be described as a function of a few moments of the size distribution of a mixture. By means of this formalism I have proven that a polydisperse mixture of PY HS never demixes despite its size distribution. I have also shown that a polydisperse mixture of PHC may demix only if the size distribution is long-tailed at large sizes, as for instance a log-normal distribution. More importantly, polydisperse BMCSL HS, also log-normally distributed, do demix for a sufficiently large standard deviation. Remarkably, log-normal distributions have a single characteristic size, so the driving mechanism of the transition in these systems is not as clearcut as in the case of binary mixtures. Finally, sizes in many polydisperse systems are log-normally distributed. Present experimentally available systems, though, are far from the

spinodal as predicted by this work. I hope that this result encourages experimental work to achieve this limit and verify the conclusions reported here.

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