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J.L. Barrat, J.P. Hansen. On the stability of polydisperse colloidal crystals. *Journal de Physique*, 1986, 47 (9), pp.1547-1553. 10.1051/jphys:019860047090154700 . jpa-00210354

HAL Id: jpa-00210354

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Submitted on 4 Feb 2008

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Classification

Physics Abstracts

05.20 — 64.70D — 82.70

On the stability of polydisperse colloidal crystals

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(Reçu le 24 février 1986, accepté le 16 mai 1986)

Résumé. — Le formalisme de la fonctionnelle de la densité est appliqué à l'étude de la stabilité mécanique et thermodynamique de cristaux colloïdaux polydispersés. Les particules colloïdales sont assimilées à des sphères dures avec une distribution continue, $p(\sigma)$, de diamètres additifs. On montre que de telles solutions solides cessent d'être stables au-delà d'un degré de polydispersité critique, qui dépend de la forme de $p(\sigma)$, mais est toujours de l'ordre de 20 %. Le problème de la détermination de la courbe de coexistence fluide-solide est brièvement évoqué.

Abstract. — The recently developed density functional theory of freezing is applied to an investigation of the mechanical and thermodynamic stability of polydisperse colloidal crystals. The colloidal particles are modelled by hard spheres with a continuous distribution $p(\sigma)$ of additive diameters. It is shown that such solid solutions cease to be stable beyond a critical degree of polydispersity, which depends somewhat on the shape of $p(\sigma)$, but is always of the order of 20 %. The problem of determining the fluid-solid coexistence curve is also briefly examined.

1. Introduction.

Dispersions of colloidal particles, like silica or polystyrene spheres, are known to undergo a « disorder-order » transition from a disordered fluid phase to an ordered crystal structure when the volume fraction of the particles or the electrolyte concentration in the solvent are varied [1]. The resulting phase diagram for monodisperse suspensions has been extensively analysed theoretically [1], generally on the basis of the standard DLVO model for the interactions between colloidal particles in charge-stabilized dispersions [2]. However rather little effort has gone into assessing the influence of the unavoidable polydispersity of particle diameters on the fluid-solid phase transition and on the stability of the colloidal crystal. The only available information comes from the molecular dynamics simulations of small samples of 108 colloidal particles due to Dickinson and co-workers [3]. The main conclusion of that work is that polydispersity favours disorder, as one would intuitively expect, and that the ordered phase disappears altogether above a certain critical degree of polydispersity. For a triangular distribution of diameters, an extrapolation of the simulation data predicts the critical degree of polydispersity to be about 27 % [4].

In this paper we examine the stability of polydisperse « solid solutions » in the framework of the modern density functional theory of freezing [5]. The polydisperse generalization of the theory is formulated in section 2 and specialized to the case of hard sphere mixtures in section 3. This specialization is necessary since detailed theoretical information on the pair structure of multicomponent fluids, a fundamental ingredient in the density functional theory, is available only for the hard sphere model [6]. Results on the stability of the polydisperse solid phase are given in section 4 for triangular and rectangular distributions of diameters and various degrees of polydispersity. The theoretical problems associated with the determination of fluid-solid coexistence of polydisperse systems are finally discussed in section 5.

2. Density functional formulation.

We consider a polydisperse suspension of spherical colloidal particles with diameters σ distributed according to a given normalized distribution $p(\sigma)$. Let $\rho = N/V$ be the total number of particles per unit volume. It will prove convenient to introduce the following moments of the distribution of diameters :

$$\xi_n = \rho \int_0^\infty p(\sigma) \sigma^n d\sigma. \quad (1)$$

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In particular the volume (or packing) fraction of the particles is :

$$\eta = \frac{\pi}{6} \xi_3. \quad (2)$$

In the uniform fluid phase the local density $\rho_\sigma(\mathbf{r})$ of particles of diameters σ is everywhere equal to $\rho_\sigma^0 = \rho p(\sigma)$, while this density has the periodicity of the crystal lattice in the solid phase. Denoting by $\mathbf{R}_j (1 \leq j \leq N)$ the lattice sites of a given crystal structure, we assume the density $\rho_\sigma(\mathbf{r})$ in the solid solution to be the sum of Gaussians centred on the \mathbf{R}_j :

$$\rho_\sigma(\mathbf{r}) = p(\sigma) \sum_{j=1}^N \left(\frac{\alpha_\sigma}{\pi} \right)^{3/2} \exp \{ - \alpha_\sigma (\mathbf{r} - \mathbf{R}_j)^2 \}. \quad (3)$$

Equation (3) constitutes the obvious generalization of the local densities used earlier to study the freezing of hard spheres [7] and of their binary mixtures [8]. A local density of the form (3) means that particles of species (i.e. diameter) σ are, on average, distributed at random on the N site of the crystal lattice.

A convenient starting point of the density functional theory is the following exact expression for the difference between the Helmholtz free energy densities of the solid and fluid phases taken at the same density and temperature, and for identical distributions of diameters :

$$\beta \Delta f = \int_0^\infty d\sigma \int \frac{d\mathbf{r}}{V} \rho_\sigma(\mathbf{r}) \ln \frac{\rho_\sigma(\mathbf{r})}{\rho_\sigma^0} - \frac{1}{2} \int_0^\infty d\sigma \times \\ \times \int_0^\infty d\sigma' \int \frac{d\mathbf{r}}{V} \int d\mathbf{r}' \Delta \rho_\sigma(\mathbf{r}) \bar{c}_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') \Delta \rho_{\sigma'}(\mathbf{r}') \quad (4a)$$

with :

$$\bar{c}_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = 2 \int_0^1 d\lambda (1 - \lambda) c_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \{ \rho_\sigma^\lambda \}) \quad (4b)$$

where $\beta = 1/k_B T$ and $c_{\sigma\sigma'}$ denotes the direct correlation function between particles of species σ and σ' corresponding to a system with local densities :

$$\rho_\sigma^\lambda(\mathbf{r}) = \rho_\sigma^0 + \lambda \Delta \rho_\sigma(\mathbf{r}) \\ = \rho_\sigma^0 + \lambda [\rho_\sigma(\mathbf{r}) - \rho_\sigma^0].$$

Equation (4) is the straightforward generalization of the one and two-component expressions used in earlier theories of freezing [7, 8]. The first term on the r.h.s. of equation (4a) is the ideal part of the free energy, while the interaction part involves a coupling-constant integration over a linear path in one-particle density space, in the manner first introduced by Saam and Ebner [9] (an exhaustive presentation of density functional techniques is given in the excellent review by Evans [10]).

Equation (4) is exact; the pair correlations embodied in the $c_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \{ \rho_\sigma^\lambda \})$ are, however, in general unknown. Systematic approximations are obtained by making a Taylor expansion of these functions around their uniform fluid values $c_{\sigma\sigma'}(|\mathbf{r} - \mathbf{r}'|; \{ \rho_\sigma^0 \})$ corresponding to $\lambda = 0$. If only the lowest order term is retained, $\bar{c}_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') \equiv c_{\sigma\sigma'}(|\mathbf{r} - \mathbf{r}'|; \{ \rho_\sigma^0 \})$; higher order terms of the expansion in powers of λ involve three and more-body direct correlation functions of the uniform fluid, about which very little is known. For that reason the expansion is limited to lowest order, but, in an attempt to account approximately for the neglected higher order terms, the direct correlation functions $\bar{c}_{\sigma\sigma'}$ are taken to be those of an « effective » fluid having the same composition $\{ \rho_\sigma^0 \}$, and a total density ρ adjusted such that the position of the first peak in the total fluid structure factor :

$$\bar{S}(k) = \int_0^\infty d\sigma \int_0^\infty d\sigma' \bar{S}_{\sigma\sigma'}(k) \quad (5)$$

coincide with the first reciprocal lattice vector of the solid. The partial structure factors $\bar{S}_{\sigma\sigma'}(k)$ appearing in equation (5) are related to the Fourier transforms $\bar{c}_{\sigma\sigma'}(k)$ of the direct correlation functions by the usual Ornstein-Zernike equations :

$$\bar{S}_{\sigma\sigma'}(k) = p(\sigma) \delta(\sigma - \sigma') + p(\sigma) p(\sigma') \rho \hat{h}_{\sigma\sigma'}(k) \quad (6a)$$

$$\hat{h}_{\sigma\sigma'}(k) = \hat{c}_{\sigma\sigma'}(k) + \int d\sigma'' \hat{c}_{\sigma\sigma''}(k) \rho_{\sigma''}^0 \hat{h}_{\sigma''\sigma'}(k) \quad (6b)$$

where $\hat{h}_{\sigma\sigma'}(k)$ is the Fourier transform of the pair correlation function $\bar{h}_{\sigma\sigma'}(r) = \bar{g}_{\sigma\sigma'}(r) - 1$.

With the above prescription for $\bar{c}_{\sigma\sigma'}$, the approximate free energy difference is now given by equation (4a). This expression is then minimized with respect to the widths α_σ of the Gaussians appearing in the local density (3), for a given distribution of diameters, a given temperature T and a given total density ρ . The scenario which is observed along an isotherm, in similar studies of one or two-component systems (characterized by one or two Gaussian widths α_0) is generally the following [7, 8]. Below some threshold density ρ_a , the free energy f exhibits a single minimum for $\alpha_\sigma = 0$, corresponding to a stable fluid phase. Above ρ_a , f exhibits two minima, one for $\alpha_0 = 0$ (fluid) and a second one for $\alpha_\sigma > 0$; this second minimum is associated with a solid phase where particles are localized around the lattice sites $\{ \mathbf{R}_j \}$. In a certain range of densities $\rho_a < \rho < \rho_b$, this second minimum is higher than the minimum corresponding to the fluid phase, signalling that the solid is mechanically, but not thermodynamically stable (metastable solid phase). At still higher densities ($\rho > \rho_b$), the second minimum drops below the fluid minimum and the solid becomes the thermodynamically stable phase. The fluid-solid coexistence is determined, as usual, by equating the pressures P and

chemical potentials μ of both phases. In sections 3 and 4 we show that the bifurcation scenario which we have just described also occurs in a polydisperse system of hard spheres; in section 5 we point out the difficulties encountered if one attempts to determine the fluid-solid coexistence curve [11].

3. The polydisperse hard sphere model.

In order to calculate the free energy difference (4a) explicitly, detailed expressions for the direct correlation functions $\bar{c}_{\sigma\sigma'}(r)$ of the polydisperse fluid phase are required. Such information is at present only available for polydisperse mixtures of additive hard spheres. Indeed, using Baxter's reduction of the Ornstein-Zernike equations for finite-range potentials [12], Blum and Stell [6] were able to calculate the partial structure factors $S_{\sigma\sigma'}(k)$ of such mixtures in the Percus-Yevick (PY) approximation, which is known to be reasonably accurate for dense hard sphere fluids. This approximation supplements the set of Ornstein-Zernike equations (6b) by the closure relations :

$$g_{\sigma\sigma'}(r) = 0, \quad r < \frac{\sigma + \sigma'}{2} \quad (7a)$$

$$c_{\sigma\sigma'}(r) = 0, \quad r > \frac{\sigma + \sigma'}{2}. \quad (7b)$$

Equation (7a) expresses the exact requirement that hard spheres of diameters σ and σ' must not overlap, while equation (7b) is the PY approximation. The results of Blum and Stell [6] can be used to obtain the following solutions for $c_{\sigma\sigma'}(r)$ inside the hard cores (with $\sigma' > \sigma$) :

$$\begin{aligned} c_{\sigma\sigma'}(r) &= a_{\sigma\sigma'}, \quad r < \lambda_{\sigma\sigma'} = \frac{\sigma' - \sigma}{2} \\ &= a_{\sigma\sigma'} + \frac{1}{r} (b_{\sigma\sigma'} x^2 + 4 \lambda_{\sigma\sigma'} d_{\sigma\sigma'} x^3 + d_{\sigma\sigma'} x^4), \\ \lambda_{\sigma\sigma'} < r < \frac{\sigma + \sigma'}{2} \end{aligned} \quad (8)$$

where $x = r - \lambda_{\sigma\sigma'}$ and the coefficients a , b and d can be expressed in terms of the moments (1), of the packing fraction η and of $\Delta = 1 - \eta$ according to :

$$\begin{aligned} a_{\sigma\sigma'} &= -\frac{1}{2\Delta} \left[2 + \frac{\pi}{\Delta} \left(\sigma \xi_2 + \sigma^2 \xi_1 + \frac{\sigma^3}{3} \xi_0 \right) + \right. \\ &\quad \left. + \frac{\pi^2}{\Delta^2} \left(\frac{\sigma^2 \xi_2^2}{2} + \frac{\sigma^3 \xi_1 \xi_2}{3} \right) + \frac{\pi^3}{\Delta^3} \left(\frac{\sigma^3 \xi_2^3}{12} \right) \right] \end{aligned} \quad (9a)$$

$$\begin{aligned} b_{\sigma\sigma'} &= \frac{\pi}{4\Delta^3} \left\{ \sigma \sigma' \xi_0 + (\sigma + \sigma') \xi_1 + \xi_2 + \frac{\pi}{\Delta} \times \right. \\ &\quad \left. \times \left[\sigma \sigma' \xi_1 \xi_2 + (\sigma + \sigma') \frac{\xi_2^2}{2} \right] + \frac{\pi^2}{4\Delta^2} \xi_2^3 \sigma \sigma' \right\} \end{aligned} \quad (9b)$$

$$d_{\sigma\sigma'} = -\frac{\pi}{12\Delta^2} \left[\xi_0 + \xi_1 \xi_2 \frac{\pi}{\Delta} + \xi_2^3 \frac{\pi^2}{4\Delta^2} \right]. \quad (9c)$$

The total structure factor, which is required to determine the density of the effective fluid, as explained in section 2, is finally calculated from equations (6) and (5). Examples are shown in figure 1 for triangular and rectangular distributions of diameters.

The lattice sites $\{ \mathbf{R}_j \}$ in equation (3) are chosen to be those of an FCC lattice, which is the stable structure for a monodisperse hard sphere solid [7, 13]. This completes the specification of the ingredients of our calculation, the results of which will be presented in the following section.

Before that we briefly pause to examine the relevance of the polydisperse hard sphere model for the study of colloidal crystals. Polydispersity is an unavoidable characteristic of colloids and should hence be taken into account in any realistic calculation of the phase diagram. The hard sphere model is of course a crude oversimplification of the DLVO interaction between colloidal particles, which includes, besides a hard core repulsion, a screened Coulomb interaction and a van der Waals attraction. If the latter is neglected, and under strong screening conditions (i.e. in the presence of added salt), the DLVO potential may be reasonably well approximated by an effective hard sphere interaction with state-dependent diameters, as is routinely done in the theory of simple liquids [14]. It should be noted that the FCC structure has been predicted to be the stable one in the strong screening regime, by calculations based on a repulsive screened Coulomb interaction [15]. Experimentally, charge-stabilized colloidal crystals are observed in the opposite, weak screening limit, but crystallization of uncharged colloidal particles has also been observed [17], and the present hard sphere model applies directly to that case.

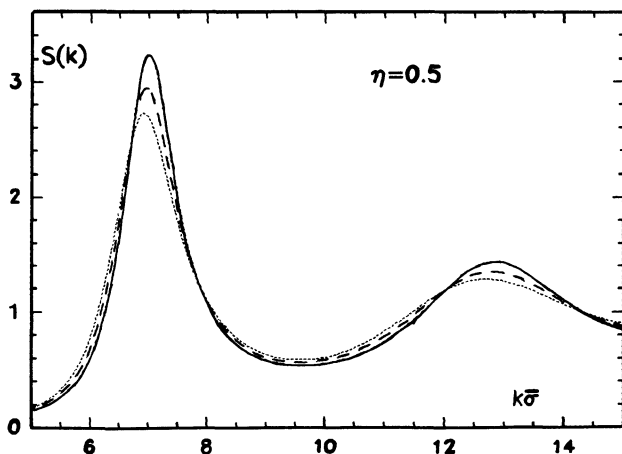


Fig. 1. — Static structure factors (5) of the monodisperse hard sphere fluid (full curve) and of polydisperse hard sphere fluids with triangular (dashes) and rectangular (dots) distributions of diameters, versus reduced wavenumber, at a packing fraction $\eta = 0.5$. The polydispersity parameter has the value $\delta = 0.15$ in the two polydisperse cases. The structure factors are calculated in the PY approximation [6].

4. Results.

We have carried out explicit free energy calculations to determine the density range of stability and metastability of polydisperse hard sphere systems with triangular and rectangular distributions of diameters. Since we are dealing with hard spheres, the results are independent of temperature. The triangular distribution is defined by :

$$p_t(\sigma) = \frac{1}{\sigma^2 \delta^2} (\bar{\sigma} \delta - |\sigma - \bar{\sigma}|); \quad \left| \frac{\sigma}{\bar{\sigma}} - 1 \right| < \delta \quad (10a)$$

while the rectangular distribution is given by :

$$p_r(\sigma) = \frac{1}{2 \delta \bar{\sigma}}; \quad \left| \frac{\sigma}{\bar{\sigma}} - 1 \right| < \delta \quad (10b)$$

where δ characterizes the dispersion ($2 \delta \bar{\sigma}$ is the total width of each distribution) and $\bar{\sigma} = \xi_1/\xi_0$ is the mean diameter, equal to the median value in these symmetric distributions. The calculations can in fact be easily carried out for any choice of $p(\sigma)$, but only the distributions (10a) and (10b) will be considered in the following. With these choices, and the forms (3) and (8) for the local densities and direct correlation functions, the integrations in equation (4a) can be carried out analytically, thus greatly simplifying the minimization procedure with respect to the α_σ . This minimization is most easily carried out in practice by discretizing the distributions (10a) or (10b) and seeking the minimum of Δf with respect to n width parameters α_i by a standard simplex algorithm. The results turn out to be practically independent of n whenever $n \geq 10$. In the monodisperse case ($\delta = 0$), we recover the results of Baus and Colot [7] : the bifurcation occurs at a packing fraction $\eta = 0.504$ beyond which a second minimum with $\alpha \neq 0$ (metastable solid) appears besides the fluid minimum ($\alpha = 0, \Delta f = 0$). The second minimum drops below the fluid minimum for $\eta = 0.548$ beyond which the solid is thermodynamically stable up to the vicinity of close packing ($\eta = 0.74$) where the second minimum disappears abruptly.

A qualitatively similar behaviour is still observed when δ is gradually increased from zero. However the abrupt vanishing of the second minimum takes place for increasingly lower values of the packing fraction (2), due to the overlap of the largest spheres at high densities; more precisely the minimum of the free energy surface vanishes in the direction of the width parameter α_σ associated with the largest spheres. Indeed, two spheres touch as soon as $\sigma + \sigma' = a\sqrt{2}$, where $a = (4/\rho)^{1/3}$ is the FCC lattice constant. Since the range of the direct correlation function $\bar{c}_{\sigma\sigma'}(r)$ is $(\sigma + \sigma')/2$ (cf. Eq. (7b)), the corresponding contribution to Δf in equation (4a), i.e.

$$-\frac{1}{2} \int \frac{d\mathbf{r}}{V} \int d\mathbf{r}' \Delta \rho_\sigma(\mathbf{r}) c_{\sigma\sigma'}(|\mathbf{r} - \mathbf{r}'|) \Delta \rho_{\sigma'}(\mathbf{r}') \quad (11)$$

increases sharply. In the monodisperse case this leads to the rapid vanishing of the second minimum around $\eta = 0.74$, as mentioned earlier. In the polydisperse case, the contribution (11) is weighted by the product $\rho(\sigma) \rho(\sigma')$ which corresponds roughly to the probability of finding two spheres of diameters σ and σ' on neighbouring sites; this weight factor explains why stability is not lost as soon as $\sigma_{\max} = \bar{\sigma}(1 + \delta) > a/\sqrt{2}$, and also why the triangular distribution has a wider range of stability than the rectangular one.

The destabilizing role of the large spheres becomes very apparent if the expression (11) is rewritten in reciprocal lattice space. The local densities can be expanded as sums over the vectors \mathbf{G} of the reciprocal lattice according to :

$$\rho_\sigma(\mathbf{r}) = \rho_\sigma^0 \sum_{\mathbf{G}} a_{\mathbf{G}}^\sigma e^{i\mathbf{G}\cdot\mathbf{r}} \quad (12)$$

Substituting (12) into (11) we arrive at the following contribution of a $\sigma\sigma'$ pair to the free energy :

$$\frac{1}{2} \rho \sum_{\mathbf{G} \neq 0} a_{\mathbf{G}}^\sigma a_{-\mathbf{G}}^{\sigma'} \hat{c}_{\sigma\sigma'}(|\mathbf{G}|) \quad (13)$$

A typical situation is shown in figure 2; the contribution to (13) due to the largest spheres is large and positive at the second reciprocal lattice vector, which makes a sizeable contribution (large amplitude $a_{\mathbf{G}}^\sigma$) to the local density $\rho_\sigma(\mathbf{r})$. As δ is increased, the desta-

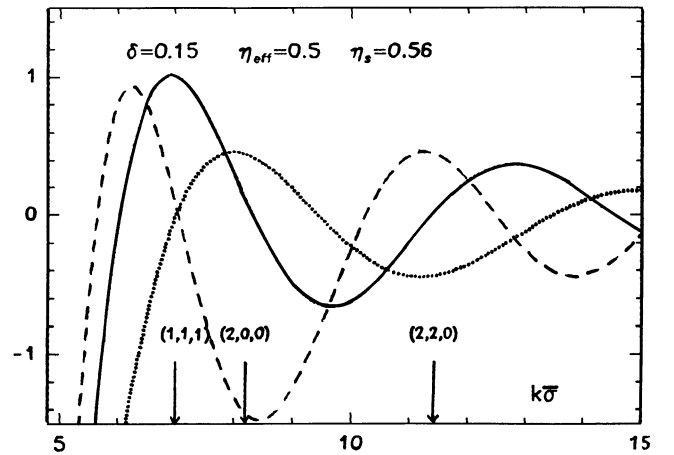


Fig. 2. — Three partial direct correlation functions $\hat{c}_{\sigma_1 \sigma_1}(k)$ (dashes), $\hat{c}_{\sigma_1 \sigma_2}(k)$ (full curve) and $\hat{c}_{\sigma_2 \sigma_2}(k)$ (dots) corresponding to the pairs of largest ($\sigma_1 = \sigma_{\max}$) and smallest ($\sigma_2 = \sigma_{\min}$) spheres in a polydisperse fluid mixture with a rectangular distribution of diameters, and $\delta = 0.15$. The effective packing fraction is $\eta_{\text{eff}} = 0.5$ and corresponds to a solid solution of $\eta = 0.56$ according to the structure factor criterion explained in the text. The moduli of the first three reciprocal lattice vectors of the FCC structure,

$$k\bar{\sigma} = 2\pi(k^2 + l^2 + m^2)^{1/2} \left(\frac{6\eta_s}{4\pi} \right)^{1/3},$$

are indicated by arrows.

bilizing contributions of the larger spheres to the free energy lead to a vanishing of the minimum for decreasing values of η , as shown in figures 3 (triangular distribution) and 4 (rectangular distribution of diameters). This second minimum, associated with the solid, vanishes completely (i.e. for all values of η) beyond $\delta \simeq 0.16$ for a rectangular distribution and beyond $\delta \simeq 0.21$ for a triangular distribution of diameters; the latter result is roughly compatible with Dickinson's molecular dynamics data [3, 4] discussed in the introduction. Beyond these critical degrees of polydispersity, a solid solution is always thermodynamically and mechanically unstable; this means that upon compression of a sufficiently polydisperse colloidal sus-

pension, one should observe either glass formation or phase separation into crystals with different compositions.

So far our calculation has allowed us to mark the boundaries of stability of the polydisperse solid solution. The problem of determining the fluid-solid coexistence curve in a polydisperse system is much more tedious in practice, and is briefly examined in the following section.

5. Comments on the fluid-solid phase equilibrium.

The difficulty in studying the equilibrium between two phases of a polydisperse system lies in the fact that the composition (i.e. the distribution of diameters) is not, in general, the same in the two coexisting phases. If we denote the two phases by A and B and the corresponding distributions by $p_A(\sigma)$ and $p_B(\sigma)$, chemical equilibrium between A and B involves in principle an infinite set of coupled equations, expressing the equality of chemical potentials over the whole range of diameters :

$$\mu_\sigma^A(T, P; p_A(\sigma)) = \mu_\sigma^B(T, P; p_B(\sigma)); \quad \sigma_{\min} < \sigma < \sigma_{\max} \quad (14)$$

If some easily tractable (e.g. analytical) form is available for the chemical potentials, the problem is usually solved by discretization, i.e. by modelling the polydisperse system by an n -component mixture, and by solving the resulting n coupled equations [11, 16]. Such a procedure cannot be implemented in any practical way in the present case, because the variational nature of our calculation renders the method numerically untractable.

The problem can be simplified further by imposing that the distributions p_A and p_B be members of a given family $p(\sigma; z)$ depending on a single parameter z ; for example z could be taken to be the position of the top of an asymmetrical triangular distribution, as shown in figure 5. By a judicious choice of the single parameter one may hope to retain the essential features of the phase coexistence, for instance the possibility of having a solid phase richer in large spheres than the fluid, as is the case in binary mixtures of hard spheres [8]. The compositions of the coexisting phases are now characterized by the values of the single parameter z , z_A and z_B say. Equilibrium between the two phases must be expressed in a way involving only z_A and z_B . The total free enthalpy of the system is :

$$G = N_A g_A(T, P, z_A) + N_B g_B(T, P, z_B) \quad (15)$$

where g_A and g_B are the free enthalpies per particle in both phases, with distributions $p_A(\sigma) = p(\sigma; z_A)$ and $p_B(\sigma) = p(\sigma; z_B)$ respectively. The total number of particles of diameter σ is :

$$N(\sigma) = N_A p(\sigma; z_A) + N_B p(\sigma; z_B) \quad (16)$$

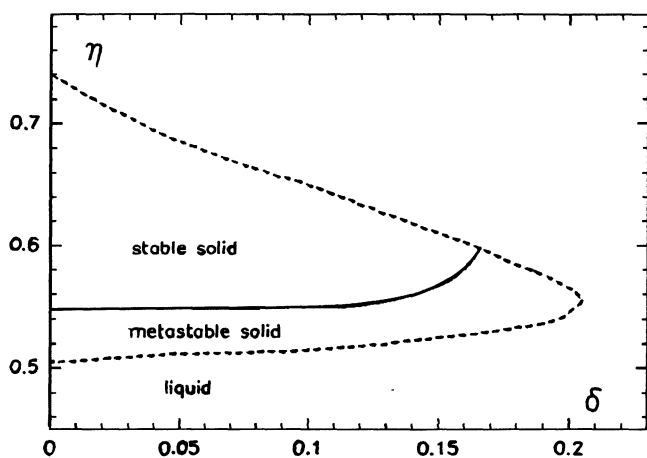


Fig. 3. — Range of stability of the polydisperse solid solution, with a triangular distribution of diameters, in the plane of packing fraction η versus polydispersity parameter δ . The dashed curve delimits the region of mechanical stability, while the full curve corresponds to the onset of thermodynamic stability; the two types of stability vanish simultaneously at large values of η (upper-part of the stability range).

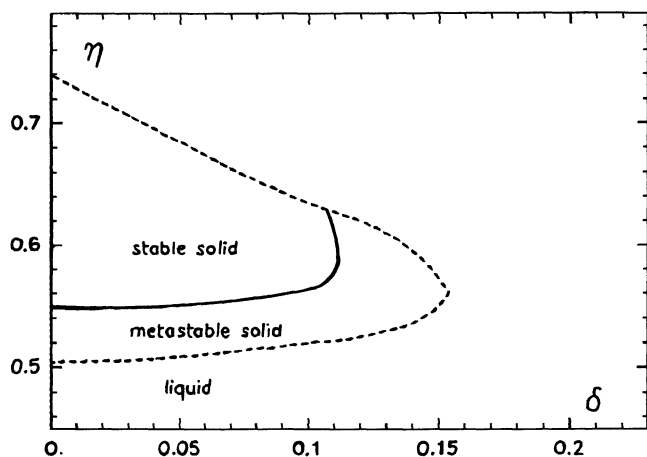


Fig. 4. — Same as figure 3, but for a rectangular distribution of diameters.

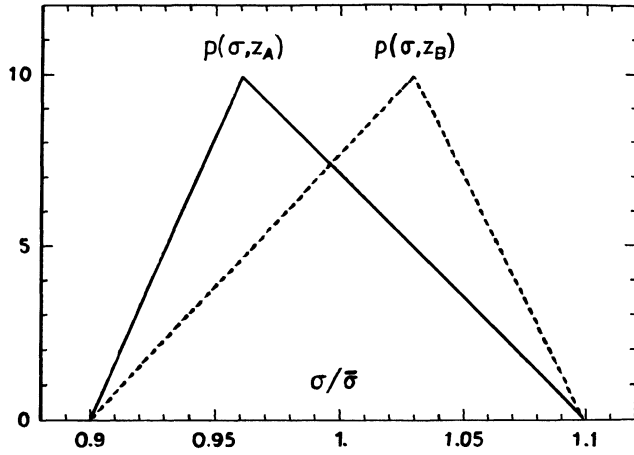


Fig. 5. — Examples of asymmetric triangular distributions of diameters characterized by a single parameter z .

The equilibrium condition $dG = 0$ and the conservation equations $dN(\sigma) = 0$ take the form :

$$(g_A - g_B) dN_A + N_A \left. \frac{\partial g_A}{\partial z} \right|_{z_A} dz_A + N_B \left. \frac{\partial g_B}{\partial z} \right|_{z_B} dz_B = 0 \quad (17)$$

$$[p(\sigma; z_A) - p(\sigma; z_B)] dN_A + N_A \left. \frac{\partial p(\sigma; z)}{\partial z} \right|_{z_A} dz_A + N_B \left. \frac{\partial p(\sigma; z)}{\partial z} \right|_{z_B} dz_B = 0; \quad \sigma_{\min} < \sigma < \sigma_{\max}. \quad (18)$$

As a consequence of the constraint imposed on the distributions $p(\sigma)$, the conservation equations (18) cannot be satisfied simultaneously. Instead we look for an approximate solution that violates the conservation conditions (18) as weakly as possible. To this end we retain the global condition $dN_A = -dN_B$ and we seek two functions $\lambda(z_A, z_B)$ and $\mu(z_A, z_B)$ such that :

$$dN_A = \lambda(z_A, z_B) N_A dz_A + \mu(z_A, z_B) N_B dz_B \quad (19)$$

and such that

$$\delta S = \int_{\sigma_{\min}}^{\sigma_{\max}} [\delta N(\sigma)]^2 d\sigma \quad (20)$$

be minimum with respect to variations of λ and μ . The solution is :

$$\lambda(z_A, z_B) =$$

$$= - \frac{\int [p(\sigma; z_A) - p(\sigma; z_B)] \left. \frac{\partial p(\sigma; z)}{\partial z} \right|_{z_A} d\sigma}{\int [p(\sigma; z_A) - p(\sigma; z_B)]^2 d\sigma} \quad (21)$$

$$\mu(z_A, z_B) =$$

$$= - \frac{\int [p(\sigma; z_A) - p(\sigma; z_B)] \left. \frac{\partial p(\sigma; z)}{\partial z} \right|_{z_B} d\sigma}{\int [p(\sigma; z_A) - p(\sigma; z_B)]^2 d\sigma}. \quad (22)$$

By inserting equation (19) into the equilibrium condition (17), and by separately equating to zero the coefficients of dz_A and dz_B , we arrive at a set of two equations for z_A and z_B :

$$\frac{\partial g_A}{\partial z_A} + \lambda(z_A, z_B) [g_A(T, P; z_A) - g_B(T, P; z_B)] = 0 \quad (23a)$$

$$\frac{\partial g_B}{\partial z_B} + \mu(z_A, z_B) [g_A(T, P; z_A) - g_B(T, P; z_B)] = 0. \quad (23b)$$

It can be easily checked that in the case of a binary mixture, where the distribution is entirely characterized by the composition parameter $x = N_2/N \equiv z$, the set of equations (23) reduces to the usual double tangent construction; in that case the minimum value of δS is exactly 0.

It is worth noting that the ideal gas terms $\rho_\sigma^0 \text{Log} \times (\rho_\sigma^0 \Lambda_\sigma^3)$, which involve the particle masses m_σ in the de Broglie thermal wavelengths Λ_σ , cancel in equations (23) if we express these masses as $m_\sigma = \alpha \sigma^3$, where α is proportional to the mass density of the material of which the colloidal particles are made. Thus equations (23) involve only T, P, z_A and z_B and may be solved to yield for example, the value of the parameter z_B of the crystal phase which is formed when the temperature T is lowered at constant z_A and P .

In the present context such a calculation of the fluid-solid coexistence, although feasible in principle, remains very cumbersome, and we made no attempt to carry it through, but we believe that the method which we have just outlined may be useful in related problems where polydispersity is an important factor.

Acknowledgments.

The calculations were carried out on the VAX 750 of Ecole Normale Supérieure with the support of the GRECO « Expérimentation Numérique ».

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