

On the spinodal instability of highly asymmetric hard sphere suspensions

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A new treatment of the binodal instability of suspensions containing a highly asymmetric mixture of hard spheres is presented. The origin of the instability is the attractive depletion interaction between the larger spheres, which is caused by the presence of the smaller spheres.

1. Introduction

Until recently it was generally believed that hard sphere mixtures are stable with respect to phase separation into two fluid phases. Indeed, at least within the Percus–Yevick closure of the Ornstein–Zernike equation and using the compressibility theorem to calculate the thermodynamic quantities this is true [1,2]. However, recently Biben and Hansen [3] have shown that starting from the Rogers–Young closure [4], which is known to be more accurate for hard spheres than the Percus–Yevick closure, such mixtures do seem to become unstable for diameter ratios larger than 5 at sufficiently high volume fractions. A direct experimental test of the prediction of Biben and Hansen is obviously not any easy task as hard sphere atoms do not exist in reality. However, recently strong experimental evidence for phase separation in bimodal dispersions of sterically stabilized silica particles was obtained in our laboratory [5]. The short-ranged harshly repulsive interactions between these sterically stabilized colloidal particles closely approximate that of hard spheres [6] and therefore the thermodynamic properties of such bimodal suspensions are closely related to those of hard sphere mixtures [7].

The phenomena observed in bimodal dispersions of sterically stabilized silica particles show striking analogies with the phase separation in colloidal suspensions induced by the addition of non-adsorbing polymer [8]. The explanation

for this phenomenon, first advanced by Asakura and Oosawa [9] and also independently by Vrij [10], is based on the exclusion of polymer from the region between two colloidal particles when their surface–surface separation becomes smaller than the diameter of a free polymer coil. The resulting imbalance in osmotic pressure gives rise to an effective attractive “depletion” force between the colloid particles. This depletion force has been termed “attraction through repulsion” by Vrij. At high enough concentration of polymer this depletion force causes the suspension to separate into colloid-poor and colloid-rich phases.

Guided by the analogy with the phase separation in colloidal suspensions induced by the addition of non-adsorbing polymer we derive a new expression for the osmotic pressure of a mixture of hard sphere colloids with strongly asymmetric sizes. This osmotic equation of state indeed displays a spinodal instability that is in qualitative agreement with the predictions of Biben and Hansen [3].

2. Osmotic equilibrium treatment of the equation of state

Ever since the days Einstein, Von Smoluchowski and Perrin gave their fundamental theoretical and experimental contributions to the study of colloidal suspensions it has been clear that for these systems where there is a large size difference between the solvent molecules and dissolved particles the “osmotic” approach is the appropriate one. In this approach, the chemical potential of the solvent molecules (and of the small counter and co-ions in the case of charged colloids) is used as independent thermodynamic parameter. The osmotic pressure then plays the same role as the hydrostatic pressure in an atomic or molecular fluid. Onsager [11] provided a statistical mechanical foundation for this approach. In particular, he showed that the thermodynamic properties of colloidal suspensions can be computed by the same procedures as those used for atomic and molecular fluids as long as one replaces the bare potential by the potential of the average forces which act between the colloidal particles.

Here we extend this approach to suspensions containing small and large hard sphere colloids. Given the asymmetry in size between the colloidal particles it is now convenient to use not only the chemical potential of the solvent molecules as independent parameter but also the chemical potential of the small colloidal particles. To “visualize” this approach we consider the osmotic system illustrated in fig. 1. It consists of three compartments separated by two semi-permeable membranes, with solvent in I, a suspension of small colloidal particles in II and a mixed suspension of small and large colloidal particles in

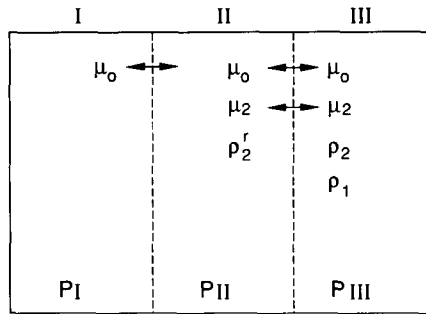


Fig. 1. Osmotic equilibrium system consisting of three compartments separated by two semipermeable membranes, with solvent in I, a suspension of small colloidal particles in II and a mixture of small and large colloidal particles in III. The solvent is denoted by the subscript 0, the large colloidal particles by the subscript 1 and the small colloidal particles by the subscript 2.

III. The solvent, denoted by the subscript 0, has a chemical potential μ_0 throughout. Membrane II/III is permeable to the small colloidal particles, denoted by the subscript 2, with number density ρ_2^r in II and ρ_2 in III (the superscript r is used to indicate that we consider compartment II as the reservoir for the system of interest). Finally the large colloidal particles denoted by the subscript 1 have a number density ρ_1 in III. The osmotic pressure Π of the colloid–colloid mixture with respect to the solvent is the pressure difference between III and I,

$$\Pi = P_{III} - P_I, \tag{1}$$

and similarly the osmotic pressure of the reservoir is given by

$$\Pi^r = P_{II} - P_I. \tag{2}$$

From here on, we shall consider the solvent as a structureless continuum that does not influence the interaction between the colloidal components which are assumed to interact as hard spheres. Then the thermodynamic properties of the mixed colloid–colloid suspension do not depend on the solvent chemical potential μ_0 and therefore the solvent molecules will not be considered explicitly in the following calculation. The appropriate thermodynamic potential to use here is the grand potential

$$\Omega = F - N_2\mu_2, \tag{3}$$

which can be obtained from the grand canonical partition function

$$\Xi(N_1, \mu_2, V) = \sum_{N_2=0}^{\infty} z_2^{N_2} Z(N_1, N_2, V) \quad (4)$$

via the standard relationship

$$\Omega = -kT \ln \Xi. \quad (5)$$

In eq. (4), z_2 is the activity of the small colloidal particles

$$z_2 = \exp(\mu_2/kT) \quad (6)$$

and $Z(N_1, N_2, V)$ is the canonical partition function of N_1 large colloidal particles and N_2 small colloidal particles in a volume V . Using the potential of mean force, the grand canonical partition function is given by

$$\Xi(N_1, \mu_2, V) = \frac{1}{N_1!} \int d\mathbf{r}^{N_1} \exp[-W(\mathbf{r}^{N_1}; \mu_2)/kT]. \quad (7)$$

Here $W(\mathbf{r}^{N_1}; \mu_2)$ is the potential of mean force, which depends on the configuration of the large particles collectively denoted by \mathbf{r}^{N_1} and the chemical potential μ_2 of the small particles. Although it is always possible to write down a formally exact expression for the potential of mean force it is of no practical use in the present case. Instead we shall give an approximate expression based on a physical argument. When the configuration \mathbf{r}^{N_1} changes, it leads to a change in the original potential $U(\mathbf{r}^{N_1})$ of the large particles and of the free volume $V_{\text{free}}(\mathbf{r}^{N_1})$ in which the small particles can move. If the free volume decreases due to a change in the positions of the large colloidal particles, work has to be done against the osmotic pressure Π^r of the reservoir leading to an increase of W . Similarly an increase of the free volume leads to a decrease of W . If we assume that the small particles are homogeneously distributed over the free volume we can write

$$W(\mathbf{r}^{N_1}; \mu_2) = U(\mathbf{r}^{N_1}) - \Pi^r(\mu_2) V_{\text{free}}(\mathbf{r}^{N_1}). \quad (8)$$

This expression for the potential of mean force is not exact since the distribution of the small particles over the free volume is not homogeneous but "structured" by the presence of the surfaces of the large particles which act as walls. However, in the limit that the small colloidal particles become point particles, the above expression for the potential of mean force is exact. We expect therefore that eq. (8) is still a good approximation for size ratios $q = a_2/a_1$ (a_1 is the radius of the large spheres and a_2 the radius of the small

spheres) much smaller than 1. Although the approximate expression for the potential of mean force looks quite simple, it is of a many-body nature since $V_{\text{free}}(\mathbf{r}^{N_1})$ depends on the mutual overlap of the excluded volume shells of two, three, four etc. particles. To make progress we use a Van der Waals type mean field approximation [12] and replace $V_{\text{free}}(\mathbf{r}^{N_1})$ by its average value in the corresponding unperturbed system of large colloidal particles,

$$\begin{aligned} \langle V_{\text{free}}(\mathbf{r}^{N_1}) \rangle &= \int d\mathbf{r}^{N_1} V_{\text{free}}(\mathbf{r}^{N_1}) \exp[-U(\mathbf{r}^{N_1})/kT] / \int d\mathbf{r}^{N_1} \exp[-U(\mathbf{r}^{N_1})/kT] \\ &= \alpha V . \end{aligned} \tag{9}$$

Obviously it is hard to justify this Van der Waals type approximation in the present case but recent computer simulations of Meijer [13] have shown that this approximation leads to good results for the phase behaviour of mixtures of hard spheres and interpenetrable spheres [14]. The free volume fraction α depends on the volume fraction of the large colloidal spheres $\phi_1 = \frac{4}{3}\pi a_1^3 \rho_1$ and the size ratio of the small and large colloidal spheres $q = a_2/a_1$. Using the potential of mean force (8) in the mean field approximation (9) to evaluate the grand canonical partition function (7), we obtain

$$\Omega = F_1(N_1, V) - \Pi^r \alpha V , \tag{10}$$

where $F_1(N_1, V)$ is the Helmholtz free energy for the pure system of the large spheres. Realizing that the last term on the right hand side of eq. (10) is just the grand potential of a pure suspension of the small particles 2 with chemical potential μ_2 and volume αV , we can write

$$\Omega = F_1(N_1, V) + \Omega_2(\mu_2, \alpha V) . \tag{11}$$

This equation can in turn be transformed into an expression for the Helmholtz free energy that has an equally suggestive form,

$$F = \Omega + N_2 \mu_2 = F_1(N_1, V) + F_2(N_2, \alpha V) . \tag{12}$$

The osmotic pressure can be readily obtained from the grand potential (10) by differentiation,

$$\Pi = - \left(\frac{\partial \Omega}{\partial V} \right)_{N_1, \mu_2} = \Pi_1^* + \Pi^r \left(\alpha - \rho_1 \frac{d\alpha}{d\rho_1} \right) . \tag{13}$$

Here Π_1^* is the osmotic pressure for the pure colloidal suspension of N_1 large

particles in a volume V . A further quantity of interest that can also directly be obtained from the grand potential is the number of small colloidal particles in the system,

$$N_2 = -\left(\frac{\partial \Omega}{\partial \mu_2}\right)_{N_1, V} = \frac{\partial \Pi^r}{\partial \mu_2} \alpha V = \rho_2^r \alpha V. \tag{14}$$

If we write this relation in the form

$$\rho_2 = \frac{N_2}{V} = \alpha \rho_2^r, \tag{15}$$

we see that in the model used here the free volume fraction α plays the role of the partition coefficient of the small colloidal particles between the system and the reservoir. Using the spinodal condition

$$\left(\frac{\partial \Pi}{\partial \rho_1}\right)_{\mu_2} = 0, \tag{16}$$

we obtain from eq. (13) the following expression for the spinodal curve:

$$\frac{\partial \Pi_1^*}{\partial \rho_1} - \Pi^r \rho_1 \frac{d^2 \alpha}{d \rho_1^2} = 0. \tag{17}$$

3. Results

Eq. (13) for the pressure and eq. (17) for the spinodal are the central results from our osmotic equilibrium treatment of asymmetric colloid–colloid mixtures. To make further progress we use for the osmotic pressure of the pure system and of the reservoir the scaled particle theory [15] result

$$Z_1^* = \frac{\Pi_1^*}{\rho_1 kT} = \frac{1 + \phi_1 + \phi_1^2}{(1 - \phi_1)^3} \tag{18}$$

and

$$Z^r = \frac{\Pi^r}{\rho_2^r kT} = \frac{1 + \phi_2^r + (\phi_2^r)^2}{(1 - \phi_2^r)^3}, \tag{19}$$

where $\phi_2^r = \frac{4}{3} \pi a_2^3 \rho_2^r$ is the volume fraction of the small particles in the reservoir. An approximate expression for the free volume fraction α can be obtained by realising that according to Widom’s particle insertion theorem

[12], the chemical potential of a test hard sphere of radius a_2 and number density $\rho_2 \rightarrow 0$ in a sea of hard spheres of radius a_1 and number density ρ_1 can be written as

$$\mu_2 = \text{constant} + kT \ln \rho_2 - kT \ln \alpha . \tag{20}$$

Comparing this expression with the well known scaled particle expression [16] or equivalently the Percus–Yevick result [17] for the chemical potential of a mixture of hard spheres of the kind indicated, one obtains

$$\alpha = (1 - \phi_1) \exp(-Ay - By^2 - Cy^3) , \tag{21}$$

in which

$$y = \frac{\phi_1}{1 - \phi_1} , \tag{22}$$

$$A = 3q + 3q^2 + q^3 , \quad B = 9q^2/2 + 3q^3 , \quad C = 3q^3 . \tag{23}$$

Using for Π^* , Π^r and α the expressions given by eq. (18), (19) and (21) we obtain from eq. (13) the following result for the osmotic pressure of a mixture of large and small colloidal particles:

$$\frac{\Pi}{(\rho_1 + \rho_2)kT} = x_1 \frac{(1 + \phi_1 + \phi_1^2)}{(1 - \phi_1)^3} + x_2 \frac{[1 + \phi_2^r + (\phi_2^r)^2](1 + Ay + 2By^2 + 3Cy^3)}{(1 - \phi_2^r)^3(1 - \phi_1)} , \tag{24}$$

where

$$x_1 = \frac{N_1}{N_1 + N_2} , \quad x_2 = \frac{N_2}{N_1 + N_2} . \tag{25}$$

From eq. (15) it follows that the volume fraction of the small spheres in the reservoir ϕ_2^r is related to the number density ρ_2 of the small spheres in the system by the relation

$$\phi_2^r = \frac{4\pi}{3} a_2^3 \frac{\rho_2}{\alpha} . \tag{26}$$

For the spinodal curve we obtain from eq. (17), again using for Π_1^* , Π^r and α the expressions given by eqs. (18), (19) and (21), the following result:

$$\frac{(1 + 2\phi_1)^2}{(1 - \phi_1)^4} - \frac{[1 + \phi_2^r + (\phi_2^r)^2]}{(1 - \phi_2^r)^3} \frac{\phi_1 \phi_2}{q^3} \times \frac{[(A^2 - 2B) + (4AB - 6C)y + (6AC + 4B^2)y^2 + 12BCy^3 + 9C^2y^4]}{(1 - \phi_1)^4} = 0. \tag{27}$$

In fig. 2 we present the spinodal obtained from eq. (27) for a size ratio $q = 0.1$. Our results lie somewhat higher than the predictions for the spinodal instability obtained by Biben and Hansen [3] using the Rogers–Young integral equation.

Clearly our results for the osmotic pressure and the corresponding spinodal curve are based on several approximations, the validity of which is hard to assess. Nevertheless we believe that our treatment in the form of eq. (17) reproduces correctly the essential physics behind the spinodal instability in asymmetric hard sphere mixtures. Increasing the number density ρ_1 of the large spheres at constant chemical potential μ_2 of the small spheres leads to an expulsion (“negative adsorption”) of the small spheres. At sufficiently high values of μ_2 this eventually leads to a point where the pressure no longer increases with increasing ρ_1 . This corresponds to the spinodal instability point.

As indicated in the introduction, our main motivation is not so much to produce an extremely accurate equation of state but rather to give a physically

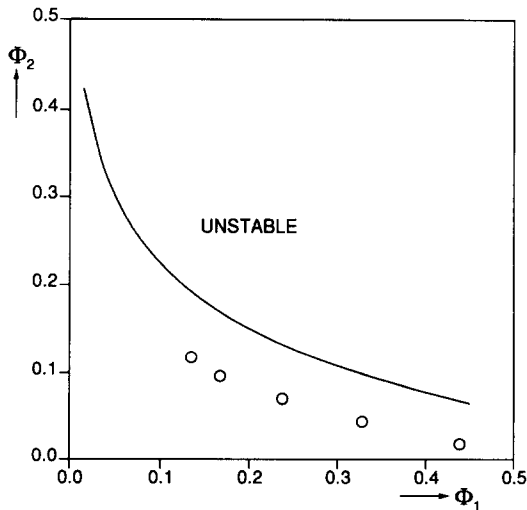


Fig. 2. Spinodal curve for an asymmetric mixture of hard spheres with a size ratio of 0.1 as a function of the volume fraction ϕ_1 of the larger and ϕ_2 of the smaller species. The spinodal instability points obtained from the Rogers and Young integral equation (Biben and Hansen, ref. [3]) are indicated as open circles.

motivated treatment of the effect of mixing small and large spheres on the pressure. Nevertheless, to have some feeling for the accuracy of our results we compare them in fig. 3 with the results obtained from the equation of state of Mansoori, Carnahan, Starling and Leland [18]. The latter equation, which has been tested against Monte Carlo and molecular dynamics simulations [19,20],

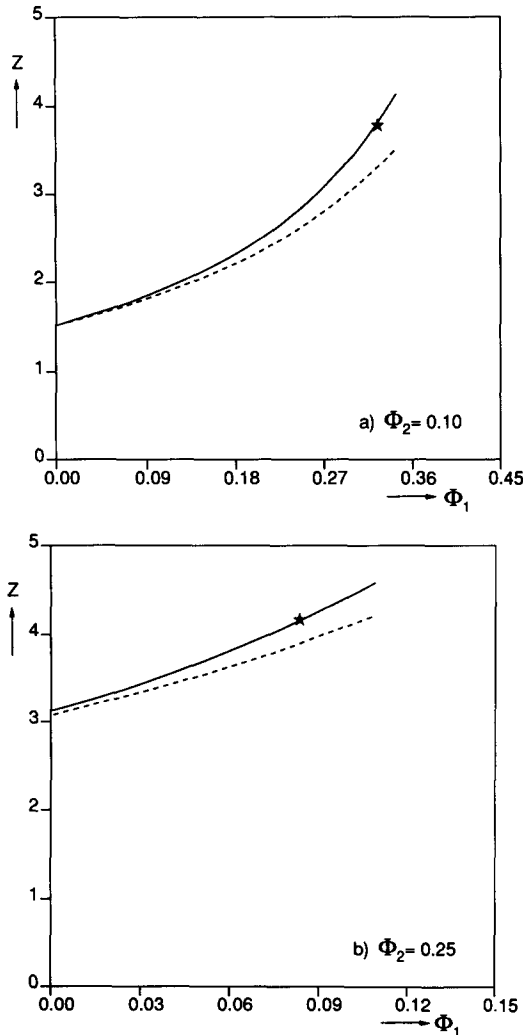


Fig. 3. The compressibility factor $Z = \Pi/(\rho_1 + \rho_2)kT$ of an asymmetric mixture of hard spheres with a size ratio of 0.10 as a function of the volume fraction ϕ_1 of the larger spheres. The volume fraction ϕ_2 of the smaller spheres is fixed at 0.1 (a) and 0.25 (b). The black stars correspond to the location of the binodal instability points. The pressure obtained from the Mansoori et al. equation is shown as a dashed line.

is believed to be very accurate. Significant deviations from simulations were found only at high densities ($\phi_1 + \phi_2 \geq 0.5$) and for large size ratios ($q \geq 5$). It is observed that our results lie somewhat above the values predicted by the Mansoori et al. equation of state. Part of the difference can be traced to the fact that our results are based on the scaled particle theory whereas Mansoori et al. use the Carnahan–Starling construction [21] which, already for one-component systems, gives lower pressures. The Mansoori et al. equation of state, however, does not give rise to a spinodal instability, whereas our supposedly less accurate equation does.

Even if hard sphere mixtures do have a spinodal instability, it is not at all certain that such mixtures will undergo a fluid–fluid phase separation of the gas–liquid type. Guided by our work on colloid–polymer mixtures [14], we rather expect that the addition of small colloidal particles will lead to a fluid–solid phase separation, preempting a fluid–fluid phase separation at a spinodal instability point. In their experiments, Van Duynveldt, Heinen and Lekkerkerker [5] were unable to determine whether the initially formed concentrated phase is a stable colloidal fluid or a metastable fluid–like suspension. The crystallization over a few weeks, observed in these experiments, could either be the result of the slow concentration dependent kinetics of formation of colloidal crystals from a supersaturated fluid or be caused by densification up to the freezing point due to sedimentation.

The question whether an asymmetric binary mixture of hard spheres does show a spinodal instability is not definitely answered. Like in other matters of principle such as the freezing transition in assemblies of hard spheres, computer simulations will be needed to further elucidate this issue. In view of the treatment given in the present work, the appropriate approach would be to simulate asymmetric hard sphere mixtures at constant chemical potential of the small spheres, in order to obtain information on the spinodal instability from the behaviour of the pressure as a function of the density of the large spheres.

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