Critical Packing Fraction
at the Phase Separation Transition in Hard-Core Mixtures

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In this paper, I relate the phase separation transition in binary hard-core mixtures in the limit of small size ratio to a bond percolation transition. It allows to estimate the critical packing fraction at the transition as a function of the size ratio and the composition of the mixture for different shapes of objects. The theoretical predictions are in excellent quantitative agreement with numerical simulations of binary parallel hard squares mixtures.

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Binary mixtures of impenetrable objects pose an easily formulated problem which is of crucial importance to understand entropic effects in colloidal systems. In this systems of “large” and “small” objects, an attractive depletion force between the large particles results from the presence of the small ones \( \langle 1 \rangle \). The main interest in such mixtures is the existence of a phase separation induced by this effective attraction of large objects.

Recent Monte-Carlo simulations \( \langle 2,3 \rangle \) have shown unequivocally that the phase separation takes place for spheres, parallel cubes and parallel squares for sufficiently dissimilar objects. Experiments \( \langle 4 \rangle \) also predict phase separation for mixtures of hard spheres. Now that estimates for the critical packing fraction at the transition have become available, theoretical work has become all the more interesting. Closures of the Ornstein-Zernicke integral equations have been studied extensively, and numerical calculations with the Rogers-Young approximation predict a demixing transition for sufficiently small size ratios \( \langle 5 \rangle \). The main drawback of this approach is that the closures are essentially uncontrolled. Other approaches have been used \( \langle 6,7 \rangle \) which lead to an instability between a homogeneous fluid phase and a demixed fluid-fluid phase. However, as shown by numerical simulations \( \langle 2,3 \rangle \) and experiments \( \langle 4 \rangle \), for small size ratio, the transition is between a fluid phase and a fluid-solid phase where the solid phase is constituted by closely packed large objects surrounded by a fluid of small ones. The actual nature of this “solid” phase is yet hotly debated \( \langle 2,4 \rangle \). The aim of this paper is not to give a better understanding of this phase but to determine the critical packing fraction at the transition.

In this article, I propose an expansion for the large-large pair distribution function in the fluid phase which is expected to be convergent in the limit of small size ratio. If two large particles are sufficiently close so that no room is left to insert a small particles between them, they are called bonded. This expansion, a virial development, allows to calculate the number of bonds between large-large objects, which is an increasing function of the packing fraction. Then, I relate the phase separation transition to a bond percolation transition and the solid phase to the percolating aggregate. Even if this heuristic mapping does not give a better understanding of the solid phase, it allows to compare the theoretical predictions of the critical packing fraction and its dependence on the composition with numerical simulations \( \langle 2,3 \rangle \) and experiments \( \langle 4 \rangle \) for objects of different shapes.

In the following, I consider large and small spheres (or disks) of diameters \( \sigma_l \) and \( \sigma_s \) and parallel cubes (or squares) of sides \( \sigma_l \) and \( \sigma_s \). The total packing fraction is \( \eta = \eta_a + \eta_b \) with \( \eta_a = N_a \nu_a / V \) and \( \eta_b = N_b \nu_b / V \) where \( V \) is the volume of a particle, \( N_a \) the number of particles and \( \nu_a \) the volume of a particle. The size ratio and the composition are defined as \( R = \sigma_s / \sigma_l \) and \( x = \eta_b / \eta_a \) respectively. For simplicity, distances are considered in units of the large particle size (\( \sigma_l = 1 \)) so that \( \sigma_s = R \).

The pair distribution functions are the relevant functions to characterize the homogeneous fluid phase. The Mayer functions \( f_{ab} \) allow to obtain density expansions of the large-large pair distribution function \( g_{ll} \) \( \langle 10,11 \rangle \). For cubes \( (d = 3) \) and squares \( (d = 2) \):

\[
f_{ab}(r) = -\prod_{i=1}^{d} \Theta(\sigma_a + \sigma_b - 2 |r_i|)
\]

where \( r_i \) stands for the difference of the \( i \)th component of the positions of particles \( a \) and \( b \) and \( \Theta \) is the Heaviside step function. For spheres and disks:

\[
f_{ab}(r) = -\Theta(\sigma_a + \sigma_b - 2 r)
\]

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where \( r \) is the distance between the particles \( a \) and \( b \). The functions \( f_{ab} \) are simply step functions with \( f_{ab} = -1 \) if the two particles \( a \) and \( b \) overlap and \( f_{ab} = 0 \) if not.

I propose the following exponential expansion of the pair distribution function which is a direct generalization of the one-component expansion (see Chap.5 in [1]):

\[
g_{ab}(r) = \exp \left[ \eta_s R^{-d} a^{-1} \bigg\{ \eta_s R^{-d} a^{-1} \bigg\} + \frac{1}{2} \eta_s^2 R^{-2d} a^{-2} \left( 2 \bigg\{ \bigg\} + 4 \bigg\{ \bigg\} + \bigg\{ \bigg\} \right) + \frac{1}{2} \eta_s \eta_a R^{-d} a^{-2} \left( 4 \bigg\{ \bigg\} + 4 \bigg\{ \bigg\} + 4 \bigg\{ \bigg\} + 2 \bigg\{ \bigg\} \right) + \frac{1}{2} \eta_a^2 a^{-2} \left( 2 \bigg\{ \bigg\} + 4 \bigg\{ \bigg\} + \bigg\{ \bigg\} \right) + \cdots \right]
\]

where \( d \) is the dimension of the space and \( a \) is a constant that depends on the shape of the objects (\( a = \pi/6 \) for spheres, \( a = \pi/4 \) for disks and \( a = 1 \) for cubes and squares). Each diagram is an integral over positions of small and large particles represented respectively by small and large black dots. Each link corresponds to a Mayer function and the two large open circles to two large particles with position difference \( r \). For example, the first diagram corresponds to:

\[
\bigg\{ \bigg\} = \int f_{ab}(r') f_{ab}(r - r') dr'
\]

and is a simple function of the position \( r \) and the size ratio \( R \). The diagrams in the expansion are all distinct connected diagrams consisting of two non-adjacent open circles, at least one black dot and such that the two open circles do not form an articulation [11]. A diagram with articulations may be reduced to a product of simpler ones (see below).

The above expansion, a density development, has negative powers of \( R \) when expressed with the pertinent parameters: \( R \), \( x \) and \( \eta \). However, three different effects may compensate the negative powers: first of all, a link between two small particles scales as \( R^d \) since the corresponding Mayer function restricts the integration to a small particle volume; second, diagrams of the same order but with odd and even numbers of links may compensate each other because the Mayer functions are negative; and last one, the critical packing fraction at the transition scales as a positive power of \( R \). Thus, we may expect that the expansion proposed in this article is convergent when written in powers of the size ratio at the phase separation transition. In that case, only the first few diagrams have to be considered in the limit of small \( R \).

In the article of Dijkstra et al. [10], another expansion up to the second order was presented for \( g_{ll} \). This expansion is not convergent in the limit of small \( R \) due to the presence of diagrams which form an articulation, like the one with two small particles without link between them. In fact, this diagram is the square of a simpler one:

\[
\bigg\{ \bigg\} = ( \bigg\{ \bigg\} )^2.
\]

It scales with a smaller power of \( R \) than the others of the same order and corresponds to the most divergent part in the second order expansion (see Eq.(5) in [10]).

\[
\bigg\{ \bigg\} = ( \bigg\{ \bigg\} )^2.
\]

FIG. 1. This figure represents the excluded volume for large disks around the disk 0 in gray. Large disks are bonded to the disk 0 if their centers stay in the ring of width equals to the small particle diameter around the excluded volume. In this case, the disks 1 and 2 are bonded to the disk 0 whereas the disk 3 is not. This case corresponds to a size ratio \( R = 1/20 \).

In the binary mixtures, \( g_{ll} \) shows a sharp peak at the contact value. In the limit of small \( R \), this peak is as narrow as \( R \) and corresponds to large particles with a distance \( 1 \leq r \leq 1 + R \) between them. Two such large particles may be considered as bonded. In this case, the mean number \( n_b \) of bonds per large particle is given by the integration of \( g_{ll} \) on the shell of width \( R \) around the excluded volume multiplied by the density of large particles \( \rho_l = N_l/V \):

\[
n_b = \rho_l \int_{1 \leq r \leq 1 + R} g_{ll}(r) dr \tag{3}
\]

where \( r \) is the usual norm of \( r \) for spheres and disks, and it is the maximum of the absolute values of the coordinates of \( r \) for cubes and squares. In the latter case, it is the relevant distance since I consider only parallel cubes (or squares). The example of disks is represented in Fig.1 where the gray region stands for the excluded volume of large disks around the disk 0. The ring around the gray region corresponds to the shell on which the integration is made. Centers of disks 1 and 2 are in this region and those disks are bonded to the disk 0 but the disk 3 is not.
From $g_0$, it is clear that the mean number $n_b$ of bonds per particle is an increasing function of the packing fraction. Thus, on increasing $\eta$, larger and larger aggregates of large particles exist in the system. There exists a critical number of bonds per particle $n_c$ for which a percolating aggregate appears. This corresponds to the phase separation transition and the percolating aggregate constitutes the solid phase. Notice that above this phase separation transition, $g_0$ is no longer defined since the translation invariance disappears due to the formation of the solid phase. If we suppose that bonds are randomly distributed, the critical number $n_c$ may be related to the bond percolation threshold $p_c$ of the lattice corresponding to the close packed configuration. The latter corresponds to the fraction of bonds necessary to obtain a percolating aggregate whereas $n_b$ counts the mean number of bonds per particle. Since the number of bonds per particle in the close packed configuration is the coordination number $z$, $n_c = z p_c$. The fact that positions of objects are not restricted to lattice sites may slightly modify the critical number $n_c$. However, $z$ is an obvious upper bound for the critical number $n_c$.

The positions of close packed spheres describe a FCC lattice of coordination number $z = 12$ and the bond percolation threshold of this lattice is $p_c = 0.199$. Thus, the critical number of bonds per particle is $n_c = 2.4$. Disks are close packed in a triangular lattice ($p_c = 0.347$ and $z = 6$) [12], which leads to $n_c = 2.1$. Cubes and squares in a cubic or square lattice ($p_c = 0.249$ or 0.5 and $z = 6$ or 4 respectively) [12] have $n_c = 1.5$ or 2 respectively.

In order to obtain the behavior of the critical packing fraction in the limit of small $R$, I consider only the first diagram of the exponential expansion assuming that the others are negligible. In this case, $n_b$ is given by:

$$n_b \approx \frac{\eta}{a} \int dr \exp \left( \frac{\eta}{a R^d} \int dr' f_{sl}(r') f_{sl}(r - r') \right) \tag{4}$$

where the integration over $r$ is restricted to $1 \leq r \leq 1 + R$. The critical packing fraction $\eta_c$ is defined by $n_b(\eta_c) = n_c$ and depends on the size ratio and the composition. An upper bound $\eta_{up}$ for this critical packing fraction is given by the condition $n_b(\eta_{up}) = z$. The estimate for $\eta_c$ is valid only for small $R$, for which the peak at the contact value of the pair distribution function of large-large particles may be related to bonds between large particles and where the diagram considered gives the dominant part of $n_b$.

Consider first parallel cubes and squares. The integration of Mayer functions $f_{sl}$ is:

$$\int dr' f_{sl}(r') f_{sl}(r - r') = \prod_{i=1}^d (1 + R - |r_i|) \Theta(1 + R - |r_i|). \tag{5}$$

For cubes, the mean number $n_b$ deduced from this equation and Eq.(3) leads to the following critical packing fraction:

$$\eta_c(\text{Cubes}) \simeq \frac{R^2}{1 - x} \log \left( \frac{n_c(1 - x)}{24 x R^3} \right). \tag{6}$$

The upper bound for the critical packing fraction is given by the same equation replacing $n_c$ by $z$. Notice that $n_c$ used to calculate $\eta_c$ is not essential to obtain the asymptotic behavior $-3R^2(1 - x)^{-1}\log R$ which is also given by the upper bound $\eta_{up}$. The packing fraction of small cubes $\eta_b = \eta(1 - x)$ at the transition is slightly dependent on composition (through a logarithmic term negligible in the limit of $R \to 0$). This result, which is observed for objects of all shapes, is not surprising since, in a first approximation, only the small particles are responsible of the effective attraction of the large ones.

The same calculation for the critical packing fraction may be done for parallel squares:

$$\eta_c(\text{Squares}) \simeq \frac{R}{1 - x} \log \left( \frac{n_c(1 - x)}{8 x R^2} \right). \tag{7}$$

It is interesting to notice that this is the first theoretical prediction of such a phase separation transition in binary mixtures of parallel hard squares.

The behavior of $\eta_c$ as a function of $R$ and $x$ has been obtained for the first time in recent simulations of mixtures of parallel hard squares [3]. Thus, it is possible to compare the theoretical predictions with the direct simulations. For this case of parallel hard squares, I have been able to push the expansion considerably farther (to second order) since the diagrams are quite simple to calculate. Mayer functions are products of one-dimensional functions and the same holds true for the diagrams. In the following table, theoretical predictions with first order and second order expansion are compared with simulations.

| $R$     | $x$  | $\eta_c^{1\text{st order}}$ | $\eta_c^{2\text{nd order}}$ | Simulation  |
|---------|------|-----------------------------|-----------------------------|-------------|
| 1/10    | 0.3  | 0.68                        | 0.52(0)                     | 0.49 ± 0.02 |
| 1/10    | 0.5  | 0.78                        | 0.54(4)                     | 0.53 ± 0.02 |
| 1/10    | 0.7  | > 1.                        | 0.58(8)                     | 0.60 ± 0.05 |
| 1/20    | 0.5  | 0.53                        | 0.42(4)                     | 0.41 ± 0.02 |
| 1/50    | 0.5  | 0.29                        | 0.26(4)                     | 0.26 ± 0.02 |

For the first order, a qualitative agreement is obtained for $R = 1/10$ and $1/20$, whereas for $R = 1/50$, the agreement is even quantitative. The agreement between numerical simulations and predictions with the second order expansion is quite striking, and indicates that this exponential expansion succeeds in summing up the essential diagrams. It is interesting to notice that, replacing the packing fraction by its critical value (Eq.(3)) in the exponential expansion, the second order terms scale at least
as $R$ whereas the first order term is of order one (neglecting logarithmic terms). It would be interesting to prove that higher orders are also negligible. Moreover, the width of the shell on which the integration is made to calculate $n_b$ does not seem to be essential as soon as we consider a width larger than the peak of the pair distribution function ($\sim R$) but still of order $R$. I have checked for $R = 1/50$ that calculations with shells of width $2R$ and $3R$ do not modify significantly $\eta_c$.

Let me now consider the mixture of spheres. The integration of the Mayer functions has already been calculated \cite{footnote1}:

$$
\int dr' f_{sl}(r') f_{sl}(r-r') = \frac{\pi}{6} (1 + R - r)^2 (1 + R + r/2)
$$

(8)

for $1 \leq r \leq 1 + R$. Including this expression in Eq. (10), I deduce the critical packing fraction:

$$
\eta_c(\text{Spheres}) \simeq \frac{2R}{3(1-x)} \log \left( \frac{3(1-x) \eta_c}{8\pi x R^2} \right)
$$

(9)

which is valid for $\eta_c \gg 2R/(3(1-x))$. This implies that the logarithm of the size ratio is sufficiently large since $\eta_c$ decreases to zero with $R$ not only linearly but with logarithmic corrections. For $x = 1/2$ and $R = 1/30$, Eq. (8) gives $\eta_c = 0.24(8)$ whereas numerical simulations \cite{footnote2} have shown that $\eta_c \leq 0.243$. Furthermore, both predictions for the critical packing fraction agree qualitatively with experimental results \cite{footnote3}. Unfortunately, in order to be able to compare quantitatively theoretical with experimental predictions, either new experiments with smaller size ratios or theoretical predictions considering further diagrams in the expansion beyond the first one are needed.

An analogous calculation may be done for disks in two dimensions, where the first diagram scales as $R^{3/2}$ in the limit $R \to 0$ for $1 \leq r \leq 1 + R$. This leads to a critical packing fraction:

$$
\eta_c(\text{Disks}) \simeq \frac{3\pi}{8\sqrt{2}} \frac{\sqrt{R}}{1-x} \log \left( \frac{\sqrt{2}(1-x) \eta_c}{2\pi x R^{3/2}} \right).
$$

(10)

The scaling prediction in $\sqrt{R}$ for $\eta_c$ has been already suggested in \cite{footnote4}, but there is not yet numerical evidence for the phase separation transition. From Eq. (10), in order to have $\eta_c \sim 0.6$ at a composition $x = 0.5$, the size ratio to consider is $R \sim 1/600$. This seems yet beyond reach since for this size ratio, we would have to take into account $360$ 000 small disks for each large one or, in order to clearly see the transition, a few dozen of large particles and more than $10^7$ small ones. On the other hand, taking into account higher orders in the expansion, the estimation of the size ratio may be strongly modified.

In conclusion, an exponential expansion of the pair distribution function of large-large particles in binary mixtures has been presented. A known limitation of such expansion is of course that it is limited to the homogeneous phase. In this work I have shown that, nevertheless, this expansion can be used to predict a fluid-solid phase separation by computing the quantity which triggers it: a large increase in the number of large particles in a thin shell around a given large particle. This was already pointed out in \cite{footnote5}. In the limit of small size ratio, the mean number of bonds between large particles at the phase separation transition is related to the bond-percolation threshold of the lattice corresponding to the close packed configuration, and the solid phase corresponds to the percolating aggregate of large particles. The critical packing fraction is then deduced. Its dependence with the composition confirms that the effective attraction of large objects is principally due to the depletion of small ones. Additional numerical simulations of mixtures of parallel hard squares reported elsewhere \cite{footnote6} confirm the theoretical predictions. The theoretical results for mixtures of spheres are in qualitative agreement with experiments, whereas the phase separation transition for mixtures of hard disks is predicted to occur at such small size ratio that the corresponding simulation above the transition seems yet out of reach.

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