Phase Behaviour of Binary Hard-Sphere Mixtures: Free Volume Theory Including Reservoir Hard-Core Interactions

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Comprehensive calculations were performed to predict the phase behaviour of large spherical colloids mixed with small spherical colloids that act as depletant. To this end, the free volume theory (FVT) of Lekkerkerker et al. [Europhys. Lett. 20 (1992) 559] is used as a basis and is extended to explicitly include the hard-sphere character of colloidal depletants into the expression for the free volume fraction. Taking the excluded volume of the depletants into account in both the system and the reservoir provides a relation between the depletant concentration in the reservoir and in the system that accurately matches with computer simulation results of Dijkstra et al. [Phys. Rev. E 59 (1999) 5744]. Moreover, the phase diagrams for highly asymmetric mixtures with size ratios \( q \lesssim 0.2 \) obtained by using this new approach corroborates simulation results significantly better than earlier FVT applications to binary hard-sphere mixtures. The phase diagram of a binary hard-sphere mixture with a size ratio of \( q = 0.4 \), where a binary interstitial solid solution is formed at high densities, is investigated using a numerical free volume approach. At this size ratio, the obtained phase diagram is qualitatively different from previous FVT approaches for hard-sphere and penetrable depletants, but again compares well with simulation predictions.

I. INTRODUCTION

Colloidal particles are ubiquitously present in everyday products such as cosmetics, foodstuffs and coatings. The stability of these products depends on the phase behaviour of the colloids that can undergo phase transitions similar to atomic or molecular systems. The conditions where these transitions occur are determined by the (effective) interactions between the colloidal particles and are affected by their environment. In colloidal products this environment is often composed of different types of other colloidal particles that interact with each other. For example, coating formulations often contain multiple colloidal components that can serve either as binder, pigment or as additive. These colloidal particles can be spherical but are also often anisotropic in the case of pigments. Moreover, the size ratio between the different particles is often quite large, for example for stratification purposes. In these types of colloidal mixtures, depletion interactions are present that can lead to phase separation which is often undesired in colloidal products since it leads to inhomogeneities. However, depletion interactions can also be used advantageously, for example in the separation or fractionation of colloidal mixtures or inducing protein crystallization. For the optimal use of colloidal mixtures it is crucial to have a good understanding of the phase behaviour of the colloidal particles.

Colloidal particles have a finite volume and therefore excluded volume interactions are always present in colloidal systems. Excluded volume is generally associated to repulsive interactions, but in mixtures of colloids with different sizes excluded volume interactions can also indirectly induce effective attractions between particles. Around the larger colloidal particles a depletion zone exists that is inaccessible to

\[ h/\sigma \]

Figure 1. (a) Schematic representation of the depletion interaction mediated by hard-sphere or penetrable hard sphere depletants. The depletion zones around the large spheres that are inaccessible for the small spheres are shown by the thick green circles and the overlap of the depletion zones resulting in more free volume available for the small spheres is highlighted. (b) Comparison between the Asakura–Oosawa depletion potential for PHS depletants (gray curve) and the depletion potential induced by hard-sphere depletants obtained from a second order perturbation theory (black curve) for a size ratio of \( q = 0.1 \) and depletant volume fraction of \( \pi/15 \). The distance between the colloidal particles \( h \) is normalized by the diameter of the depletants \( \sigma \).

the centers of the smaller particles. Once the depletion zones of different particles overlap, the total volume available for the smaller particles will increase leading to an effective depletion attraction between the larger colloids, induced by the excluded volume repulsion between the large and small particles. The depletion interaction is schematically illustrated in Fig. [1]. Due to the depletion attraction, colloidal particles can undergo phase transitions at much lower concentrations then expected for the single component dispersion.

In 1954 Asakura and Oosawa were first to theoretically consider the interaction between two spherical particles as mediated by non-adsorbing macromolecules and showed this leads to an effective attraction due to excluded volume interactions. A few years later, they explicitly quantified the case of

\[ W/k_B T \]

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the interaction between two hard spheres mediated by other hard spheres in the dilute limit. In their pioneering paper, Asakura and Oosawa speculated already about more complicated situations. Here we consider in some detail the phase behaviour of Asymmetric binary hard sphere dispersions.

An insightful and relatively simple method to elucidate the phase behaviour of mixtures with colloids and depletants is free volume theory (FVT).\(^{15}\) In FVT, phase behaviour is determined using a thermodynamic description of the system containing colloids and depletants, based on estimating the free volume available for the depletants. FVT was originally developed to study colloid-polymer mixtures, where the colloids were described as hard spheres and the polymers were considered as penetrable hard spheres.\(^{16}\) Penetrable hard spheres (PHS) are defined as non-additive spheres that can freely overlap with each other but cannot overlap with the colloidal particle,\(^{14}\) an approximation that is reasonably accurate if the polymers are ideal chains or are dilute. The PHS model was later applied in FVT studies of mixtures with the colloidal particles.\(^{17,18}\) For these reasons, FVT is a promising and versatile method to gain insight in the phase behaviour of colloidal mixtures. However, already for the binary hard-sphere mixture there is a significant discrepancy between the FVT results in comparison with results from simulations\(^{33}\) and perturbation theory\(^{20}\).

In this paper, we first show why the original FVT approach to account for the excluded volume of colloidal depletants\(^{3,16}\) does not lead to an accurate description of the phase behaviour for binary hard-sphere mixtures. Next, we propose a FVT approach that accurately takes the excluded volume of the depletants into account. We focus on highly asymmetric binary hard-sphere mixtures \((q \lesssim 0.2)\) for comparison with previous studies to validate the proposed approach. We also briefly discuss the possibility of applying FVT for a larger size ratio of 0.4 where an interstitial solid solution is formed at high densities.\(^{20,21}\)

## II. THEORY

In this section we provide an overview of the FVT used in this paper. In FVT the system of interest containing colloidal particles and depletants is assumed to be in thermodynamic equilibrium with a hypothetical reservoir through a membrane that is permeable to the solvent and depletants, but impermeable to the large colloidal particles. This equilibrium is used as a starting point for the derivation of the thermodynamic properties of the binary system. First, we provide the original equations of FVT for hard spheres mixed with penetrable hard spheres\(^{20}\) and an adjusted description of the free volume in a face-centered-cubic (FCC) crystal based on geometrical arguments.\(^{19}\) Then we show the correction on the semi-grand potential for hard-sphere depletants first discussed by Lekkerkerker and Stroobants\(^{20}\) and argue why this correction is not sufficient to accurately describe binary hard-sphere mixtures. Finally, we provide a novel description of the semi-grand potential and free volume fraction in a binary hard-sphere system and explain how this can be used to calculate phase coexistence binodals. The focus in this paper is on highly asymmetric binary hard-sphere mixtures \((q \lesssim 0.2)\), however, we also briefly discuss the applicability of FVT for a larger size ratio of \(q = 0.4\). All calculations were performed using Wolfram Mathematica 12.

### A. Semi-grand potential

The semi-grand potential \(\Omega\) describing a system containing \(N_c\) colloidal particles and \(N_d\) depletants, in contact with a depletant reservoir, is a Legendre transformation of the Helmholtz free energy \(F\):
\[ \Omega(N_c, V, T, \mu_d) = F(N_c, N_d, V, T) - \mu_d N_d \ , \] 

where \( \mu_d \) denotes the chemical potential of depletants in the system, and the volume and temperature are given by \( V \) and \( T \) respectively. In this approach, the solvent is treated as background. From Eq. 1 the following thermodynamic relation is obtained:

\[ \left( \frac{\partial \Omega}{\partial \mu_d} \right)_{N_c, V, T} = -N_d \ , \] 

from which it follows that:

\[ \Omega(N_c, V, T, \mu_d) = F_0(N_c, V, T) - \int_{-\infty}^{\mu_d} N_d(d\mu_d')d\mu_d' \ , \] 

where the equality \( \Omega(N_c, V, T, \mu_d \to -\infty) = F_0(N_c, V, T) \) was used. In this equation, \( F_0 \) is the Helmholtz free energy of a pure system of hard spheres (i.e. colloids without depletants). Eqs. 1-3 are exact and hold for any type of binary colloidal mixture.

1. Penetrable hard spheres

In original FVT, which was developed to describe mixtures of colloids and polymers, polymers were described as penetrable hard spheres (PHS) that can freely overlap with each other but cannot overlap with the colloidal particles. To obtain an expression for the number of depletants in the system \( (N_d) \), Widom’s insertion theorem is used, which gives for the chemical potential of PHS depletants in the system:

\[ \mu_d = \text{const} + k_B T \ln \left( \frac{N_d}{\langle V_{\text{free}} \rangle} \right) \ , \] 

where \( \langle V_{\text{free}} \rangle \) is the ensemble-averaged volume that is available for the depletants. The chemical potential of PHS depletants in the reservoir is simply given by the chemical potential of an ideal solution:

\[ \mu_d^R = \text{const} + k_B T \ln n_d^R \ , \] 

with \( n_d^R \) the number density of depletants in the reservoir. By equating both expressions for the chemical potential of depletants, assuming equilibrium, an expression for \( N_d \) is found:

\[ N_d = n_d^R \langle V_{\text{free}} \rangle \ . \] 

Substituting Eq. 6 into Eq. 3 and applying the Gibbs–Duhem relation:

\[ n_d^R d\mu_d = d\Pi^R \ , \] 

yields the following expression for the semi-grand potential of the system:

\[ \Omega(N_c, V, T, \mu_d) = F_0(N_c, V, T) - \int_{0}^{\Pi^R} (V_{\text{free}}) d\Pi^R \ , \] 

where \( \Pi^R \) is the osmotic pressure of depletants in the reservoir. Finally it is assumed that the PHS depletants do not influence the configuration of the colloids in the system. This implies that the free volume available for the depletants is equal to the free volume for depletants in the pure hard-sphere system; \( \langle V_{\text{free}} \rangle = \langle V_{\text{free}} \rangle_0 \). This leads to the following approximate result for the semi-grand potential of a mixture of hard spheres and penetrable hard spheres:

\[ \Omega(N_c, V, T, \mu_d) = F_0(N_c, V, T) - \langle V_{\text{free}} \rangle_0 \Pi^R \ . \] 

To compute phase equilibria it is useful to rewrite this equation in terms of dimensionless quantities as:

\[ \tilde{\Omega} = \tilde{F}_0 - \alpha \tilde{\Pi}^R \ , \] 

where the following definitions are used:

\[ \tilde{\Omega} = \frac{\Omega}{V k_B T} \ , \quad \tilde{F} = \frac{F}{V k_B T} \ , \quad \alpha = \frac{\langle V_{\text{free}} \rangle}{V} , \quad \tilde{\Pi} = \frac{\Pi v_c}{k_B T} \ . \] 

Here \( v_c \) denotes the volume of a colloidal sphere. Furthermore, the size ratio \( q \) is defined as the ratio of the radii of the depletants and colloids, \( q = R_d/R_c \). Since the depletants do not have interactions with each other (i.e. ideal depletants), the osmotic pressure \( \Pi^R \) is given by (dimensionless form of) the van ’t Hoff equation:

\[ \tilde{\Pi}^R_{\text{ideal}} = q^{-3} \phi_d^R \ . \] 

Here, \( \phi_d^R \) is the volume fraction of depletants in the reservoir given by \( n_d^R v_d \). Furthermore, the Helmholtz free energy \( \tilde{F}_0 \) of the pure hard-sphere fluid phase is given by:

\[ \tilde{F}_{0, \text{fluid}} = \phi_c \left[ \ln \left( \phi_c A^3/v_c \right) - 1 \right] + 4\phi_c^2 - 3\phi_c^3 \left( \frac{1 - \phi_c}{1 - \phi_d} \right)^2 \ , \] 

where the first term on the right-hand side is the ideal contribution and the second term originates from the Carnahan–Starling equation of state. For the hard-sphere solid, a face-centered-cubic (FCC) crystal, the result from Lennard-Jones and Devonshire cell theory is used:
\[
\tilde{\Omega}_{\text{solid}} = \phi_c \ln \left( \Lambda^3 / \nu_c \right) + \phi_c \ln \left( \frac{27}{8 \phi_c^3} \right) + 3 \phi_c \ln \left( \frac{\phi_c}{1 - \phi_c / \phi_{\text{cp}}} \right) . \tag{14}
\]

In Eqs. \([13]\) and \([14]\) \(\Lambda\) is the De Broglie wavelength, \(\phi_c\) is the volume fraction of colloidal spheres, and \(\phi_{\text{cp}}\) denotes the volume fraction of a close-packed FCC crystal \((\phi_{\text{cp}} = \pi / 3 \sqrt{2} \approx 0.74)\). The final ingredient for the semi-grand potential \(\Omega\) in Eq. \([10]\) is the free volume fraction \(\alpha\) which can be obtained from the reversible work \(W\) required to insert a depletant into the system \([16]\):

\[
\alpha = \exp \left( - \frac{W}{k_B T} \right) . \tag{15}
\]

The work of insertion \(W\) is determined with scaled particle theory (SPT)\([19]\), resulting in:

\[
\frac{W}{k_B T} = - \ln (1 - \phi_c) + \frac{3 q \phi_c}{1 - \phi_c} + \frac{1}{2} \left( \frac{6 q^2 \phi_c}{1 - \phi_c} + \frac{9 q^2 \phi_c^2}{(1 - \phi_c)^2} \right) + q^3 \tilde{\Pi} . \tag{16}
\]

For the osmotic pressure \(\tilde{\Pi}\) in the last term on the right-hand side of Eq. \([16]\) the Carnahan–Starling equation\([22]\) is used for the fluid phase:

\[
\tilde{\Pi}_{\text{fluid}} = \frac{\phi_c + \phi_c^2 + \phi_c^3 - \phi_c^4}{1 - \phi_c^3} . \tag{17}
\]

For the solid phase, the osmotic pressure as derived from cell theory for an FCC crystal\([23]\) is used:

\[
\tilde{\Pi}_{\text{solid}} = \frac{3 \phi_c}{1 - \phi_c / \phi_{\text{cp}}} . \tag{18}
\]

It is noted here that the Percus–Yevick osmotic pressure (Eq. \([22]\)) was used in original FVT\([16]\), as this osmotic pressure is internally consistent with SPT, both for the fluid phase and the solid phase.

The free volume fraction in the solid phase can also be determined using geometrical arguments\([22]\), which gives a more accurate result for the solid phase at high volume fractions:

\[
\alpha_{\text{solid}} = \begin{cases} 
1 - \phi_c \tilde{v}_{\text{exc}} & \text{for } \phi_c < \phi_c^* \\
1 - \phi_c \tilde{v}_{\text{exc}} & \text{for } \phi_c^* \leq \phi_c < 2^{3/2} \phi_c^* \\
0 & \text{otherwise} \end{cases} . \tag{19}
\]

Here it is assumed that the centers of the spherical colloids are perfectly located on the FCC lattice points. In this equation, \(\phi_c^* = \phi_{\text{cp}} / \nu_{\text{exc}}\) denotes the volume fraction of large spheres above which the depletion zones overlap. Furthermore, the normalized excluded volumes are given by:

\[
\tilde{v}_{\text{exc}}^0 = (1 + q)^3 , \quad \tilde{v}_{\text{exc}}^0 = \left[ 1 + q - \left( \frac{\phi_{\text{cp}}}{\phi_c} \right)^{3/4} \right] ^2 \left[ 1 + q + \frac{1}{2} \left( \frac{\phi_{\text{cp}}}{\phi_c} \right)^{3/4} \right] . \tag{21}
\]

Note that Eq. \([19]\) only holds if there is no multiple overlap of depletion zones, i.e. for size ratios smaller than \(q = \frac{3}{2} \sqrt{3} - 1 \approx 0.15\).

2. First \(\Omega\) correction for HS depletants

The semi-grand potential \(\Omega\) can also be used to describe a mixture of large and small spheres in equilibrium with a reservoir of small spheres. For this purpose, Lekkerkerker and Stroobants\([20]\) proposed to use a different expression in Eq. \([10]\) for the osmotic pressure in the reservoir to account for the excluded volume interactions between the depletants. Instead of assuming ideal behaviour, the "compressibility" result of the Percus–Yevick (PY) closure was used, which describes the osmotic pressure of monodisperse hard-sphere dispersions with reasonable accuracy:

\[
\tilde{\Pi}_{\text{PY}}^R = q^{-3} \phi_{\text{d}}^R \left( \phi_{\text{d}}^R \right)^2 + \left( \phi_{\text{d}}^R \right)^3 \left( 1 - \phi_d^R \right)^3 . \tag{22}
\]

Fig. 2 shows the phase diagram for a hard-sphere mixture with size ratio \(q = 0.1\) determined using original FVT for hard-sphere depletants\([20]\), compared with direct coexistence simulation results of Dijkstra et al.\([23]\). The results are shown both for the SPT expression (Eq. \([15]\)) and the geometrical expression for the free volume fraction in the solid phase (Eq. \([19]\)). Also shown for comparison are the binodals obtained with FVT using the PHS approximation (gray curves). The SPT expression was originally used in FVT for hard-sphere depletants and the resulting binodals are in slightly better agreement with simulation results than the binodals for PHS deplets. However, still a significant discrepancy remains and also when the geometrical expression for \(\alpha_{\text{solid}}\) is used this discrepancy is present. The reason for this mismatch is that the excluded volume of the depletants is still not explicitly taken into account in the FVT of Lekkerkerker and Stroobants\([20]\). The excluded volume of the depletants is not accounted for in the free volume fraction, for both the reservoir and the system, and therefore the chemical potential of the depletants is not accurately taken into account. The chemical potential for depletants in the system given by Eq. \([4]\) still...
holds for hard-sphere depletants, but the volume excluded by the depletants has to be accounted for properly in the free volume \((V_{\text{free}})\). The chemical potential for depletants in the reservoir given by Eq. 5 is no longer valid since hard spheres at finite concentrations do not behave ideally. Moreover, the approximation used in Eq. 9 is no longer valid because the free volume available to the depletants is no longer independent of depletant concentration. In the next subsection we derive an adjusted expression for the semi-grand potential of binary hard-sphere mixtures that accounts for the excluded volume of the depletants more accurately.

It is noted that the binodals of FVT for PHS depletants in Fig. 2 are in remarkable agreement with the simulation results of the binary hard-sphere mixture, except for the low depletant concentration region. This similarity in phase behaviour for PHS depletants and hard-sphere depletants for large size discrepancies \((q \gtrsim 0.2)\) was also found by Velasco et al.\(^{29}\). Using a perturbation theory they determined the phase behaviour of a colloidal mixture using a variety of different model pair potentials. It was found that the exact shape of the depletion potential barely affects the phase behaviour of the system as various hard-sphere pair potentials yield essentially the same phase diagram as the Asakura–Oosawa pair potential. Moreover, a mismatch between simulation and theoretical results in the region of low depletant concentrations and high colloid concentrations was found by Velasco et al. for both the Asakura–Oosawa pair potential and the hard-sphere pair potentials, similar to the mismatch in FVT that can be seen in Fig. 2b. A downside of the perturbation theory is that it relies on a pair potential to account for depletion, which makes it difficult to apply to colloidal mixtures with large size discrepancies or containing anisotropic depletants, whereas FVT does not use a pair potential but is solely based on the free volume available to the depletants.

3. Adjusted \(\Omega\) for HS depletants

Next, the excluded volume of hard-sphere depletants is accounted for in both the reservoir and the system. We start from the definition of the semi-grand potential given by Eq. 3. An equation for the number of small hard-sphere depletants in the system is again obtained by equating the chemical potentials of the small spheres in the system and in the reservoir. Non-ideal behaviour can be accounted for in the chemical potential of the small spheres, both in the system and in the reservoir, by the work of small sphere-insertion:

\[
\bar{\mu}_d = \text{const} + \ln(\phi_d) + \frac{W^S}{k_B T},
\]

\[
\bar{\mu}_d^R = \text{const} + \ln(\phi_d^R) + \frac{W^R}{k_B T},
\]

where \(W^S\) is now the work of inserting a hard-sphere depletant in the system consisting of a binary sphere mixture, and \(W^R\) is the work of inserting a hard-sphere depletant in the reservoir, which is a dispersion containing only hard-sphere depletants. Combining Eq. 15 with Eqs. 23 and 24 the following expressions are found for the volume fraction of depletants in the system \(\phi_d\) for the fluid phase and solid phase, respectively:

\[
\phi_d = \phi_d^R \frac{\alpha_{\text{fluid}}^S(q, \phi_c, \phi_d)}{\alpha_{R}^R(\phi_d^R)}.
\]

\[
\phi_d = \phi_d^R \frac{\alpha_{\text{solid}}^S(q, \phi_c, \phi_\alpha)}{\alpha_{R}^R(\phi_d^R)}.
\]

In Eqs. 25 and 26 it is stressed that the free volume fraction in the reservoir is no longer unity and \(\alpha_{\text{fluid}}^S\) and \(\alpha_{\text{solid}}^S\) do not only depend on the volume fraction of large spheres \(\phi_c\), but also on the volume fraction of the depletants. The volume fraction of depletants in the system \(\phi_d\), in coexistence with the reservoir with a certain depletant volume fraction \(\phi_d^R\), can be found numerically by solving Eqs. 25 and 26. Substituting Eqs. 25 and 26 into the definition of the semi-grand potential given by Eq. 3 and applying the Gibbs–Duhem relation (Eq. 7) finally yields expressions for the semi-grand potential for the fluid and solid phases of a binary hard-sphere mixture:

\[
\bar{\Omega}_{\text{fluid}} = F_{0,\text{fluid}} - \int_0^{\phi_d^R} \frac{\alpha_{\text{fluid}}^S(q, \phi_c, \phi_d)}{\alpha_{R}^R(\phi_d^R)} \left( \frac{\partial \bar{\Pi}^R}{\partial \phi_d^R} \right) d\phi_d^R,
\]

\[
\bar{\Omega}_{\text{solid}} = F_{0,\text{solid}} - \int_0^{\phi_d^R} \frac{\alpha_{\text{solid}}^S(q, \phi_c, \phi_\alpha)}{\alpha_{R}^R(\phi_d^R)} \left( \frac{\partial \bar{\Pi}^R}{\partial \phi_d^R} \right) d\phi_d^R.
\]
where the dimensionless quantities from Eq. [11] are applied and the integration variable \( d\mu_0 \) in Eq. [3] is changed to the volume fraction of depletants in the reservoir \( d\phi^\text{R} \). The free volume fraction for depletants in the reservoir \( \alpha^\text{R} \) can be calculated by using Eqs. [15] and using \( q = 1 \). It is noted that Eqs. [27] and [28] recover the original semi-grand potential given by Eq. [10] when the PHS approximation is applied. In the next section we discuss how to obtain expressions for the free volume fraction of hard-sphere depletants in the binary system for both the fluid and solid phase. Even though the excluded volume of the small spheres will be accounted for in the free volume fractions, it is still assumed that the presence of the depletants does not alter the configurations of the large spheres in our approach outlined below.

### B. Free volume fraction for HS depletants

#### 1. Fluid phase

The free volume fraction in the fluid phase of a binary hard-sphere mixture can again be determined using the work for depletant insertion in a binary mixture given by SP [80], resulting in:

\[
\alpha^\text{fluid}_\text{s} = \exp \left[ - \ln(1 - \phi_c - \phi_d) + \frac{3q\phi_c + 3\phi_d}{1 - \phi_c - \phi_d} \right] \\
= \frac{1}{2} \left( \frac{6q^2\phi_c + 6\phi_d}{1 - \phi_c - \phi_d} + \left( \frac{3q\phi_c + 3\phi_d}{1 - \phi_c - \phi_d} \right)^2 \right) + q^3\tilde{\Pi}_\text{BM} \right] ,
\]

(29)

where \( \tilde{\Pi}_\text{BM} \) is the osmotic pressure of the binary mixture of hard spheres. An expression for \( \tilde{\Pi}_\text{BM} \) is given by the Boublik–Mansoori–Carnahan–Starling–Leland (BMCSL) equation of state for binary hard-sphere mixtures [51-54].

\[
\tilde{\Pi}_\text{BM} = \frac{\phi_c + q^{-3}\phi_d}{1 - \phi_c - \phi_d} \\
+ \frac{\phi_c^2 + q^{-1}\phi_c\phi_d + q^{-2}\phi_c\phi_d + q^{-3}\phi_d^2}{(1 - \phi_c - \phi_d)^2} \\
+ \left( \frac{\phi_c^3 + 3q^{-1}\phi_c^2\phi_d + 3q^{-2}\phi_c\phi_d^2 + q^{-3}\phi_d^3}{(1 - \phi_c - \phi_d)^3} \right) \\
\times (3 - \phi_c - \phi_d) .
\]

(30)

#### 2. Solid phase (\( q \leq 0.2 \))

The same approach cannot be followed for the solid phase since the osmotic pressure of a hard-sphere solid containing smaller hard spheres is not known. Moreover, as mentioned in Sec. [1A.1] the scaled particle theory approach does not accurately describe the free volume available in the solid phase at high concentrations [48]. The free volume fraction in the solid phase is approximated here by considering an FCC crystal of the larger spheres and assuming that the small spheres behave as a fluid in the free space left by the large spheres, which is valid for highly asymmetric binary sphere mixtures [33, 44] with \( q \leq 0.2 \). With this assumption, the free volume fraction \( \alpha^\text{solid}_\text{s} \) can be approximated by a product of the free volume fraction of the hard-sphere solid and the free volume fraction in the small sphere fluid that surrounds the larger spheres:

\[
\alpha^\text{solid}_\text{s} (q, \phi_c, \phi_d) = \alpha^\text{solid}_\text{s} (q, \phi_c) \alpha^\text{fluid}_\text{s} (q = 1, \phi_d^+) ,
\]

(31)

where \( \phi_d^+ = \phi_d/(1 - \phi_c) \) is the effective volume fraction of the small spheres in the space that is not occupied by large spheres and \( \alpha^\text{solid}_\text{s} (q, \phi_c) \) is given by the geometrical free volume fraction in Eq. [19]. This expression is only a rough approximation, as it does not accurately account for the overlap between the depletion zones of large and small spheres. To take this overlap into account, we make the same approximation for the fluid phase and use the ratio of this approximation and \( \alpha^\text{fluid}_\text{s} \) from SPT given by Eq. [29] as a correction factor that takes the overlap between the depletion zones of small and large spheres into account:

\[
\alpha^\text{approx}_\text{s} (q, \phi_c, \phi_d) = \alpha^\text{fluid}_\text{s} (q, \phi_c) \alpha^\text{fluid}_\text{s} (q = 1, \phi_d^+) ,
\]

(32)

\[
\alpha^\text{approx}_\text{solid}_\text{s} (q, \phi_c, \phi_d) = \frac{\alpha^\text{solid}_\text{s} (q, \phi_c, \phi_d)}{\alpha^\text{approx}_\text{s} (q, \phi_c, \phi_d)} = \alpha^\text{solid}_\text{s} (q, \phi_c) \alpha^\text{fluid}_\text{s} (q, \phi_c) \alpha^\text{fluid}_\text{s} (q = 1, \phi_d^+) .
\]

(33)

The result in equation [33] implies that the ratio between the free volume for a depletant in the binary system (denoted as \( \alpha^\text{R} \)) and in a system with only large particles is independent of the phase of the large particles. In Sec. [III A] it is shown that Eq. [33] accurately matches simulation data for dense colloidal hard-sphere mixtures with size ratios \( q = 0.1 \) and \( q = 0.05 \).

### 3. Solid phase (\( q > 0.2 \))

The analysis in the previous section only holds when the small spheres behave as a fluid in the FCC crystal of the large particles, but for \( q > 0.2 \) this is no longer the case and at these size ratios either an interstitial solid solution or a cocrystal is formed [33, 44]. Due to the large variety of crystal structures that can be formed for hard-sphere mixtures with larger size ratios [33, 35], a general FVT cannot be derived because each different cocrystal requires an accurate thermodynamic description and free volume fraction. However, for specific size ratios FVT might still be applicable. The Monte Carlo approach of Filion and Dijkstra [44] can be used to predict the crystal structures of binary mixtures with a specific size ratio. This may be used to obtain the required input for an accurate FVT approach for specific mixtures. Here we focus on the case of a mixture of hard spheres with size ratio \( q = 0.4 \). At
this size ratio the binary mixture forms an interstitial solid solution at high densities. In this relatively simple binary system, the large spheres organize in an FCC structure where the small spheres do not fit in the tetrahedral holes and there is space for one small sphere in the octahedral holes of the FCC crystal formed by the large particles.

A new expression is needed for the free volume available in the FCC crystal formed by the hard spheres \( \alpha _{\text{solid}} \) since Eq. 19 can no longer be applied for \( q = 0.4 \) due to multiple overlap of depletion zones. Finding an analytical equation for \( \alpha _{\text{solid}} \) for \( q > 0.15 \) is more difficult since already accounting for overlap of three depletion zones is mathematically laborious. However, it is possible to find an equation for the free volume available in an FCC crystal, or any other given (binary) crystal structure, accounting for multiple overlaps with a numerical approach. One way to do this is using Wolfram Mathematica’s built-in Region function. The free volume fraction of the one component FCC crystal obtained for \( q = 0.4 \) following this approach is given by:

\[
\alpha _{\text{solid}}^{\text{fit}}(q = 0.4, \phi _c) = 1.33 - 9.38 \phi _c + 28.5 \phi _c^2 - 48.0 \phi _c^3 + 47.1 \phi _c^4 - 25.5 \phi _c^5 + 5.97 \phi _c^6 . \tag{34}
\]

This result is used to determine the free volume fraction of the interstitial solid solution. Given that the number of octahedral holes in the FCC crystal of the large particles is the same as the number of large particles, and assuming that the excluded volume of a small sphere present in an octahedral hole completely fills the hole, the total free volume fraction in the system can be described as:

\[
\alpha _{\text{solid}}^S(q = 0.4, \phi _c, \phi _d) = \alpha _{\text{solid}}^0(q = 0.4, \phi _c) \left( 1 - q^{-3} \phi _d / \phi _c \right), \tag{35}
\]

where the term \( q^{-3} (\phi _d / \phi _c) \) can be interpreted as a filling fraction of small spheres in the octahedral holes.

C. Phase coexistence calculations

Two-phase coexistence densities of a system containing hard spheres and depletants are determined by applying the coexistence criteria of an equilibrium between a phase I and a phase II:

\[
\bar{\mu }_c^I = \bar{\mu }_c^{II} , \quad \bar{\Pi }_c^I = \bar{\Pi }_c^{II} . \tag{36}
\]

The chemical potential of the large spheres and the osmotic pressure are calculated with the following thermodynamic relations:

\[
\bar{\mu }_c = \left( \frac{\partial \bar{\Pi }}{\partial \phi _c} \right)_{\phi _c, T} . \tag{37}
\]

III. RESULTS & DISCUSSION

Here we present and discuss results of the theoretical method described in the previous section and verify the validity. First, we show how the adjusted description of the semi-grand potential that explicitly takes the excluded volume of the depletants into account deviates from the original semi-grand potential used in FVT for binary hard-sphere mixtures. Second,
we test the validity of the expressions used for the free volume fraction $\alpha^f$ in the binary mixture by comparing the relation between the concentration of depletants in the reservoir and in the system with computer simulation results. Next, we show how multiple overlap influences the free volume fraction in the solid phase. Subsequently, we present phase diagrams for size ratios $q = 0.05, 0.1, 0.2$ and $0.4$ and make a comparison with phase diagrams obtained from simulations. Finally, possible extensions of our approach are discussed.

A. Free volume fraction

The main difference between the theory presented in Secs. II A 3 and II B 3 with respect to the original FVT for binary hard-sphere mixtures is that the excluded volume of the depletants is explicitly taken into account in the free volume descriptions. Due to this, the free volume available to the depletants in the system and in the reservoir is significantly lower. Fig. 3 shows a schematic picture of the FVT approach presented in this paper. Both the large and small colloidal particles are surrounded by a depletion zone that is inaccessible to the small particles and the white areas in both the system and the reservoir show the free volume available to the depletants. In original FVT the excluded volume of the depletants was not fully taken into account and as a result the free volume fraction is always unity in the reservoir and the free volume fraction in the system is independent of the depletant concentration. When the excluded volume interactions of the depletants are taken into account this is no longer the case, as presented in Sec. II A 3 and both the free volume in the reservoir ($\alpha^R$) and the system (\(\alpha^S\)) depend on the depletant concentration. The effect of this excluded volume interaction is demonstrated in Fig. 3b where the ratio $\alpha^S/\alpha^R$, the relative fraction of the volume available in the system with respect to that available in the reservoir, is plotted as a function of the depletant volume fraction for different large particle concentrations $\phi_c$. This ratio is given by Eqs. (25) and (26) and is an important contribution to the semi-grand potential of the system given by Eqs. (27) and (28). Fig. 3b shows that $\alpha^S/\alpha^R$ is no longer constant as originally assumed by Lekkerkerker and Stroobants but increases as a function of the depletant concentration in the reservoir. The difference with respect to original FVT becomes more significant at higher concentrations of either the large or small hard spheres.

Fig. 4 shows the relation between the volume fraction of depletants in the system $\phi_c$ and in the reservoir $\phi^R_c$ for the fluid phase (a) and the solid phase (b). As mentioned above, this relation is given by the $\alpha^S/\alpha^R$ ratio. Also shown in Fig. 4 is the relation from original FVT theory and computer simulation data by Dijkstra et al. The results from the adjusted FVT follow the simulation data remarkably well, which confirms the validity of the equations obtained for the free volume fractions in the fluid phase and the solid phase given by Eqs. (29) and (33). The free volume approach followed here also compares strikingly well with an alternative relation between $\phi^R_c$ and $\phi_c$ derived by Roth et al. using a density functional theory approach.

As mentioned previously, the geometrical description of the free volume in a single component FCC crystal given by Eq. (19) is not valid anymore for $q > 0.15$ due to multiple overlap of depletion zones and a numerical method is used to obtain a description for $\alpha_{\text{solid}}$ as described in Sec. II B 3. Unfortunately, for these size ratios there is no simulation data on the free volume or on the equilibrium between $\phi_c$ and $\phi^R_c$ available in the literature for comparison. Fig. 5 shows the results of the numerical free volume fraction in the solid phase (\(\alpha^{R}\)) as a function of the volume fraction of the large particle solid $\phi_c$ for a depletant with size ratios $q = 0.1, 0.2$ and $0.4$. Also shown for comparison is Eq. (19) which does not account for multiple overlap. The free volume $\alpha^R$ matches with the analytical result of Eq. (19) for $q = 0.1$, as expected because no multiple overlap occurs for this size ratio. For $q = 0.2$ the numerical method also corresponds to Eq. (19) for low particle concentrations, however at a certain point multiple overlap of depletion zones occurs and the free volume fraction starts to deviate from Eq. (19). The volume fraction above which this occurs can be determined by:

$$\phi_c = \frac{4\pi \sqrt{2}}{9(1+q)^3},$$  \(39\)

which results in $\phi_c = 0.66$ for $q = 0.2$, indicated by the black dot in Fig. 5. For $q = 0.4$, multiple overlap of depletion zones already occurs at $\phi_c = 0.42$ and the free volume fraction strongly deviates from Eq. (19) showing the importance of taking multiple overlap of depletion layers into account for large size ratios $q$. 

![Figure 4. Relation between $\phi^R_c$ and $\phi_c$ as determined with Eqs. (25) and (26) (solid curves). The free volume fraction in the system $\alpha^S$ is given by Eq. (29) for the fluid phase (a) and Eq. (33) for the solid phase (b). The values used for the volume fraction of large spheres $\phi_c$ and the size ratio $q$ are indicated in the figure. The dashed curves show the results for PHS depletants using Eq. (19) for $\alpha_{\text{solid}}$. The symbols denote Monte Carlo computer simulation data from Dijkstra et al.](image)
Figure 5. Free volume fraction based upon geometrical arguments for a PHS depletant in a colloidal FCC crystal with the colloidal particles fixed at their respective lattice positions. The solid black curves show the results for the numerical procedure explained in Sec. [II B 3] that takes multiple overlap of depletion zones into account. The dashed gray curves show the results of Eq. [19] which is analytical but no longer holds when multiple overlap occurs. The size ratios considered are \( q = 0.1 \) where no multiple overlap occurs (a), \( q = 0.2 \) where multiple overlap occurs at high densities (\( \Phi_c \geq 0.66 \)) (b) and \( q = 0.4 \) where multiple overlap occurs for all concentrations where a solid phase is expected (c).

B. Phase behaviour of HS mixtures

1. Highly asymmetric (\( q \lesssim 0.2 \))

Phase diagrams were computed for binary hard-sphere mixtures with size ratio \( q = 0.05 \), 0.1 and 0.2 using the semi-grand potential descriptions given by Eqs. 27 and 28. The free volume fraction in the solid phase of the binary mixture is described using Eq. 33. For \( q = 0.05 \) and \( q = 0.1 \), the free volume fraction of the one-component solid \( \alpha_{\text{solid}} \) given by Eq. 19 is used. Multiple overlap of depletion zones is possible for \( q = 0.2 \) at high densities, therefore \( \alpha_{\text{solid}} \) is determined following the numerical procedure described in Sec. II B 3. It is noted that the phase diagram for \( q = 0.2 \) determined with Eq. 19 showed no significant difference from the phase diagram calculated with the numerical \( \alpha_{\text{solid}} \), which is most likely due to the fact that the deviations between both methods are quite small for this size ratio as shown in Fig. 5b.

A comparison with the theoretical phase diagrams and phase coexistence data obtained from direct coexistence simulations from Dijkstra et al. is shown in Fig. 6 for both the resinove and the system representation. Metastable isostructural coexistence lines are not shown in the theoretical phase diagrams except for the solid-solid phase coexistence for \( q = 0.1 \).

The theoretical binodals are in qualitative agreement with the simulation results. The binodals shift to lower depletant concentrations when the size ratio \( q \) becomes smaller and an isostructural solid-solid coexistence region appears at low values of \( q \). The solid-solid coexistence region in the theoretical phase diagram is metastable for \( q = 0.1 \), whereas a small stable isostructural solid-solid coexistence region was found in simulations. The discrepancy between the solid-solid coexistence regions and the mismatch of the fluid-solid binodals at low depletant concentrations is mostly likely because the geometrical description of the free volume fraction in the solid phase becomes less accurate for low packing fractions \( \Phi_c \) since a perfect FCC crystal is assumed. For \( q = 0.2 \) there is a slight underestimation of the fluid branch of the binodal compared to the simulation data. Overall, the phase diagrams are in much better agreement with the simulation data than the original FVT for binary hard-sphere mixtures as can be seen for example by comparing Fig. 6b with Fig. 2. Moreover, the FVT phase diagrams presented in Fig. 6 are very similar to phase diagrams determined with FVT using the PHS approximation, and Eq. 19 for the free volume fraction in the solid phase, which is in line with the perturbation theory predictions of Velasco et al. The agreement of the phase diagrams obtained with the FVT presented in this paper with simulation data and previous perturbation and DFT studies indicates that the excluded volume of the depletants is now accurately taken into account and FVT can be accurately applied to hard depletants. For future applications, FVT can be extended to study the phase behaviour of colloidal mixtures containing hard anisotropic depletants. It must be noted that anisotropic depletants have already been studied with FVT how-
ever the same approximations are made in these studies as the approximations in the original FVT for binary hard-sphere mixtures. It is expected that explicitly taking the excluded volume of the depletants into account in FVT has a large influence on the phase behaviour predictions for anisotropic depletants since these have a larger effective excluded volume than spherical depletant particles.

2. Interstitial solid solution ($q = 0.4$)

In Fig. 7b, we present the phase diagram of a binary hard-sphere mixture with a size ratio $q = 0.4$, determined using the numerical free volume fraction given by Eq. 35. Also shown is the phase diagram resulting from Monte Carlo free energy simulations by Filion. Fig. 7b shows the FVT results from the PHS approximation, with Eq. 34 for the free volume fraction in the solid phase, are shown in (b). The dashed lines indicate the fluid-fluid-solid triple coexistence region, the fluid phase is denoted with F, the solid phase with S, the fluid-solid coexistence region with F+S and the isostructural fluid-fluid coexistence region with F+F.

C. Outlook

It is interesting to extend our approach to binary colloidal mixtures in which interactions beyond hard core interactions are accounted for. In this paper the focus is on binary mixtures of hard spheres, while classical FVT focused on hard-sphere + PHS mixtures. It may be interesting to vary the additivity of the depletants to investigate the transition from PHS (non-additive) to HS (fully additive), along the lines of Roth and Evans. Also, it is useful to vary, for an asymmetric binary mixture only the degree of the interactions between the dissimilar particles as Wilding et al. did for a symmetrical mixture. A further step may be to induce a simple Baxter stickiness between the particles. This would involve three stickiness parameters. Finally, this may be extended by investigating binary hard-core Yukawa (HCY) mixtures, where each hard-core particle species interacts with its own and other type of particles through an additional Yukawa interaction with adjustable sign, strength and range. This has been done for HCY + PHS mixtures. An important element for all these extensions is to obtain knowledge of the preferred solid structures that appear in such mixtures, for which the simulation method of Filion and Dijkstra may provide a useful starting point.

IV. CONCLUSIONS

A FVT approach that explicitly takes the excluded volume of hard-sphere depletants into account was developed. The descriptions of the free volume fractions in a highly asymmetric binary hard-sphere fluid and solid were verified by comparing the volume fraction of depletants in the system as a function of the volume fraction in the reservoir with computer simulation results. Explicitly taking the excluded volume of the depletants into account leads to a significantly better match with the simulation data than original FVT for binary hard-sphere mixtures. Moreover, the phase diagrams obtained with the FVT approach presented in this paper are in qualitative agreement with simulation results. For highly asymmetric mixtures, FVT for hard-sphere depletants and PHS depletants lead to very similar results as expected from perturbation theory.

FVT is more difficult to apply for large size ratios due to the possibility of multiple overlap of depletion zones ($q > 0.15$) and the wide variety of binary solid phases that can be formed for $q > 0.2$. However, we have shown that the phase behaviour...
of a binary hard-sphere mixture with a size ratio of $q = 0.4$, where a simple interstitial solid solution is formed at high densities, can be described reasonably well using FVT. Although it is not possible to develop a general FVT method for binary hard-sphere mixtures with size ratios $q > 0.2$, a similar approach as for $q = 0.4$ could in principle be followed for specific size ratios, as long as the binary solid phases that can be formed are known in advance.

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DATA AVAILABILITY

All data computed in this work and copies of the Mathematica codes are available upon request.

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