



Isostructural solid–solid coexistence of colloid–polymer mixtures

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HIGHLIGHTS

- Phase behavior of penetrable hard spheres plus hard spheres from free-volume theory.
- Improved description of free-volume available for penetrable hard spheres in the solid phase.
- Depletion-driven isostructural solid–solid transition.

ABSTRACT

Hard spheres mixed with penetrable hard spheres display an isostructural solid–solid transition. This phase transition is fully driven by the entropy gain of the depletants without invoking explicit pair potentials between the colloidal particles. The solid–solid phase coexistence terminates at a critical endpoint with a size ratio $q \approx 0.09$. Colloid–polymer mixtures are an excellent candidate for the experimental realization of this intricate solid–solid transition, first predicted by Bolhuis and Frenkel for hard spheres with short range pair attractions [PRL 72, 2211–2214 (1994)].

Interactions between colloidal particles determine the phase behavior of colloidal dispersions [1,2]. Control over the interactions may be achieved through various surface modifications, such as functionalization of the particles with polymers, surfactants, or charged groups [3,4]. A systematic method to effectuate well-defined attractions is through the addition of non-adsorbing polymers to colloids [5–8]. The polymers are excluded from a region with thickness δ near the particle surface, the so-called depletion zone, due to excluded volume interactions. Therefore, when two colloidal spheres are brought in close proximity such that their depletion zones overlap, the free volume for the non-adsorbing polymer increases. This leads to an increase in entropy of the polymers. The magnitude and range of the resulting depletion attraction between the spheres are set by the concentration and size of the non-adsorbing polymer [7].

We focus here on a model system for the depletion attraction, which arises when hard spheres (HS, with diameter σ) are mixed with penetrable hard spheres as depletants (PHS, with diameter 2δ). PHS can freely overlap with each other, but feature hard-core repulsions with HS [7]. All length scales involved in the problem of interest are captured in terms of the depletant-to-colloid size ratio $q \equiv 2\delta/\sigma$. PHS are an approximation to polymeric depletants at relatively low concentrations in θ -solvents [9,10].

Different thermodynamic approaches can be followed to reveal the phase behavior of these HS–PHS mixtures. For instance, depletion effects may be mapped onto an effective pair potential between the colloidal particles, as done originally by Asakura and Oosawa [5,6] and Vrij [7], often denoted as the AOV potential. These pair potentials can be used in Monte Carlo routines [11,12] or other theoretical approaches [13–16] for phase stability studies. More sophisticated approaches account for multiple overlap of depletion zones [17] or the statistics of polymer chains [10,18].

Independent of the approach followed, it is the size ratio q that defines the possible thermodynamically stable phases. It is well-known that a collection of pure HS only exhibits a fluid–solid (F–S) phase transition [19,20]. Upon adding large depletants ($q \gtrsim 0.33$), the range of the effective attractions is sufficient to display additionally an isostructural F_1 – F_2 transition: the colloidal gas–liquid (G–L) transition [8,21,22]. In this work we show that, in the opposite limit of sufficiently small PHS, an isostructural solid–solid phase transition can be realized on purely entropic grounds.

We will do this on the basis of free volume theory (FVT), developed by Lekkerkerker and co-workers in the early 1990s [23,24]. FVT is an instructive approach to describe the phase behavior of colloid–polymer mixtures, because it accounts explicitly for the partitioning of

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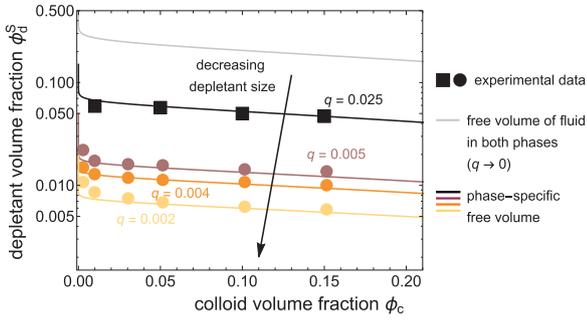


Fig. 1. Fluid branch of the fluid–solid binodals from free volume theory, (gray curve) using free volume expressions of the fluid phase for both phases in the limit of depletant-to-colloid size ratio $q \rightarrow 0$; and (black and colored curves) using phase-specific free volume expressions for the indicated q -values. Symbols represent experimental results from (squares) Piazza and Di Pietro [33] and (circles) Bibette et al. [34]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

depletants over the different phases by considering the free (accessible) volume of the depletants in the HS dispersion [8]. Several improvements have been incorporated into FVT to bring it closer to reality [25–28], for instance by accounting for configurations of large polymer chains *around* smaller colloidal particles [9,29–32], that effectively increase the free volume available to the depletants.

One remaining particularity of FVT for HS–PHS mixtures in the small depletant limit ($q \lesssim 0.1$) is the prediction that the F–S binodal becomes *independent* of q [8], see Fig. 1 (gray curve). This is unphysical, because in the small q limit the depth ε of the depletion potential for two spheres at contact in the AOV model is [8]

$$\frac{\varepsilon}{k_B T} \simeq -\frac{3}{2} \frac{\phi_d^R}{q}, \quad (1)$$

where $k_B T$ is the thermal energy and ϕ_d^R the bulk volume fraction of PHS. If the location of the binodal in terms of depletant concentration would be independent of q , the potential depth ε at the binodal would diverge. Instead, one would expect ε at the binodal to be nearly independent of depletant size, so that the depletant concentration at the binodal should be approximately proportional to q . Experiments indeed show this trend (Fig. 1, data points). We show that this unphysical behavior of FVT for small q is a consequence of an imprecise description of the free volume for PHS in the HS solid phase: an improved description brings FVT in line with experimental results and, crucially, yields the aforementioned solid–solid phase transition.

Within FVT, the system (S) containing HS and PHS is held in equilibrium with a reservoir (R) that contains PHS at constant concentration. System and reservoir are connected via a membrane, only permeable for the depletant. The thermodynamic properties of each phase k are described via the semi-grand potential Ω of the system, given exactly by $\Omega_k = F_k - V \int_0^{\phi_d^R} \alpha_k (\partial \Pi_d^R / \partial \phi_d^R) d\phi_d^R$, where F_k is the Helmholtz free energy of a reference HS-only system, Π_d^R is the osmotic pressure of depletants in the reservoir, ϕ_d^R the volume fraction of depletant in the reservoir, and $\alpha_k \equiv V_k^{\text{free}}/V$ is the free volume V_k^{free} accessible to the depletant relative to the total volume V [8]. It is this free volume fraction α_k that is the quintessential ingredient of free volume theory, fully determining phase behavior.

The free volume fraction is assumed independent of depletant concentration [23], so the dimensionless grand potential $\tilde{\Omega}_k \equiv \frac{\Omega_k v_c}{V k_B T}$ (with v_c the HS volume) has the form:

$$\tilde{\Omega}_k = \tilde{F}_k - q^{-3} \alpha_k \tilde{\Pi}_d^R, \quad (2)$$

where \tilde{F}_k is the dimensionless free energy of pure HS and the second term on the r.h.s. incorporates depletion effects. Due to the ideal nature

of the depletants, the dimensionless osmotic pressure of the reservoir is $\tilde{\Pi}_d^R \equiv \Pi_d^R v_d / (k_B T) = \phi_d^R$, with v_d the volume of a PHS. The depletant volume fraction in the system follows from the free volume fraction in each phase as $\phi_{d,k}^S = \alpha_k \phi_d^R$. Provided expressions are available for the reference free energy \tilde{F}_k and the free volume fraction α_k , the binodals may now be computed from the conditions of equal chemical potential and pressure for two coexisting phases using standard thermodynamic relations. Here, we leave all mathematical details to the SI and focus on the free volume fraction for depletants in the different phases.

The free volume fraction for depletants in the system in a fluid state, α_F , can be derived by combining Widom’s insertion method [35] with scaled particle theory (SPT) [36,37] for the work W required to bring a depletant from the reservoir to the system. It is assumed here that the free volume fraction $\alpha_F = \frac{\langle V_{\text{free}} \rangle_0}{V} = \exp[-W/(k_B T)]$ can be approximated from the average free volume $\langle V_{\text{free}} \rangle_0$ in a pure HS dispersion. This work is obtained by connecting the limits of inserting a very small depletant and a very big depletant in the system of interest. This leads to:

$$\alpha_F = \underbrace{(1-\phi_c)}_{\text{point depl.}} \underbrace{\exp(-Q_s)}_{\text{small depl.}} \underbrace{\exp(-q^3 \tilde{\Pi}_F^0)}_{\text{cavity}}. \quad (3)$$

The first term on the r.h.s. represents the free volume of point-sized depletants. The second term is a correction for small depletants, accounting for the overlap of depletion zones. The third term contains the osmotic pressure $\tilde{\Pi}_F^0$ of pure HS and is a representation of the work required to create a cavity in the HS system by the depletants.

Traditionally, Eq. (3) is used not only for the fluid phase, but also for the solid state [8]. The argument for this is that the free volume fraction in the solid phase is very low, so that the absolute difference between α_F and the actual free volume of a solid phase will be small. A slightly improved estimate for the free volume in a solid phase can be obtained by replacing $\tilde{\Pi}_F^0$ in Eq. (3) by the osmotic pressure of a HS solid, $\tilde{\Pi}_S^0$. However, this does not drastically improve the phase diagrams in the small q limit, as the free volume is dictated by the first two terms in Eq. (3), due to the q^3 dependence of the third term. This motivated us to investigate the free volume of the solid state in more detail.

We will determine the free volume fraction α_S of the solid state on the basis of geometrical arguments. Consider HS occupying fixed positions in a face-centered cubic (FCC) lattice. In terms of the excluded (inaccessible) volume v_{exc} for PHS in such a lattice, the free volume is given by

$$\alpha_S = 1 - \frac{v_{\text{exc}}}{V}. \quad (4)$$

For small q , only overlap between two depletion zones is possible and overlap between three or more depletion zones can be neglected. In this case we find an analytical function for the free volume fraction in the solid phase:

$$\alpha_S = \begin{cases} 1 - \phi_c \tilde{v}_{\text{exc}}^0 & \text{for } \phi_c < \phi_c^* \text{ (no overlap),} \\ 1 - \phi_c \tilde{v}_{\text{exc}}^* & \text{for } \phi_c^* \leq \phi_c < 2^{3/2} \phi_c^* \text{ (overlap),} \\ 0 & \text{otherwise,} \end{cases} \quad (5)$$

where $\phi_c^* \equiv \phi_c^{\text{CP}} / \tilde{v}_{\text{exc}}^0$ is the HS volume fraction where the depletion zones start to overlap, represents the normalized volume of depletion zones (in case of no overlap), and

$$\tilde{v}_{\text{exc}}^* \equiv \tilde{v}_{\text{exc}}^0 - 6 \left[1 + q - \left(\frac{\phi_c^{\text{CP}}}{\phi_c} \right)^{1/3} \right]^2 \left[1 + q + \frac{1}{2} \left(\frac{\phi_c^{\text{CP}}}{\phi_c} \right)^{1/3} \right]$$

accounts for the overlap between depletion zones, with $\phi_c^{\text{CP}} \equiv \pi / (3\sqrt{2}) \approx 0.74$ the volume fraction at close packing. The regime $\phi_c < \phi_c^*$ of Eq. (5) represents the situation where there is no overlap of depletion zones: the surface-to-surface distance between two neighboring colloidal particles is larger than 2δ . The interval $\phi_c^* \leq \phi_c < 2^{3/2} \phi_c^*$ accounts for two-body overlaps of depletion zones. In the SI, we show

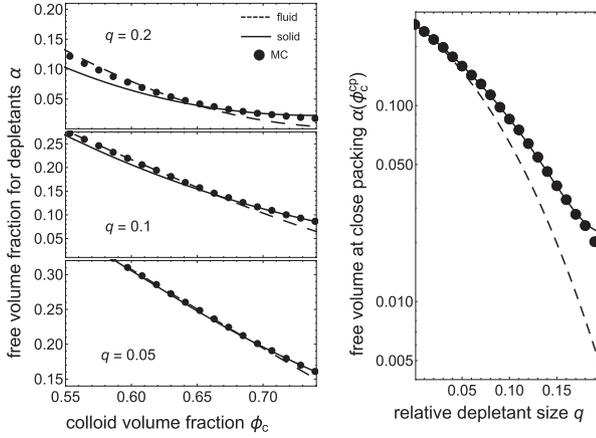


Fig. 2. Comparison between the free volume fractions for penetrable hard spheres in a system of hard spheres (dashed curves) from scaled particle theory for the fluid phase [Eq. (3)], (solid curves) from our analytical expression for the solid phase [Eq. (5)], and (points) from Monte Carlo simulations.

that for $q \lesssim 0.2$ three-body overlaps are not present in the solid phase. Finally, the situation of no free volume for the depletants within the FCC unit cell is accounted for, which occurs when the depletants are larger than the voids of the HS FCC lattice.

Monte Carlo (MC) simulations provide a way to verify the validity of Eq. (5) [38]. To this end we performed simulations on an NVT -ensemble of $N_c = 256$ hard spheres with an initial FCC state of 2×10^5 MC steps (one step corresponding to N_c trials of moving a randomly selected particle). In each of the last 50% of the MC steps, a virtual attempt was made to insert a PHS. The free volume fraction is given as the number of accepted insertions over the number of trials performed. The reported values correspond to the averages of 10 different runs.

The free volume fractions for HS in the solid state are presented in Fig. 2 as obtained from Eqs. (3) and (5) and are compared to our MC simulations. We focus first on the case of $q = 0.2$. Up to $\phi_c \approx 0.65$, the free volume from MC simulations follows the SPT fluid prediction, Eq. (3). For larger HS volume fractions, there is a crossover to our new prediction for the solid state, Eq. (5). For $q = 0.1$, this crossover happens also at $\phi_c \approx 0.65$. For even smaller depletants ($q = 0.05$), both the fluid and the solid state free volume fractions become an adequate description at lower volume fractions, but only the solid phase prediction matches the MC simulations at larger volume fractions. On each occasion, in the close packed regime, $\phi_c \rightarrow 0.74$, Eq. (5) predicts the MC results much better than Eq. (3): α_F underestimates the free volume for depletants for $q \lesssim 0.2$ at high ϕ_c (see Fig. 2, right panel). It is important to note that the thermodynamic properties of colloid–polymer mixtures do not only depend on the absolute value of α , but also on its derivative. As can be seen from Fig. 2 (left panel), the slopes near close packing are also different and this bears important consequences for the phase behavior.

We now turn our attention to the phase behavior of these HS–PHS mixtures. Calculation of phase diagrams is straightforward from Eq. (2) and basic thermodynamics. Fig. 3 shows phase diagrams for $q \leq 0.1$ using our expression [Eq. (5)] for the free volume of the solid phase (black curves) and following the usual practice of using the free volume of the fluid phase [Eq. (3)] for the solid phase (solid gray curves). The pure HS F–S coexistence is recovered at $\phi_d^R = 0$ [19]. Contrary to the phase diagrams generated when the fluid free volume α_F is used for the solid phase, we now do observe a shift of the binodal to lower depletant concentrations upon decreasing q , in agreement with experiments (see also Fig. 1, curves through the experimental points). Further, we observe a shift of the F–S coexistence towards higher HS volume fractions with increasing ϕ_d^R . At small ϕ_d^R the F–S coexistences quantitatively follow the predictions from thermodynamic perturbation theory (dashed gray curves) [39].

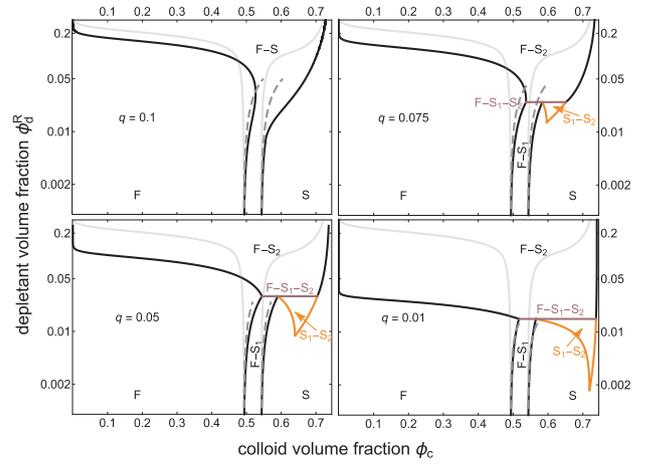


Fig. 3. Phase diagrams of hard spheres mixed with penetrable hard spheres as depletants for various relative depletant sizes q . The various curves are obtained (black, orange, purple curves) using the solid free volume [Eq. (5)] for the solid phase and (solid gray curves) using the fluid free volume [Eq. (3)] for the solid phase. The triple lines (purple) and isostructural solid–solid binodals (orange) are indicated. The dashed gray curves correspond to the fluid–solid coexistence calculated using thermodynamic perturbation theory. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The phase diagrams for $q \lesssim 0.1$ also display an *isostructural solid–solid* (S_1 – S_2) coexistence (orange and purple curves). Due to the piecewise nature of α_S , the curvature of the S_1 – S_2 binodal to the left and right of the critical point differs. This S_1 – S_2 critical point is found precisely at the HS volume fraction ϕ_c^* where overlap of depletion zones starts to take place: the colloid–polymer mixture phase separates into a high density solid with large overlap of depletion zones and a dilute solid with no overlap.

Isostructural S_1 – S_2 coexistence has been predicted theoretically [40–45] and reported in MC simulation studies [46,47] for systems with short-range attractive pair potentials, as well as for additive binary hard sphere mixtures [11]. Many of these authors hypothesized that mixing HS with depletants might be a way to realize such an S_1 – S_2 coexistence experimentally. So far, no experiments have demonstrated this transition. However, much like experiments, our computations do not invoke explicit pair potentials: the isostructural solid–solid coexistence arises from the partitioning (or entropy gain) of depletants. It must be noted that the wide presence of glassy states at such small ranges of attraction may make this isostructural solid–solid coexistence hard to find experimentally [48–50].

We now turn our attention to the critical behavior of the S_1 – S_2 coexistence, detailed in Fig. 4. We observe that the solid–solid critical point (CP) moves to lower HS volume fraction with increasing q , because $\phi_c^* \simeq \phi_c^{\text{CP}}(1-3q)$ for small q [see Eq. (5)]. This trend is in qualitative agreement with results from Dijkstra et al. for binary mixtures of hard spheres of different sizes [11]. Similarly, the PHS volume fraction at the CP increases linearly with q , since the depth ϵ of the potential [Eq. (1)] at the CP is expected to be approximately constant. Indeed, we find a limiting value of $\epsilon \approx -0.25k_B T$ for $q \rightarrow 0$ from the ratio of q and ϕ_d^R at the CP in terms of the AOV potential. This is considerably lower than found previously for HS interacting through square-well and Yukawa potentials, for which limiting contact potentials of $\epsilon \approx -0.59k_B T$ [46] and $-1.49k_B T$ [47] were found, respectively. This suggests that the S_1 – S_2 transition is sensitive to the precise shape of the (effective) interactions. In particular, we expect the shape of the binodal near the S_1 – S_2 critical point to become more rounded in real systems, as Brownian motion makes the transition from non-overlapping to overlapping depletion zones more gradual. For the triple point (TP), a soft reentrant behavior is observed: the PHS volume fraction first increases and then

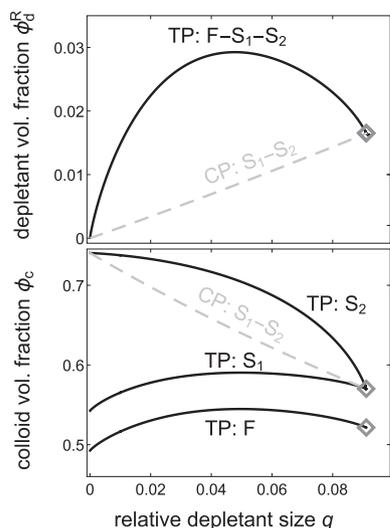


Fig. 4. Depletant volume fraction (ϕ_d^R) and colloid volume fraction (ϕ_c) at the fluid–solid–solid triple point (black curves) and solid–solid critical point (gray dashed curves) as a function of the relative depletant size q . The open symbols denote the critical endpoint.

decreases, in agreement with previous studies on hard spheres with short-range Yukawa attractions [45].

The conditions for which a critical point (dis)appears is denoted the critical endpoint (CEP). More specifically, a CEP is found when two phases are at a CP while they are in equilibrium with a third distinct phase, for instance when the S_1 – S_2 CP coexists with the fluid phase. This can be identified graphically in Fig. 4, where the S_1 – S_2 CP meets the TP. Thus, we find an upper q -limit for solid–solid coexistence of about $q \approx 0.091$; for larger PHS the S_1 – S_2 coexistence becomes metastable.

In conclusion, we have shown that mixtures of hard spheres plus small penetrable hard spheres as depletants exhibit an isostructural solid–solid phase transition. The finding of this phase coexistence follows from an accurate description of the free volume for depletants in the HS solid phase within free volume theory. Crucially, the solid–solid coexistence is caused solely by the partitioning of the depletants reflecting the situation of depletion-induced phase separation in experiments. The solid–solid coexistence is terminated by a critical endpoint at a depletant-to-colloid size ratio of $q \approx 0.091$. We note that, in general, the overall phase diagram is sensitive to the quantitative details of the free volume fractions. Our work contributes to the fundamental understanding of phase transitions in mixed colloidal dispersions and paves the way towards experimental realization of this solid–solid coexistence.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.cplett.2018.08.028>.

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