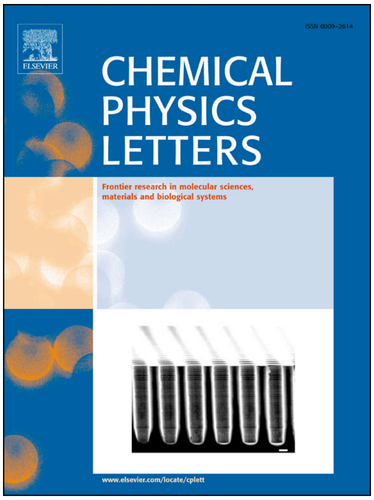

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Isostructural Solid–Solid Coexistence of Colloid–Polymer Mixtures

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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)].

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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, 6, 7, 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, 14, 15, 16] for phase stability studies. More sophisticated approaches account for multiple overlap of depletion zones [17] or the statistics of polymer chains [18, 10].

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 depletants over the different phases by con-

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