Polymer-Enforced Crystallization of a Eutectic Binary Hard Sphere Mixture

*Anna Kozina, †Pedro Díaz-Leyva, ‡Eckhard Bartsch, and Thomas Palberg

1Institut für Makromolekulare Chemie, Albert-Ludwigs Universität Freiburg, D-79104 Freiburg, Germany
2Institut für Physikalische Chemie, Albert-Ludwigs Universität Freiburg, D-79104 Freiburg, Germany
3Institut für Physik, Johannes Gutenberg Universität Mainz, D-55128 Mainz, Germany

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We prepared a buoyancy matched binary mixture of polydisperse polystyrene microgel spheres of size ratio $\Gamma = 0.785$ and at a volume fraction of $\Phi = 0.567$ just below the kinetic glass transition. In line with theoretical expectations, a eutectic phase behavior was observed, but only a minor fraction of the samples crystallized at all. By adding a short non-adsorbing polymer we enforce inter-species fractionation into coexisting pure component crystals, which in turn shows signs of intra-species fractionation. We show that in formerly inaccessible regions of the phase diagram binary hard sphere physics is made observable using attractive hard spheres.

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Binary colloidal mixtures are valuable model systems for fundamental studies of crystallization [1–3]. Detailed predictions of their phase behavior exist for binary hard sphere (HS) systems of different size ratio $\Gamma = R_S/R_L$ (where the $R_i$ are the radii of small ($S$) and large ($L$) spheres, respectively). These show a sequence of spinodal to azeotropic to eutectic phase diagram types with decreasing $\Gamma$, vanishing miscibility in the crystal phase for $\Gamma < 0.85$ and a huge variety of crystal structures for compounds [4–9]. For zero miscibility eutectics the inter-species fractionation is expected to cause a pronounced slowing of nucleation [8]. As the crystal phase becomes unstable for polydispersities above 6% [11, 12] (10% in 2D [10]) an additional intra-species fractionation is expected for strongly polydisperse systems [13, 14]. Indications of polydispersity altered solidification dynamics have been observed in several experiments [15, 16] including subtle influences of the skewness of the size distribution [17] but direct evidence of intra-species fractionation is still missing. While many of the predicted crystal structures have by now been observed [1, 2, 7, 18, 19] and also the general sequence of phase diagrams was confirmed [20], most parts of the phase diagram escape a detailed experimental investigation. In particular, the exact locations of phase boundaries in compound forming systems have not yet been determined. Crystallization kinetics has not been obtained and, except for a recent 2D-study [21], fractionation into coexisting $L$- and $S$-crystals has not yet been observed. The main reason for this is the interference of crystallization with the glass transition at large volume fractions [22]. The second reason is the presence of gravity, which seemingly enhances the trend to dynamically arrest the systems [23]. As seen in other systems, gravity, moreover, may lead to differential sedimentation and inhomogeneities in composition [24, 25].

In the present paper we circumvent sedimentation by investigating a binary mixture of buoyancy matched microgel particles. Exploiting observations made earlier on HS, copolymer micelles and binary HS [26–28], vitrification, on the other hand, is suppressed and crystallization is enforced by adding a short chained, non-adsorbing polymer. By adding polymer we move from HS to attractive HS (AHS), which, in principle, may significantly alter the phase behavior and crystallization kinetics [29–36]. For the present case, however, we may state that the phase diagram type for binary AHS at this size ratio is identical to that of the corresponding HS system. For the first time we demonstrate a eutectic solidification process over the full range of compositions for a binary mixture of size ratio $\Gamma = 0.785$. We observe simultaneous precipitation of $S$- and $L$-crystals and give a preliminary account of their crystallization kinetics. As both species own a large polydispersity, we are, in addition, able to also observe intra-species fractionation from the superposition of individual Bragg reflections. Further analysis suggests that the conversion efficiency is controlled by both the sample specific polydispersity and the polymer-induced mobility enhancement.

Cross-linked polystyrene (PS) microgel spheres were synthesized by emulsion polymerization, cleaned, dried and re-suspended in 2-Ethynylnaphtalene (2EN) as described previously [37]. In this good solvent the particles swell to hydrodynamic radii of $R_{h,S} = (152 \pm 4)$ nm and $R_{h,L} = (193 \pm 3)$ nm giving a size ratio of $\Gamma_h = 0.785$. The hardness of interaction was probed in oscillatory rheological measurements following the procedure described in [38]. Assuming an inverse power potential $U(r) \propto 1/r^n$ we find $n = 40 \pm 2$ [39] which is sufficiently steep to regard the particles as hard spheres. From form factor measurements the polydispersity index $\sigma = \sqrt{\langle R^2 \rangle - \langle R \rangle^2 / \langle R \rangle}$ is about 0.08 for both pure species. Sedimentation exper-
ments following [10] revealed the expected HS-like phase behavior. The freezing concentration was then identified with the ideal HS value and the melting points scaled accordingly to obtain \( \Phi_{M,i} = 0.528 \) and \( \Phi_{M,L} = 0.531 \). Further, from the position of the first Bragg reflection of samples at coexistence the lattice spacing and from that the effective radii were obtained as \( R_{\text{eff},L} = (170.5 \pm 2) \) nm and \( R_{\text{eff},S} = (126.2 \pm 3) \) nm (effective size ratio \( \Gamma_{\text{eff}} = 0.74 \) [41]. The volume fraction chosen for our experiments is just below the HS glass transition at \( \Phi_{GT} = 0.573 \pm 0.002 \) [42]. The phase diagram of the HS mixtures (R1 - R5) is shown in Fig. 1. To monitor the effects of attraction, a sample series (E1 - E10) of eutectic composition (\( x_S = 0.77 \)) and increasing concentrations, \( c_p \), of linear PS (\( R_g = 13.1 \) nm, \( M_W = 133000 \) g/mol; PSS GmbH, Germany) was prepared. Strongly attractive samples (A1 - A5) of different molar fraction of S-particles, \( x_S \), were prepared at \( c_p = 12.54 \) g/l. Respecting the volume occupied by the colloids, the polymer concentration in the free volume is \( c_p,\text{free} = 43 \) g/l [43], roughly 1.8 times larger than the overlap concentration \( c_p^* = 3M_W/(4\pi N_A R_g^2) = 23.5 \) g/l.

Start of crystallization measurements \((t = 0)\) was defined by taking a sample off the homogenizing tumbler and mounting it on a static light scattering goniometer (modified Sofica, SLS Systemtechnik, Germany, \( \lambda = 405 \) nm, 1 mW laser illumination, angular range 25° - 135°, resolution 1°). Structure factors, \( S(q,t) \), were obtained by time resolved measurements of the scattered intensity, \( I(q,t) \), for the concentrated dispersions, dividing by the appropriate form factors, \( P(q) \), obtained from a dilute sample and normalizing by the number density ratio: \( S(q,t) = [I_{\text{conc}}(q,t)P_{\text{dilute}}]/[P(q)\rho_{\text{conc}}] \). Here \( q = (4\pi n_D/\lambda)\sin(\Theta/2) \) is the scattering vector with \( n_D \) denoting the suspension refractive index. Zero time structure factors, \( S(q,0) \), only show the meta-stable melt, while at later times \( S(q,t) \) is a superposition of the contributions from fluid and crystalline phases. After two months most \( S(q,t) \) stopped evolving. The crystal scattering contribution, \( S_C(q,t) \), was obtained following [45]: \( S_C(q,t) = S(q,t) - \beta S(q,0) \). The scaling factor \( \beta \) represents the fraction of remaining melt and the total fraction of crystals \( X_C(t) = 1 - \beta(t) \). In this approximation we neglect the small changes of melt and crystal composition and thus scattering power with time.

The final \( S(q,\infty) \) for the \( R \)-samples in Fig. 2(a) are dominated by the scattering from the melt. \( R5 \) did not crystallize within two years and presented a single exponential decay of its intermediate scattering function. All other samples showed isolated small crystallites. The final crystallinities \( X_C(\infty) \leq 0.2 \) appear to be rather small. Presumably, values given by the lever rule applying to the coexistence regions are further diminished due to polydispersity [13]. In each sample we could isolate individual narrow Bragg-peaks appearing at different \( q \). Their average scattering vectors (dotted lines) reasonably well coincide with the melt maxima. The calculated osmotic pressures of the mixtures [44] are below the eutectic pressure \( P_E = 28k_BT(2R_L)^{-3} \) at \( \Gamma = 0.8 \) [8]. Hence, the observed phase behavior is consistent with theoretical expectations but also with previous results on a 3% polydisperse mixture with \( \Gamma = 0.72 \) [19].

The \( E \) samples in Fig. 2(b) show fluid order up to \( c_p = 9.05 \) g/l and a minimum of the structural relaxation time at \( c_p = 8.12 \) g/l. For \( c_p = 10.43 \) g/l we observe crystallization, while for \( c_p \geq 15.08 \) g/l the samples initially are amorphous again. Here the intermediate scattering functions show indications of a plateau-like feature. \( E9 \) and \( E10 \) finally started crystallizing after two years.

Fig. 2(c) shows the \( S_C(q,\infty) \) of the \( A \)-samples with \( c_p = 10.43 \) g/l. Large numbers of small crystallites appeared within days and grew to final sizes \((0.4 - 0.8) \) mm within several weeks. Neither additional peaks nor a shift in peak positions appears for the mixtures. This excludes the formation of compounds and of substitutional crystals. By comparison to the \( S_C(q,\infty) \) of the two pure samples we identify \( A2 \) and \( A3 \) to show crystals of both species, while \( A4 \) contains \( S \)-crystals only. The simultaneous occurrence of both crystal species shows that the systems are above the eutectic pressure (c.f. Fig. 1). In all mixtures the observed lattice constants equal those of the pure samples within experimental uncertainty. Using the effective radii, \( R_{\text{eff},i,t} \), and the number densities inferred from the peak maxima we may calculate the vol-

![Fig. 1: (Color online) Phase behavior of the pure binary mixture in the pressure-composition plane. The solid line gives the osmotic pressures for samples of \( \Phi = 0.567 \pm 0.006 \) and experimental size ratio \( \Gamma_h = 0.785 \) as calculated using the fundamental measure theory equation of state [44]. Circles indicate the values for samples R1 - R5 with partial volume fractions \( \Phi_S = \Phi_S/\Phi \) of 0.26, 0.57, 0.83 and 1 corresponding to molar fractions \( x_S \). \( \Phi_S/\Phi = 0.47, 0.77, 0.92 \) and 1 (where \( \rho_i = 4\pi N_A R_i^3 \)) is the particle number density. Thick solid lines are the phase boundaries adapted from [8] for a HS mixture at \( \Gamma_{th} = 0.8 \).](image-url)
Summarizing, we find that the addition of non-adsorbing polymer to a buoyant binary mixture allows investigations in regions of the phase diagram, in which under gravity much more complicated scenarios occur [25, 32] and which in pure HS usually are blocked by a kinetic glass transition. For the particular system investigated here the reference system without polymer shows fluid-solid coexistence or pure fluid. The observed phase behavior is consistent with the theoretically expected eutectic [4–8]. By contrast, \((L + S)\) coexistence is obtained, when the pressure, \(P\), surmounts the eutectic pressure \(P_E(x_F, c_{P,E})\), corresponding to the eutectic composition and a polymer concentration \(9.05\, g/l < c_{P,E} \leq 10.43\, g/l\). Recent work on one component HS [35, 36] showed that both \(P(\Phi)\) and \(P_E\) shift to lower values upon increasing the attraction. The present work suggests that for binary AHS \(P_E\) drops faster than \(P(\Phi = 0.567)\). However, theoretical predictions for composition dependent equations of state and the phase diagram of binary attractive HS are eagerly awaited to quantitatively rationalize our observations in a plot analogous to Fig. 1.

Being above \(P_E\), our mixtures should convert completely to \(S\) or \(L\)-crystals. Instead, we find a pronounced amorphous background signal and broad pyramid-shaped peaks composed from a superposition of a large number of individual Bragg reflections located at slightly different \(q\). This supports theoretical expectations that conversion proceeds via combined inter- [8] and intra-species fractionation [46]. In both cases the conversion efficiency should be correlated with the possibility to form combined density and composition fluctuations. The addition of polymer generally enhances the dynamics of such fluctuations [7] as long as the system remains untrapped by the attractive glass. However, conversion efficiency

\[
X_L(t) = c \int dq S_C(q), \text{ choosing } c \text{ such that } X_L(t) + X_S(t) = X_C(t) = 1 - \beta(t). \tag{2d}\]

\[
\Phi(R1) = 0.54, \Phi(R2, R3, R4) = 0.567, \Phi(R5) = 0.505. \tag{54}\]

Dashed lines indicate location of Miller-indexed reflections averaged over several individual crystallites. (b) Final structure factors for the \(E\)-samples of \(x_S = 0.77 \neq x_E\) and \(\Phi = 0.567\) with indicated amounts of added polymer. (c) Crystal structure factors of \(A\)-samples with location of Miller-indexed reflections of the pure samples averaged over several individual crystallites (dashed lines). (d) Temporal development of the fraction of crystals for the three mixtures \(A4 - A2\). Filled symbols denote \(S\)-crystals, open symbols denote \(L\)-crystals.

\[
\int dq S_C(q) \tag{4}\]

\[
\Phi(0, t) + \Phi(x_S, t) \tag{47}\]

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\Phi(0, t) + \Phi(x_S, t) \tag{47}\]

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\Phi(0, t) + \Phi(x_S, t) \tag{47}\]

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also relies on the availability of similar sized partner particles to form a stable fluctuation. We here observe an absence of L-crystals at large \(x_0\) (already seen in [19, 25]), an increased initial formation of S-crystals in A4, their delayed formation in A2, and an overall incomplete conversion. This suggests that depletion of the minority components (initial and/or in time) and their enrichment in the melt (by formation of majority crystals) govern their fluctuation spectrum and conversion efficiency. Particles from the wings of the size distributions are simply too diluted to crystallize.

In this study we have recovered important aspects of HS-crystallization in an AHS system. In future the controlled use of depletion attraction in formerly inaccessible regions of the phase diagram may allow detailed and quantitative studies of the phase behavior at other size ratios, kinetics of compound formation or other interesting problems of condensed matter physics.

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