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# Influence of the polymer size on depletion attraction—induced gel and glass transitions of microgel colloids

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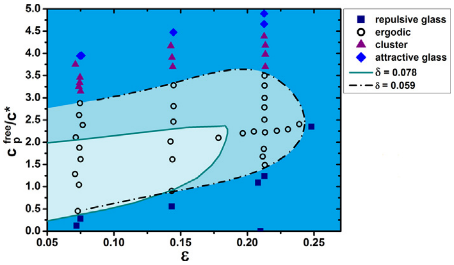
## HIGHLIGHTS

- Investigation of phase behaviour of a binary colloidal system in dependence of $\xi$.
- The re-entry region was shifted to higher volume fractions than theory predicted.
- We found colloidal fluid states up to 0.673 even considering osmotic deswelling.
- We used a qualitative model to classify samples to their phase state.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In previous work of our group on the re-entrant melting of colloidal glasses we observed an unexpectedly huge re-entry region for a binary system of 1:50 crosslinked polystyrene (PS) microgel spheres when a depletion attraction range $\xi = R_{g,polymer}/R_{colloid} = 0.08$ was induced by non-adsorbing (free) PS chains. To investigate whether this fluid region can even be increased by reducing polymer size and therefore the attraction range as predicted by mode coupling theory (MCT), we studied an almost identical system. It consists of a binary 1:50 PS microgel mixture ($R_{h,L} = 105.8$ nm, $R_{h,S} = 82.9$ nm; $\Gamma = R_{h,S}/R_{h,L} = 0.85$) with a reduced attraction range of $\xi = 0.059$ by use of an appropriate free PS polymer ($M_w = 79,600$ g/mol, $R_{g,polymer} = 9.18$ nm). Here the glass transition is shifted from $\phi_g = 0.577$ to higher values, allowing for fluid states up to volume fractions of $\phi = 0.715$. This is significantly higher than the maximum fluid state of $\phi = 0.69$ reached for $\xi = 0.08$. Tentatively correcting for osmotic deswelling these volume fractions reduce to 0.673 and 0.66, respectively. This is in qualitative agreement with MCT, but in quantitative disagreement because the theory predicts a shift of only a few percent. Such fluid states beyond the maximum amorphous packing of hard spheres ($\phi_{rcp} \sim 0.64$) do not occur for PMMA colloids and 1:10 crosslinked PS microgel spheres that can both be considered as hard spheres. Thus, we tentatively attribute the observation of fluid states at such high volume fractions to a combination of the slight softness of the 1:50 microgels, leading to osmotic deswelling and particle deformability. In addition, polydispersity and polymer non-ideality effects should be taken into account.

## 1. Introduction

Understanding the phase behaviour of concentrated colloidal dispersions has profited significantly from a well-established analogy between colloidal systems and atomic fluids [1]. This has allowed transferring concepts and theories from simple liquids [2] to colloidal dispersions. At the same time colloids have become very useful model systems to study fundamental problems of condensed

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matter physics such as crystal nucleation and growth [3,4] or the glass transition [5]. This successful application of colloids as model atoms has mainly been possible due to the availability of well-characterized model colloids with a well-defined interaction potential. Here sterically stabilized poly(methylmethacrylate) (PMMA) particles have played an outstanding role. It is generally accepted that they are the closest approximation to a (model) hard sphere (HS) system achieved so far, even though some open questions of their model character remain [6]. When transferring concepts from model systems to real, i.e. technical dispersions, one faces the fact that such dispersions are usually more complex than HS systems. This includes particle interactions and additives. The latter can affect colloidal interactions as these are potentials of mean force that depend not only on particle properties, but also on the properties of the surrounding medium [7]. Fortunately, it is in many cases possible to map the behaviour of other colloids onto that of HS by defining an effective HS radius or by matching the experimental volume fraction of freezing, $\phi_F$, onto the known value of the HS system [8]. This procedure has been demonstrated to be valid for particles with slightly soft repulsive interactions. These can be described by an inverse power potential $u(r) \propto r^{-n}$ with a “hardness” exponent $n > 18$ [9] which can be successfully applied, for example, to map microgel or core–shell microgel colloids onto the HS system [10,11].

Additives to colloidal dispersions are in many cases non-adsorbing polymers, micelles or some small particles (e.g. nano particles). It is long since known that such additives introduce an attractive part into the interaction potential due to the depletion effect [12–14]. This depletion attraction leads to significant modifications of dispersion properties. This concerns for example gelation in diluted dispersions [15] as well as widening of the fluid–crystal coexistence region and a fluid–fluid phase separation in concentrated dispersions [16,17]. Recently studies of the depletion effect have been extended to cover the phase behaviour of highly concentrated dispersions close to a colloidal glass transition [10,18–21]. These works have been inspired by the predictions of the mode coupling theory (MCT) of interesting effects concerning the glass transition [22–25]. The most prominent phenomenon is the so-called re-entrant melting or re-entry effect. On addition of a certain amount of free (i.e. non-adsorbing) polymer to a vitrified colloidal dispersion one observes a re-fluidization. The colloidal glass melts when “switching on” depletion attraction. By increasing polymer concentration the dispersion becomes even more fluid until reaching a maximum and then starts to become more viscous until it arrests again at higher polymer concentrations. The physics of the re-entry phenomenon can be understood by a transition between two glassy states – from a repulsive (=packing-driven) glass at low polymer concentrations to an attractive (=bonding-driven) glass at high polymer concentrations via an intervening fluid phase. At low polymer concentration the repulsive part of the potential between the colloid particles dominates and the dispersion is frozen due to packing constraints – particles are trapped in cages of their neighbours. These cages are tight and in order that one particle is able to move many surrounding particles have to move at the same time. Such a concerted motion is improbable and does not occur to a significant amount during the time of an experiment. When the strength of depletion attraction has increased sufficiently by the addition of free polymer (attraction strength being proportional to polymer concentration), particles have a significant probability to form transient bonds. This leads to transient doublets, triplets etc. and therefore sufficient free volume for neighbouring particles to move. By increasing the packing fraction of the repulsive glass, more free polymer is necessary to create free volume for melting. This results in a (repulsive) glass transition line that moves to higher polymer concentrations and eventually meets the attractive glass line at a limiting volume fraction. This behaviour has been predicted by MCT and has also been verified by computer simulations [26]. It leads to a fluid pocket which extends to higher volume fractions than the glass transition of the HS system at $\phi_g = 0.58$ [27].

Besides the interest of a better understanding of the physics of the glass transition and the proof of the applicability of MCT for the description of the colloidal glass transition, the re-entry phenomenon is also of practical interest. Highly concentrated dispersions with concurrent high fluidity are desired for most applications of synthetic dispersions like paints, inks or paper coatings. The benefits then are higher space–time-yield in synthesis, less storage and transport cost, less energy consumption and high formulation variability. So far, the classical route to achieve high particle packing at low viscosity levels in dispersions is to provide bimodal or broad particle size distributions [28,29]. However, for many applications a narrow monomodal size distribution would be preferred. Here the re-entry effect may be an alternative route to the preparation of highly concentrated, yet still fluid dispersions.

In previous work [30] we have demonstrated that the re-entry effect which has mainly been observed by monitoring (microscopic) particle dynamics via dynamic light scattering (DLS) techniques [18–21] is reproduced by the (macroscopic) flow behaviour as observed with rheological techniques. This is, again, consistent with the predictions of MCT: approaching the glass transition the zero shear viscosity diverges with the same power law as the structural relaxation time measured by DLS [31]. We could show that the concept of preparing highly concentrated dispersions by introducing depletion attraction and the thus induced re-entry effect can be transferred to commercial, water-based dispersions as well. However, significant differences were observed between studied systems concerning the dimension of the re-entry effect, i.e. the extension of the fluid pocket. Whereas for the generic HS PMMA system fluid samples have been achieved up to a volume fraction of 0.62 [19], the PS microgel system has allowed to reach fluid volume fractions of 0.69 with the commercial dispersions showing a behaviour in between (maximum fluid volume fraction 0.64) [30].

Given the importance of the re-entry effect we embarked on a systematic study – varying both colloidal and polymer properties. MCT predicts that reducing the range of depletion attraction increases the re-entry region (the attraction range is determined by the size ratio of polymer to colloid, i.e. $\xi = R_{g,polymer}/R_{colloid}$, with $R_{g,polymer}$ being the radius of gyration of the polymer and $R_{colloid}$ the effective hard sphere radius of the particles; see below for its determination). This effect could be responsible for the observation of the higher maximum fluid volume fraction reached by the commercial dispersion compared to the PMMA system. In the former system a size ratio of $\xi = 0.05$ has been employed, the latter size ratio was $\xi = 0.09$. However, this could not explain the extent of the re-entry region of the PS microgel system where volume fractions well above random close packing ($\phi_{rcp} = 0.64$) were found since here a size ratio ($\xi = 0.08$) [32] quite similar to that of the PMMA system was used. One particular feature distinguishing the microgel particles from other systems is their swelling in a good solvent by a factor of 5–6 in volume. This imparts a certain softness of particle interactions which can be tuned by varying the degree of internal crosslinking. To assess how far the huge re-entry effect is connected to this feature we reduced the crosslinking density from 1:50 (ratio of crosslinks to monomer units) to 1:10. Consequently the volume swelling is reduced to a factor of 2 and particle interactions are more hard-sphere like, but all other system parameters remain unchanged. In a first preliminary study we found that the re-entry region is significantly reduced in size and becomes very similar to that of the PMMA system, even though differences in detail still exist [33]. Obviously, the extent of the re-entry region is an intrinsic feature of the microgel particles and connected to their crosslink density. The large re-entry region of the 1:50 crosslinked particles could be caused by particle deformation, particle deswelling, partial