



Effect of cross-link density on re-entrant melting of microgel colloids

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ABSTRACT

We investigated concentrated suspensions of newly synthesized highly cross-linked (1:10) polystyrene (PS) microgel particles dispersed in a good, iso-refractive organic solvent that allowed for a detailed study using light scattering techniques. Inducing depletion attraction by addition of non-adsorbing (PS) polymer, we analyzed the re-entrant melting behavior of the particle system. We compared our results with that of previous studies on polystyrene microgel particles with a lower cross-linking ratio (1:50) and on PMMA suspensions. In contrast to the (softer) 1:50 microgels where an unexpectedly huge re-entry effect was found with fluid samples extending up to a volume fraction $\phi \approx 0.69$, the re-entry region here extends only up to $\phi \approx 0.61$ and the attractive glass transition line is found at significantly lower polymer concentrations.

Instead we find a closer similarity of the re-entry behavior with that observed for hard sphere-like PMMA particles. Whereas the highest volume fractions up to which fluid states could be observed are comparable, the polymer concentration needed to induce re-entrant melting and the formation of attractive glass is shifted to higher polymer concentrations. While the latter effect may be attributed to the non-ideal behavior of the free polymer, the extension of the fluid region with respect to colloid volume fraction appears to depend sensitively on system details like particle softness or particle size distribution.

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1. Introduction

Colloidal dispersions are commonly used as model systems for investigating fundamental principles of condensed-matter systems. The glass transition in particular has long been investigated with light scattering techniques using suspensions of hard sphere (HS) particles, such as sterically stabilized polymethylmethacrylate (PMMA) in cis-decalin [1–3]. The fundamental physics of the processes involved in vitrification has been successfully described within the framework of mode coupling theory (MCT) [4–6], even though some discrepancies between theory and experimental observation still remain under debate [7,8]. In addition to catching the essence of glass transition phenomena in hard sphere-like colloidal dispersions, mode coupling theory predicted the possibility of melting colloidal glasses by inducing short range attraction between the colloidal particles [6,9,10]. Attraction reduces the average distance of the particles in the suspension, freeing more

volume for particle movement and thus melting the glass. This is commonly achieved by adding non-adsorbing polymer to the colloidal suspensions, which gives rise to the so-called, well known depletion attraction [11–13]. This behavior – usually addressed as re-entrant glass transition or re-entry phenomenon – has been confirmed in several studies, using e.g. the aforementioned PMMA particles dispersed in cis-decalin [14,15] or polystyrene (PS) microgel particles dispersed in 2-ethylnaphthalene (2-EN) [16–19]. In the case of PMMA particles fluid states up to volume fractions of $\phi \approx 0.62$ were found, while it was possible to increase the fluid volume fraction up to $\phi \approx 0.69$ in the case of the PS microgel particles.

The unexpectedly large re-entry region where fluid states could be induced by adding free polymer to the colloidal glass in the case of the previously studied 1:50 cross-linked PS microgels (1 crosslink per 50 monomer units) as compared to the PMMA system raised the question to its physical origin. Even though the phase behavior, rheology, and glass transition dynamics of such microgel particles without free polymer are comparable to that of hard spheres-like colloids – such as PMMA – once an appropriate mapping of the volume fraction scale is performed [17,19], one could imagine that the discrepancies in the re-entry behavior are connected with the microgel character of the PS particles. Their inherent (slight) softness which is expressed by an inverse power interaction potential

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