

PHASE BEHAVIOR OF HARD-SPHERE PARTICLE IN A COLLOIDAL BINARY MIXTURE

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ABSTRACT

The researchers investigated the pair correlation function $g(r)$ between sterically stabilized polystyrene particles in a binary mixture with poly (N-isopropylacrylamide-co-acrylic acid) (pNipam-co-AAc) colloidal microgels as a function of temperature. The intensity peak of $g(r)$ for polystyrene particles increases with increase in temperature indicating apparent attraction. The interaction potential ranges from repulsive at low temperature to attractive interaction as the temperature increases due to the collapse of the steric stabilizing surface layer, whose hydrogen bond is broken at low pH value. The experiment shows that tuning external factors in colloidal systems is possible to design complex materials that response to multicomponent.

Keywords: pair correlation function $g(r)$, colloidal systems, standard particle-tracking techniques.

INTRODUCTION

The phase behavior of colloidal dispersions are determined largely on the pair interactions between the particles (Kodger *et al.*, 2015). The interparticle forces such as Van der Waals attractions, Coulombic interactions, steric repulsions and hydrogen-bonding are essential to control colloidal phase behavior (Cho *et al.*, 2009). With well controlled microscopic structures and interactions, colloidal suspensions are an ideal model system for exploring how matter organizes itself (Manopharan, 2015). Because their thermal motions can be directly visualized by optical video microscopy (Baumgartl and Bechinger, 2005) and tracked by image processing, they have also become a key constituents of model for the study of fundamental Statistical Physics (Stil *et al.*, 2005).

The stability of colloidal systems depends on the balance between the attractive Van der Waals forces and any repulsive forces (e.g. electrostatic and/or steric repulsion) acting on the particles. When the range of attraction is much bigger than the repulsive force, aggregation is induced. Both the strength and range of attraction affect the phase behavior of the colloidal systems. Thermosensitive polymers have been used as additives of the colloidal suspension. Adding polymer to colloidal suspension is an effective way to tune attractive force between colloidal particles (Zhao *et al.*, 2012). The properties of the mixed systems can be easily tuned by adjusting temperatures. In addition to the possibility of tuning the nature of colloidal particles themselves, is to form a binary mixture of two different colloids. This gives rise to an effective colloid-colloid interaction.

Several pieces of experimental evidences have shown like-charged colloidal particles cluster when in confined geometries (Crocker and Grier, 1994, 1996; Kepler and Fraden, 1994; John *et al.*, 1999).

This seemed to suggest the existence of an attractive minimum in the thermodynamic pair potential. Recently, Huai and Simon (2013) probed the behavior of sterically stabilized temperature

sensitive colloidal particles as a function of temperature and electrolyte concentration. Their results, show that the degree of particle aggregation, is more prominent at high electrolyte concentrations and temperatures, due to the dehydration of the steric stabilizing layer. Therefore, the study of binary suspensions of particles which are sterically stabilized carrying like charge electric and a reversible temperature-responsiveness which also changes to pH and ionic strength is important. Breedveld's group have previously reported that pNipam-co-AAc is pH-sensitive and changes from attractive to repulsive as the pH increases (Jac Kyu *et al.*, 2009; Zhiyong *et al.*, 2009). It is expected that the introduction of this responsive microgel in the system with a hard sphere particles, will alter the pH of the total vicinity of the system causing insufficient stabilization on the surface layer of the hard sphere.

To this end, we experimentally investigated the influence of adding pNipam-co-AAc microgel on the clustering behaviour of sterically stabilized hard-sphere particles. These colloids are composed primarily of Polystyrene (PS) particles that are sterically stabilized on the surface layer with polyvinyl pyrrolidone (PVP) which is known to be pH-sensitive (Rui *et al.*, 2011) and thermosensitive poly (N-isopropylacrylamide-co-acrylic acid) (pNipam-co-AAc) colloidal microgels which readily permit *in situ* variation. We observed both qualitatively and quantitatively Polystyrene particles in the binary mixture showing attraction and clustering at high temperatures due to the dehydration of the steric stabilizing surface layer. This attractive interaction in our system can be attributed to the effect of low pH induced by the presence of pNipam-co-AAc. The present experiments would be a good way to induce attraction *in situ* in micro-sized colloidal systems.

EXPERIMENT

The experiment employed ensembles of particles sandwiched between a glass slide and cover slip (Fisher Scientific), creating a quasi-2D chamber. Polystyrene (PS) particles had a diameter

of 1.0 μm and poly (N-isopropylacrylamide-co-AAc) (pNipam-co-AAc) particles had diameter of $\sim 1.0 \mu\text{m}$. Polystyrene particles are much more hard sphere-like (Dinsmore *et al.*, 1995; Zhang *et al.*, 2011; Royall *et al.*, 2013) while pNipam-co-AAc particles have a soft interparticle potential (Han *et al.*, 2008; Peter *et al.*, 2014). First, we loaded a prepared sample of Polystyrene only, which we used as the control experiment into a glass slide and cover slip. A small amount of Fluorescein sodium salt dye ($\sim 0.3\%$ w/v) was added to the aqueous suspension of particles in order to improve imaging contrast. The dye was excited using light from a mercury lamp that was directed through a 488-nm wavelength bandpass filter. The sample was hermetically sealed by using optical glue (Norland 63). Images of the samples were acquired at 30 frames/s by using fluorescent video microscopy at temperatures ranging from 24.0 $^{\circ}\text{C}$ to 40.0 $^{\circ}\text{C}$. Sample temperature was controlled by thermal coupling to a resistively heated microscope objective

(EHEM Professional 3), and the sample was allowed to equilibrate for 30 mins at each temperature before data

acquisition. In a separate experiment, a binary mixture consisting of pNipam-co-AAc particles and Polystyrene (PS) particles under the same experimental conditions as the control experiment above was loaded between two glass cover slips to create a colloidal monolayer. The resulting video images of both control experiment (PS only) and binary mixture experiments consisted of dark particles on a bright background (Figure 1). The raw images (dark particles on a bright background) were then inverted to yield images of bright particles on a dark background (Figure 1). Images of the system with resolution of 640 x 480 pixels were digitalized and analyzed. The trajectories of each particle in the video was then extracted using standard particle-tracking techniques (Crocker and Grier, 1996).

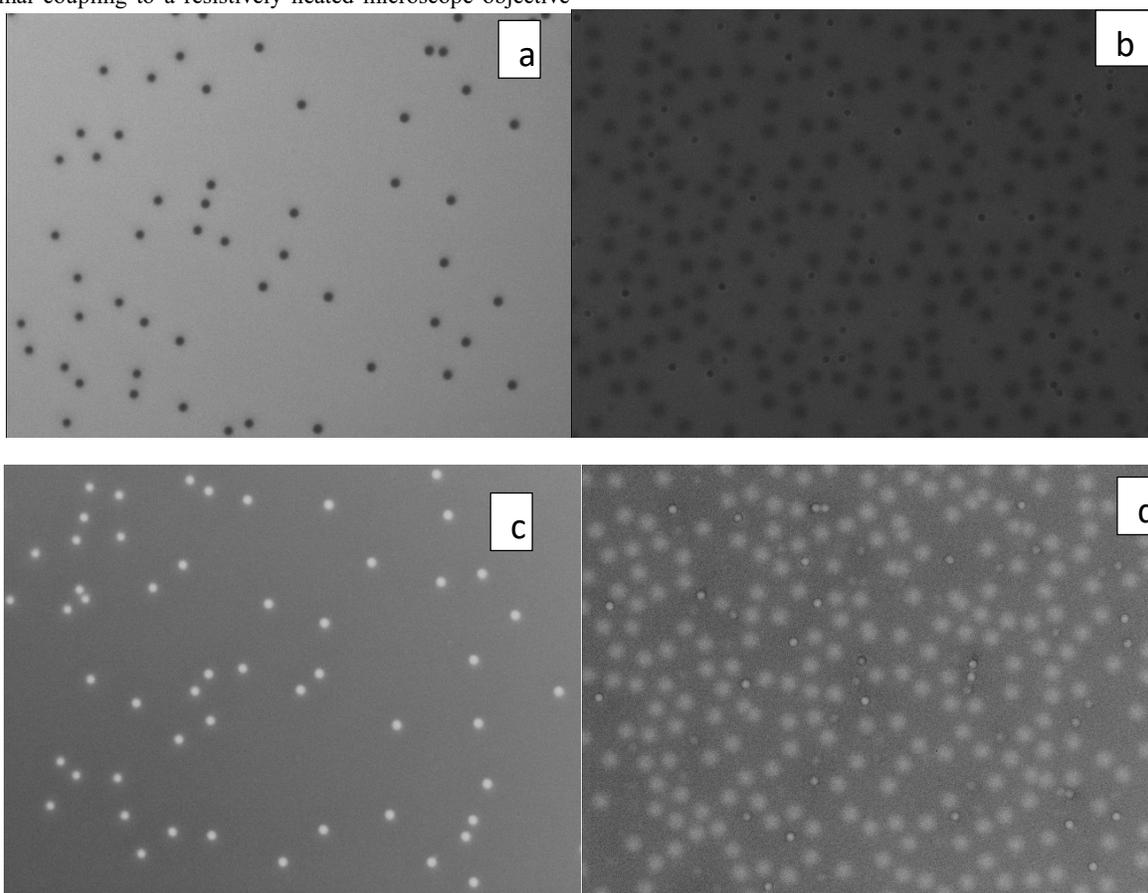


Figure 1: Images PS only and PS + pNipam-co-AAc colloidal suspensions in the quasi-2D confinement. (a) dark particles of PS only on a white background (b) dark particles of PS + pNipam-co-AAc on a white background (c) White particles of PS only on a dark background (d) White particles of PS + pNipam-co-AAc on a dark background.

RESULTS AND DISCUSSIONS

To characterize the phase behavior of the colloidal systems, we employed the pair-wise interaction measurement analysis. The method devised by Crocker and Grier (1996) allows us to locate the centroid of each particle within a precision of 1/5 pixel (\sim

0.02σ), particles' x and y coordinates in each image are determined. The pairwise

interaction potential between colloidal particles in a medium can be determined from the equilibrium structure of particle suspensions (Ramirez-Saito *et al.*, 2006). This is quantified through the two dimensional radial distribution $g(r)$, which provides the probability of finding neighboring particles at

specific separation distances (Cho *et al.*, 2009). We calculated $g(r)$ by averaging over 10000 frames to reduce the statistical noise, with r being the measured in-plane interparticle distance. Theoretically, the effective pairwise interaction potential $U_{eff}(r)$ in the equilibrium distribution of particles in a suspension is related to $g(r)$ through the Boltzmann distribution as (Cho *et al.*, 2009; Crocker and Grier, 1996):

$$g(r) = \exp\left(-\frac{U_{eff}(r)}{k_B T}\right), \quad (1)$$

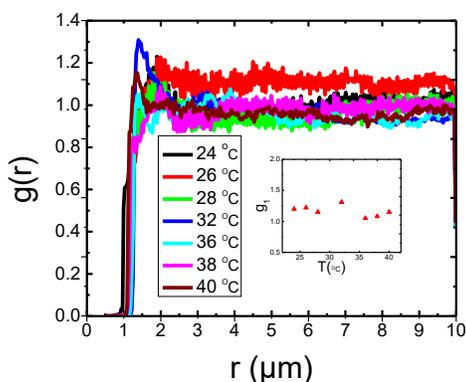


Figure 2a: $g(r)$ as a function of distance for PS particles only: shows that purely repulsive interaction occurs at all temperatures.

As one can see here, $g(r)$ follows a qualitative behavior within the range of temperatures studied. However, both measurements of $g(r)$ differ quite dramatically from each other. The intensity of the pair correlation function $g(r)$ for the PS only is close to 1, almost uniform probability for all temperatures considered, with the highest peak of $g(r) = 1.3$ at 32 °C (figure 2a). As expected for a hard-sphere model, this shows purely repulsive interaction occurs at all temperatures. Comparably, the binary system of pNipam-co-AAc and Polystyrene exhibit both qualitative and quantitative different behavior from the control experiment. As we can see in figure 2b, the intensities of the peaks are clearly above the uniform probability ranging from $g(r) = 1.72$ at 24°C to 4.17 at 40°C. This clearly shows a shift from repulsive interaction at low

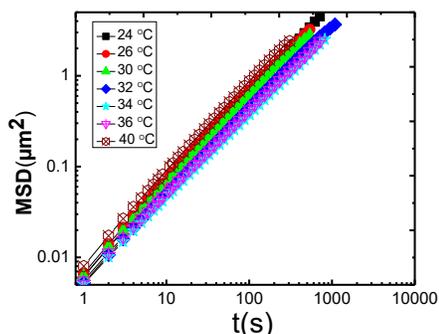


Figure 3a: Mean square displacement (MSD) of PS alone: The colloidal dispersion shows nearly fast diffusive fluid behavior.

where

$$g(r) = \langle \int \rho(x-r) \rho(x) dx \rangle / [\int \rho(x) dx]^2 \quad (2)$$

is the two-particle correlation function and angle brackets indicate an average over angles.

Our experimental results of $g(r)$ for PS only (control experiment) and binary sample as a function of temperature appear in figure 2.

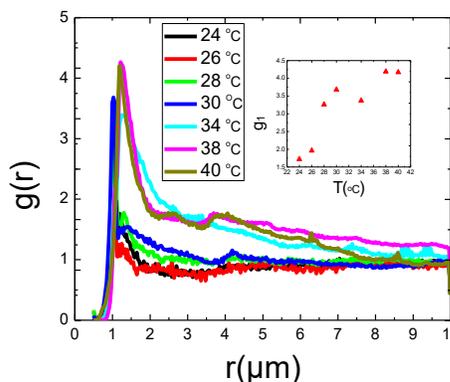


Figure 2b: $g(r)$ as a function of distance (r) for PS in mixture: Shows, repulsive interaction at low temperature, however, as the temperature is increased, the interaction changes from repulsion to attraction.

temperature to attractive interaction as the temperature increases, with noticeably strong attraction occurring from 30°C. Note that similar qualitative behavior of the pair correlation function has been reported in Quasi-2D aqueous suspensions of nonfluorescent polystyrene and silica sphere, as well as in suspensions of fluorescent polystyrene spheres, measured by optical microscopy in the white-image mode and in the fluorescent image mode respectively (Han *et al.*, 2008; Peter *et al.*, 2014).

In addition to the direct visualization of particle dynamics and spatial organization, the microscopy data can offer a quantitative assessment of the particle diffusion. To illustrate this, a log-log plot of the particles' mean square displacement (MSD) versus time as a function of temperature is shown in figure 3.

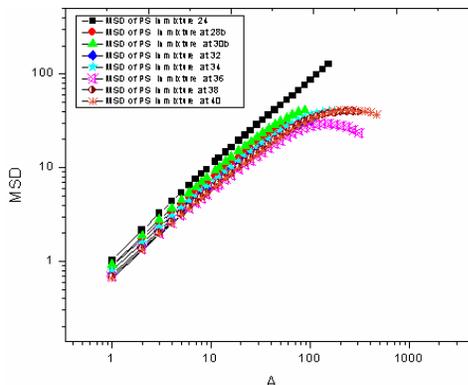


Figure 3b: Mean square displacement (MSD) of PS in mixture: At temperature 24C, the colloidal dispersion shows fast diffusive fluid behavior, as the temperature increases with the attraction of the particles, the particle displacement decreases with the sample progressing from a fast, diffusive fluid to a slow, subdiffusive fluid.

The MSD of the Polystyrene particles in an ensemble is given by

$$MSD(\tau) = \langle [r_i(t+\tau) - r_i(t)]^2 \rangle_{i,t} \quad (3)$$

where $r_i(t)$ is the position vector of the i th particle at time t , τ is the lag time and $\langle \rangle_{i,t}$ indicates the spatial average over both the ensemble of particles and all starting times t .

The MSD plots for Polystyrene only (control experiment) in figure 3a shows nearly diffusive fluid behavior with repulsive interactions for all temperatures considered. On the other hand, the MSD plot for the Polystyrene in the binary mixture figure 3b illustrate a marked slowing of the particle motion with increase in temperature. At 24°C after sample preparation, the colloidal dispersion shows nearly diffusive fluid behavior with repulsive interactions. As the temperatures increases, the MSD of the sample at long lag time decreases. Thus, as the temperature reaches the critical temperature 32°C, the maximum particle displacement decreases with the particles progressing from a fast

diffusive repulsive interactions to a slow sub-diffusive, fluid with attractive interactions forming clusters.

With the pairwise interactions between the polystyrene particles in the binary mixture apparently being attractive at high temperatures, as evidenced by the clustering in the dispersions, it is likely that the redistribution of pNipam-co-AAc in the system with increase in temperature completely altered the pH of the total suspension. These observations can be explained by the pH-sensitivity behavior of pNipam-co-AAc. We also confirmed that pNipam-co-AAc changes in pH and ionic strength with response to temperature by performing experiments at different temperatures. Our result in figure 4 is in agreement with several reports which shows that the incorporation of ionizable functional groups such as acrylic acid (AAc), as co-monomers, to pNipam, it responds not only to temperature but also to pH as well as ionic strength (Cho *et al.*, 2009).

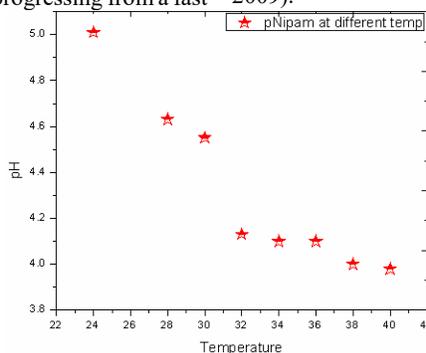


Figure 4: pNipam particles at different temperatures, shows that increase in temperature causes a decrease in pH

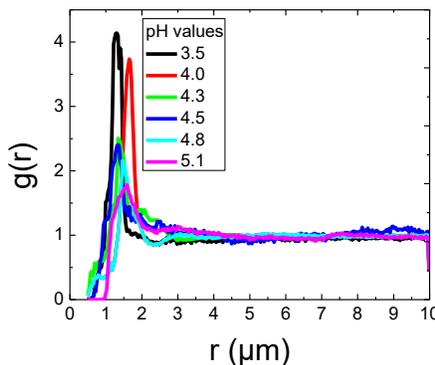


Figure 5: $g(r)$ of PS at different pH values

Figure 5 exhibit the plot of $g(r)$ as a function of pH and the intensity of the peaks respectively, for the slightly charged, sterically stabilized polystyrene particles. This is to further probe the effect of change in pH on the particles. Clearly, one can see the dependence of $g(r)$ on pH. This is in agreement with the foregoing, that the presence of pNipam-co-AAc altered the behavior of the hard sphere particles.

At high temperatures, the hydrogen bond between protonated AAc groups breaks and changes from repulsive to attractive. Thus, altering the pH of the total vicinity.

Following this, the ionic strength of the slightly charged, sterically stabilized particles in the system is also affected. This further leads to the dehydration of the steric stabilizing layer, which induces greater instability on the particles. Hence, the form clusters at high temperatures. Another interesting feature is that the attractive interparticle interactions are apparently long range.

CONCLUSION

This research has employed binary colloidal suspensions of temperature-sensitive soft particles and slightly charged sterically stabilized hard sphere particles to probe the clustering behavior of the hard sphere particle as a function of temperature. Interestingly, our result shows both qualitatively and quantitatively evidence of repulsive to attractive interaction as a function of temperature in the polystyrene particles. Our findings suggest that the hard sphere particles not only responds to temperature but also pH. This pH sensitive long range interaction suggest that by introducing pNipam-co-AAc to a system of sterically stabilized hard sphere, one can enhance tunability of interactions between the hard sphere colloidal particles. Furthermore, our result clearly suggest that the attractive interactions arises from the collapse of the steric stabilizing surface layer, whose hydrogen bond is broken at low pH value.

In the future, this will serve as a good way to manipulate micro-sized particle interaction *in situ* from repulsive to attractive.

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