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# Direct Observation of Phase Transition Dynamics in Suspensions of Soft Colloidal Hydrogel Particles

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**Abstract.** Due to the tunability of their softness and volume as a function of temperature, poly(N-isopropylacrylamide) (pNIPAm) hydrogel particles have emerged as a model system for soft colloidal spheres. By introducing AAc as comonomer, one can also tune the particle volume via pH. We report on the phase behavior of these stimuli-responsive colloids as measured with a microdialysis cell. This device, which integrates microfluidics with Particle Tracking Video-microscopy allows for simple and quick investigation of the phase behavior of suspensions the soft colloidal hydrogel as a function of pH as well as its packing density. In particular, we demonstrate the existence of an unusually broad liquid/crystal coexistence region as a function of effective particle volume fraction. Additionally, we reveal that non-equilibrium jammed states can be created in the coexistence region upon sudden large changes of pH. The phase diagram is indicative of complex interparticle interactions with weakly attractive components.

**Keywords:** Stimuli-responsive Hydrogel, Phase behavior, Particle Tracking Microscopy, Microfluidics.

**PACS:** 47.57.J-, 83.80.Hj, 64.75.Xc, 87.64.M

## INTRODUCTION

The phase behavior of colloidal dispersions has been studied over the past few decades, because they provide an excellent model system for atomic systems with time- and length-scales that are more readily accessible for experiments. Depending on effective particle volume fraction ( $\phi_{eff}$ ), the dispersions tend to phase transitions from a liquid state to crystal or glass state with increasing concentration<sup>1</sup>. While sterically stabilized poly(methyl methacrylate) (PMMA)<sup>1</sup>, and silica<sup>2</sup> have been widely used as hard-sphere model systems, recently hydrogels consisting of mesoscopic, covalently crosslinked polymer have attracted attention as useful soft-sphere model systems. The most popular colloidal hydrogel system is poly(N-isopropylacrylamide) (pNIPAm), which can be synthesized to form monodisperse, cross-linked colloidal particles. In aqueous media, pNIPAm undergoes a reversible and continuous volume phase transition<sup>3</sup>, which provides temperature-sensitive tunability to modulate  $\phi_{eff}$ <sup>4</sup>. By introducing acrylic acid (AAc) as comonomer, additional responsiveness of particle size to pH and ionic strength (I), can be acquired<sup>5</sup>.

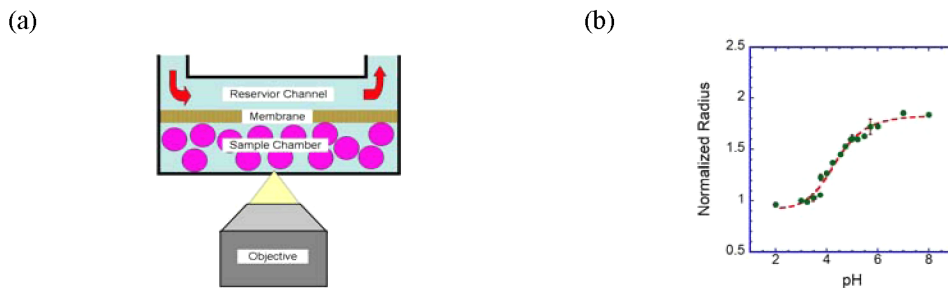
In this work, we fabricated poly(dimethylsiloxane, PDMS)-based microfluidic device, microdialysis cell<sup>6</sup>, and used this device to investigate the dynamics and phase behavior of suspensions of stimuli-responsive poly(N-isopropylacrylamide-co-acrylic acid) (pNIPAm-co-AAc) ionic hydrogels. Particle Tracking Microscopy (PTM)<sup>7</sup> is used to directly observe dynamics of particles in concentrated suspensions of these particles in real time in the microdialysis cell.

## EXPERIMENTAL

Figure 1 (a) illustrates the schematic of the microdialysis cell. It consists of three main compartments; reservoir channel, membrane, and sample chamber. The experimental set-up can be mounted onto an inverted optical

microscope with x100 emulsion oil objective for direct observation of the sample via Videomicroscopy (CCD camera at 30 frame/sec). The microdialysis cell is connected with two syringes and by controlling the fluid flow through the reservoir via a four-way valve, the solvent composition in the reservoir channel can be switched rapidly. Mass transfer between the sample chamber and the reservoir channel through the rigid membrane yields control over the solvent composition in the sample under investigation, in particular the sample pH. Since the size of the hydrogel particles is at least 50 times larger than the membrane pore size, the number density of colloids is kept constant. With PTM, we can extract the mean-squared displacement (MSD) of the colloids and from the Stokes-Einstein equation, we can determine the hydrodynamic radius ( $R_H$ ) of the colloids in dilute suspensions. Figure 1 (b) shows  $R_H$  of the pH-responsive pNIPAm-co-AAc as a function of pH for colloids with 10 wt.% AAac. The response curve can accurately be modeled by following equation:

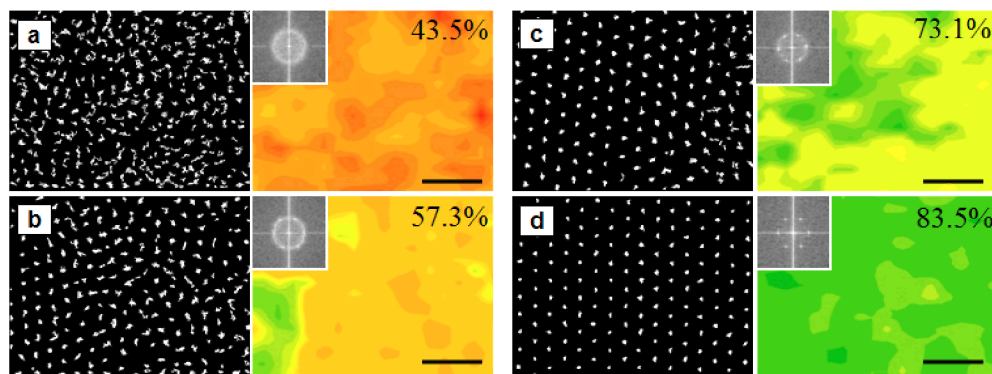
$$R_H = 0.9235 + \frac{0.9072}{1 + \left(\frac{pH}{4.3543}\right)^{-7.389}} \quad (1)$$



**FIGURE 1.** (a) Schematic of Microdialysis cell, (b) Normalized radius of pNIPAm-co-AAc as function of pH. Dotted line represents curve fitting. Measurements were carried out at 24°C in dilute suspensions with I=15mM.

## RESULTS AND DISCUSSION

For concentrated suspensions of the same particles, the phase behavior was investigated by gradually increasing  $\phi_{eff}$  ( $\Delta\phi_{eff} < 0.04$ ) via the pH, using the dilute suspension data in Fig. 1(b) to relate  $\phi_{eff}$  to pH. Because the sample chamber in the dialysis cell is thin, the mass transfer in the microfluidic device is rapid and enables quick transitions between phases. To ensure that our measurements represented the equilibrium state we waited about one hour after pH changes. More than 90% volume of the ionic microgel is water, so that difference in density and resulting gravity effects on crystal growth in the sample chamber are negligible.

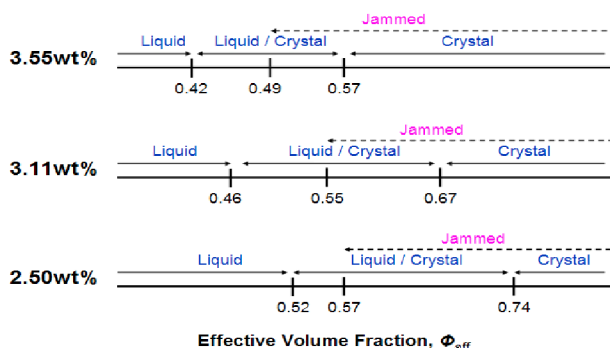


**FIGURE 2.** Structural Evolution during liquid-crystal phase transition. In each figure, left and right cartoon represent particle trajectories and contour plot of MSD, respectively. In set show Fourier Transform of original image. Each number in the contour plot represents  $\phi_{eff}$  and scale bar is 5μm.

Like hard-sphere suspensions, these ionic hydrogel suspensions display phase transitions from liquid to crystal (Figure 2). At low  $\phi_{eff}$ , they show liquid-like diffusive motion, as  $\phi_{eff}$  increases, the suspension crystallizes after going through liquid/crystal coexistence region. The MSD contour plot visualizes transitions from fast motion (red color) to slow motion (green color) and direct Fourier Transforms of microscope images exhibit pronounced hexagonal peak evolution during crystal growth.

Figure 3 shows the phase diagram of the ionic microgel suspension at 3 different concentrations (particle number densities). The most interesting feature is the broad liquid/crystal coexistence region; in contrast, for hard-spheres, this region ranges from  $\phi_{eff}$  between 0.49 and 0.54. Since the ionic hydrogels are deformable and compressible surface, the energy penalty for overlap is relatively small compared to hard-spheres, thus exhibiting unusual broad coexistence domain. More concentrated dispersion show a narrower coexistence window at lower values of  $\phi_{eff}$ .

When the experiments were conducted with large “abrupt” changes in effective volume fraction ( $\Delta\phi_{eff} > 0.2$ ), an interesting non-equilibrium jammed state was formed in which the colloids are kinetically trapped. Surprisingly, the jammed state can be formed inside the liquid/crystal coexistence region and was found to be very stable ( $> 24$  hr).



**FIGURE 3.** Phase diagram for various colloidal concentrations; effective volume fraction was changed by adjusting the sample pH and calculated from dilute suspension data (Fig. 1(b) and Eq. (1)). Blue letter and magenta letter represent equilibrium and non-equilibrium state, respectively.

## CONCLUSION

In conclusion, we introduce a microfluidic device which allows us to control solvent composition reversibly in a controlled manner. By integrating the microfluidic device with Particle Tracking Microscopy, we are able to investigate the phase behavior of pH-responsive pNIPAm-co-AAc ionic hydrogel dispersions. Ionic hydrogel displays liquid/crystal phase transition like hard-sphere suspensions. However, we observe an extended liquid/crystal coexistence region which is dependent on particle swelling ratio and concentration due to soft and deformable surface. Moreover, we investigate a non-equilibrium jammed state, and found that the boundary between non-jammed and jammed states resides in liquid/crystal coexistence domain for equilibrium structures.

## ACKNOWLEDGMENTS

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