Abstract

Poly(N-isopropylacrylamide) (PNIPAM) microgel particles are thermo-responsive, which show decrease in the particle size with increase in temperature and undergo volume phase transition (VPT) with a sudden collapse at 34°C. Dense suspensions of monodisperse PNIPAM microgel particles exhibit structural ordering (gas, liquid, glass and crystalline) similar to that observed in atomic or other colloidal systems. Tunability of microgel particle’s size and hence interparticle interactions with temperature allows variation of phase behavior of the dense suspensions using temperature. Unlike hard sphere or charged colloidal particles, PNIPAM microgel particles are soft and heterogeneous (core-shell structured) in density with dense solvent penetrable polymer core and dangling polymer chains forming a shell. In dense suspensions (where interparticle separations are of the order of particle diameter) the soft and the core-shell nature of PNIPAM microgel particles is expected to influence their structural ordering, dynamics and yielding behavior. Motivated by this, we have investigated dense microgel suspensions for the deswelling behavior of microgel particles, their dynamics and yielding behavior using techniques of UV-Visible spectroscopy, dynamic light scattering and non-linear rheology, and the results are reported in this thesis. The major findings of the thesis are as follows: i) PNIPAM microgel particles are shown to deswell in dense suspensions due to osmotic pressure from the surrounding microgel particles, ii) The dynamical criterion (which says that at the freezing/melting of a colloidal liquid/crystals,
ratio of long time diffusion coefficient to short time diffusion coefficient is a universal number 0.1) is found to deviate for melting of dense PNIPAM microgel crystals, iii) The behavior of mean square displacement (MSD) in dense PNIPAM microgel crystals and glasses is found to be subdiffusive at short times, iv) The dense PNIPAM microgel glasses are found to yield in two steps (by exhibiting two peaks in the loss modulus $G''$). The subdiffusive behavior of MSD in dense microgel suspensions is argued to arise due to entanglements of dangling polymer chains from the shells of neighboring microgel particles, which is responsible for the deviation of dynamical criterion for melting of PNIPAM microgel crystals. The two step yielding of PNIPAM microgel glasses arises from two microscopic mechanisms, i) due to breaking of entanglements of dangling polymer chains between neighbouring particles and ii) due to breaking of near neighbour cages. Our investigations suggest that the soft and core-shell structured PNIPAM microgel particles constitute yet another model colloidal system with an interesting dynamics and flow behaviour.

List of publications

Journals and published conference proceedings

1. “Dynamics in thermo-responsive nanogel crystals undergoing melting”


3. “Subdiffusive dynamics and two step yielding of dense thermo-responsive microgel glasses”
   R. G. Joshi and B. V. R. Tata (submitted)

4. “Yielding behavior of dense microgel glasses”

5. “Pressure Tuning of Bragg Diffraction in Stimuli Responsive Microgel Crystals”