

GLASSY DYNAMICS AND ELASTICITY IN TEMPERATURE SENSITIVE NANOPARTICLE PASTES

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Nano- and mesoscopic colloidal particles with adjustable interaction potential have been of scientific and technological interest in recent years. Tuning the interaction between such particles opens the possibility to control bulk properties such as viscous flow or optical properties [1]. To achieve such behavior *thermo-sensitive hydrogels* have been widely used. These materials have also received attention due to their potential applications in drug delivery or as sensors. The majority of investigated systems are based on *poly(N-Isopropyl-Acrylamide)* (PNIPAM), a polymer which has a critical solution temperature of approximately 33°C [2]. Colloidal systems based on PNIPAM have been prepared by cross linking PNIPAM resulting in microgel particles with tunable softness, the latter depending on the cross link density [3,4]. PNIPAM Microgel particles thus display properties due to the tunable network combined with properties of classical colloids, e.g. crystallization or aggregation. This is very useful to tailor colloidal systems that can be kept close to the liquid solid transition thus having the possibility to “temper” these materials. This process is not possible using most “classical” colloidal systems that require a change in composition in order to cross a phase boundary.

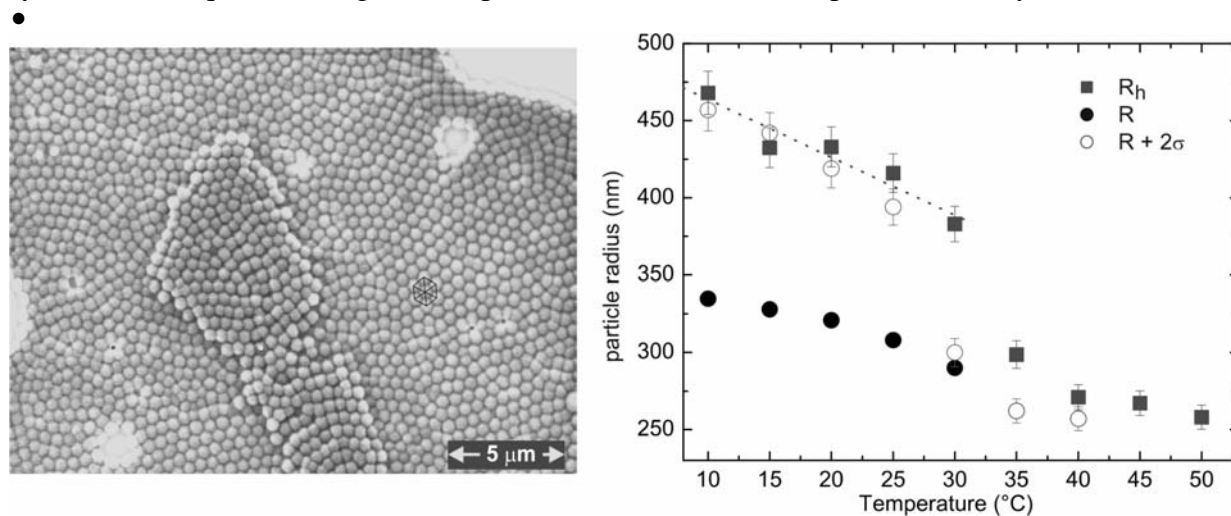


Figure: Left: Scanning electron microscopy picture of PNIPAM particles on a solid substrate. The particles are ordered in hexagonal arrays, giving us a qualitative idea about the rather low polydispersity of approximately 9-10% in the collapsed state. From the analysis of several dozen particle positions we obtain a SEM radius of 260 ± 5 nm. Right: Temperature dependence of the PNIPAM particle size from static and dynamic light scattering. Solid squares: hydrodynamic radius, Full circles: Mean radius R from a Rayleigh-Gans Debye fit assuming a radially inhomogeneous density profile [5]. Open circles: mean radius R plus diffuse layer $2 \int$.

We use the free radical cross-linking polymerization of the monomer *N-Isopropyl-Acrylamide* (NIPAM) from Acros Organics (Acros Organics BVBA, Geel, Belgium) and the (tetra-functional) cross-linker *N,N'-Methylene-Bis-Acrylamide* (BIS) from Fluka (Fluka Chemie GmbH, Buchs, Switzerland) to make highly cross-linked PNIPAM microgel particles. Since

NIPAM is not soluble in hot water [2] the cross-linked PNIPAM gels collapse at elevated temperatures whereas at room temperature and below, water is a good solvent leading to a strong swelling. This means we can control the hydrodynamic size of the particles simply by adjusting the temperature.

In this work we present a study of concentrated PNIPAM microgel particle suspensions using a combination of standard light scattering and Diffusing Wave Spectroscopy (DWS). In the expanded state the effective particle volume fraction reaches almost 100% and the system is a visco-elastic solid.

In our study we cover the microscopic dynamic and the rheological properties spanning the hard to the soft sphere regimes. We analyze in detail the particle morphology and the viscoelastic response of the dense particle assemblies over an extended range of temperatures. We show that existing models are insufficient to describe the behavior of these interesting tunable materials, and we discuss some central elements needed for a quantitative theoretical description [6].

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