

Sizing Thermo-responsive Colloidal Particles with Dynamic Light Scattering

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Primary CNF Tools Used: Malvern Zetasizer Nano

Abstract:

We are synthesizing transparent, thermo-responsive core-shell colloidal particles for use as a model system in studies of the glass transition. The particles consist of an optically-dense polystyrene core surrounded by a nearly-transparent poly-N-isopropylacrylamide shell. We use dynamic light scattering (DLS) to measure the size of the particles during and after their preparation. We also use DLS to examine the response of the core-shell particles to temperature changes.

Summary of Research:

Understanding the mechanical behavior of glasses, which have liquid-like structure but solid-like moduli, is an important open question in condensed matter physics. Colloidal suspensions are useful as model systems for studying condensed-matter phenomena like the glass transition. Specifically, colloidal particles can be used as “model atoms” that can be engineered to exhibit interactions similar to those in atomic systems, but are large enough to be directly visualized in real space using optical microscopy.

Recently, Perro and co-workers introduced a core-shell particle that could potentially be useful as a model system for studying glasses [1]. The particles consist of a small, optically-dense, mechanically-rigid core surrounded by a thermo-responsive, nearly-transparent, soft hydrogel shell (Figure 1). These particles are expected to have

soft-sphere interactions, which may be more relevant to atomic systems than colloidal particles with hard-sphere interactions, which have been much more extensively studied. The particles reversibly deswell when heated above room temperature, which would allow the particle volume fraction, a key thermodynamic parameter, to be tuned *in situ*. Finally, since the shells are nearly refractive index-matched in water, it is possible to image deep within dense suspensions using techniques such as confocal microscopy. Our overall goal is to measure the interactions between these core-shell particles and how the interactions affect the rheology of dense suspensions of the particles.

First, however, we need to synthesize the particles since they cannot be purchased commercially. Measuring particle sizes with dynamic light scattering (DLS) using the Malvern Zetasizer Nano at CNF is important in the synthesis. We need to know both the size of the cores alone as well as the size of the completed core-shell particles. We also need to measure the temperature dependence of the shell size.

The Zetasizer is useful for these measurements for several reasons. DLS is particularly appropriate for sizing our particles: because our cores are smaller than the optical diffraction limit and the shells are nearly-index matched, sizing the particles by direct optical imaging would not be effective, and electron microscopy would most likely destroy them. In addition, the Zetasizer allows us to easily regulate the sample temperature over the relevant range (25-40°C). Finally, we can also use

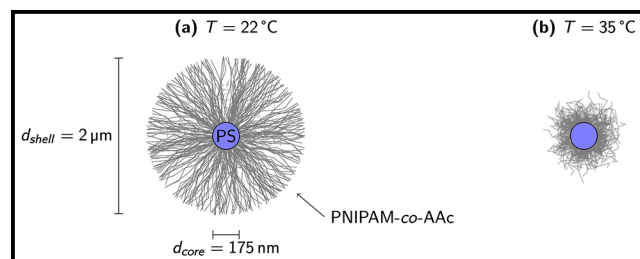


Figure 1: Schematic illustration of core-shell polymer particles characterized using dynamic light scattering. The particles consist of a polystyrene (PS) core surrounded by a thermo-responsive poly-N-isopropyl acrylamide/acrylic acid (PNIPAM-co-AAc) shell. At room temperature, the shells are highly swollen and nearly index-matched in water. At higher temperatures, the shells collapse.

the intensity autocorrelation functions measured in DLS to determine whether or not the particles are monodisperse.

Figure 2 shows two intensity autocorrelation functions, one for cores alone and one for completed core-shell particles. The autocorrelation functions exhibit an exponential decay characteristic of monodisperse suspensions. Notably, the longer decay time scale for the core-shell particles indicates that they are larger than the bare cores as expected. Moreover, fitting a refined model based on a cumulant expansion of the particle size distribution to the measured autocorrelation functions allows us to quantify the particle size as well as estimate the small but nonzero polydispersity index of the suspensions [2].

While the core-shell particles we have prepared thus far have not exhibited the expected thermoresponsive behavior, we are currently working to optimize the synthesis reaction parameters. We expect DLS measurements with the Zetasizer at CNF to remain an important part of our ongoing work.

References:

- [1] A. Perro, G. Meng, J. Fung, and V. N. Manoharan, "Design and synthesis of model transparent aqueous colloids with optimal scattering properties." *Langmuir*, 25 (19), 11295-11298 (2009).
- [2] B. J. Frisken, "Revisiting the method of cumulants for the analysis of dynamic light-scattering data." *Applied Optics*, 40 (24), 4087-4091 (2001).

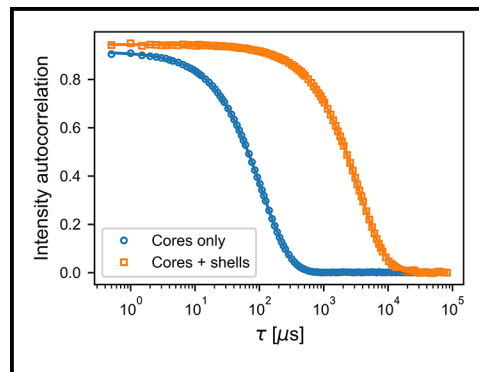


Figure 2: Intensity autocorrelation functions measured for cores only (blue circles) and core-shell particles (orange squares). Solid lines are fits to a second-order cumulant model for the particle size distribution [2]. The autocorrelation function for the core-shell particles decays over a longer time scale than the autocorrelation function for the cores only, indicating that the core-shell particles are larger than the cores alone as expected.