Microgel Dynamics Characterization Using SEM

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Abstract. A methodology for imaging the dynamics of individual microgel particles using high resolution scanning electron microscopy (SEM) is presented. To enable this, the microgels are dispersed in an ionic liquid, which due to its low vapor pressure allows them to remain in suspension even under the high vacuum conditions present in a typical electron gun. Thus, compared with conventional electron microscopy studies of microgels, no sample drying or freezing is necessary which preserves their morphology while also allowing to probe microgel dynamics in solution. The results based on the individually tracked particles are compared with results from dynamic light scattering (DLS) which measures the mean size and diffusion properties of large collectives of particles. For the size measurements, the SEM and DLS data are in general agreement. For the particle dynamics, monitoring individual microgel motion reveals complex dynamics in which, aside from the expected thermal motion, one observes effects such as clustering, rotation and drift. This is in contrast with a control sample of hard sphere-like silica particles where the motion is primarily diffusional in good agreement with DLS studies.

INTRODUCTION

Microgels are polymer-based particles that exhibit a reversible swelling in water, making them a system of interest for bio-sensing and drug delivery applications [1]. The experimental data on the size and dynamics of these systems is typically collected using optical techniques, such as dynamic light scattering (DLS). DLS relies on averaging data collected from sample volumes containing large numbers of particles. Thus, these methods often have to rely on the approximation of dilute, monodisperse particles of a certain shape (e.g. spheres) [2]. In this context having the ability to observe the dynamics of individual particles is particularly important for multicomponent systems, assemblies for non-spherical particles, or particles that have complex interactions with their environment.

Electron microscopy methods are an important set of tools used for the characterization of micro- and nano-scale systems, owing to their very high spatial resolution. They have been used in previous studies to characterize the morphology and size of microgel particle systems [3]. One has to note though, that the imaging in an electron microscope requires samples that: (i) are compatible with the high vacuum conditions in an electron gun required to prevent the scattering of the electron signal and electric discharges; (ii) are conductive so that they can dissipate charge accumulation due to beam exposure; and (iii) can withstand the potential thermal damage associated with exposure to the high energy electron beam. For the microgel example, meeting these stringent requirements involves drying or cryofreezing the samples. This might change microgel morphology [4], and more importantly prevents studies of dynamics of their motion or response to environmental conditions.

In this work, an alternative sample preparation methodology for microgel systems has been explored, enabling their high-resolution imaging in a scanning electron microscope (SEM). The method relies on dispersing the system of interest (microgels) in an ionic liquid. Owing to the very low vapor pressure of the ionic liquid used at room temperature, even under the high vacuum in the SEM, the suspension remains in liquid state. Moreover, the electrical and thermal conductivity of the ionic liquid also limits sample charging and thermal damage. This allows the imaging of the motion of individual microgel particles in conditions similar with those used for studying dynamics of large ensembles of microgels using DLS. Aside from SEM imaging of microgel ionic liquid samples, this work presents SEM results for a control sample of monodisperse hard sphere silica particles in ionic liquid.

EXPERIMENTAL PROCEDURE

Hydroxypropylcellulose (HPC) microgels were synthesized in water following refs. [2]. The final concentration of microgels in the aqueous solution was 2% by volume. Following the synthesis, the microgels were dispersed in the ionic liquid using equal amounts of stock solution and ionic liquid. The mixture was purged with dry N_2 for 24 to 72 hours. In the process the water evaporated, while the mass of the solution was monitored, resulting in a microgel suspension in ionic liquid of 2% by volume. The ionic liquid used in this study was 1-n-Butyl-3-methylimidazolium (98% purity, Sigma Aldrich), chosen to maximize the mutual solubility of the ionic liquid with that of water [5]. A control sample of silica monodispersed microspheres (Cospheric LLC, 890 nm SiO_2) in ionic liquid was prepared with the same volume concentration.

Solutions of the microgels in both water and ionic liquid were characterized using DLS setup described in ref. [6]. Figure 1 shows the temperature dependence of microgel hydrodynamic diameter ($2R_H$) in ionic liquid and water. While ionic liquid DLS runs are noisier, the measured $2R_H$ in ionic liquid agrees well with the $2R_H$ in water below the microgel phase transition temperature (~41°C). The larger error bars in the ionic liquid are indicative of stronger thermal fluctuations. To limit thermal effects of the laser beam on microgel ionic liquid solution all of the DLS data was collected at laser powers below 0.035 W. Heating the samples above the phase transition temperature, i.e. 41°C, did show differences between the water and ionic liquid suspensions, as the microgels showed no apparent deswelling in ionic liquid while deswelling by a factor of 2 in diameter in water, as expected.

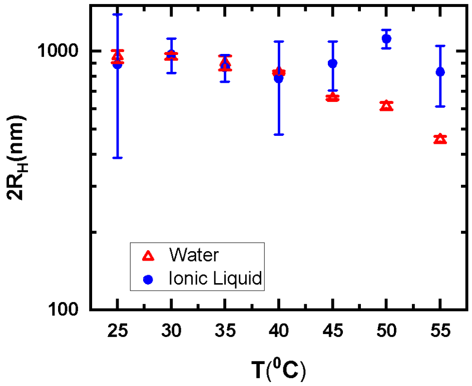
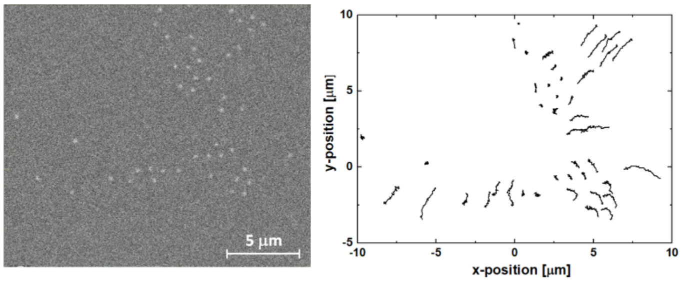


FIGURE 1. Hydrodynamic diameter ($2R_H$) of microgels as a function of solution temperature in water and ionic liquid.

To prepare samples for SEM studies, the ionic liquid microgel suspension was dispersed ultrasonically for 10 minutes, and then a 1 μL sample drop was deposited on a TEM copper grid. The excess liquid was removed using a piece of filter paper touched to the side of the grid, leaving the ionic liquid film as membranes suspended in the grid openings. The grid was then mounted on a standard SEM pin holder or an adaptor holder for TEM grids (Ted Pella #16111 or #15469). The imaging was done at room temperature in a field emission electron microscope Inspect F50 (FEI). It was observed that high magnification, high acceleration voltages, and long exposure resulted in the crosslinking of the ionic liquid leading to quenching of the particle dynamics. To mitigate this, the acceleration voltage was limited to 2kV and the diffusion data was collected for less than 1 minute to limit the overall dose.

RESULTS AND DISCUSSION

SEM imaging of the particles suspended in ionic liquid allowed size measurements on individual particles. The secondary electron signal is used for imaging, with the contrast arising mainly from the topography of the microgel particles rising above the liquid ion – vacuum interface. These values were consistent with the distribution values extracted from DLS data. Moreover, the actual motion of individual particles could be monitored over times sufficiently long to observe their relevant dynamics. Figure 2a shows an SEM frame snapshot of 44 silica particles, the control sample. Using similar time stamped frames, the time evolution of the x- and y- position coordinates of the particles are extracted using an open source particle tracking package (Tracker 5.0 [7]). Figure 2b shows the reconstructed trajectories for the 44 particles shown in Figure 2a over 33 seconds.



(a) (b)

FIGURE 2. (a) Scanning electron microscopy snapshot of silica particles in ionic liquid (t = 0 s). (b) Trajectories of the 44 silica particles tracked over a period of ~ 33 seconds.

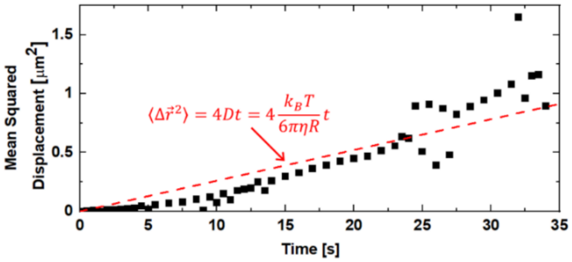
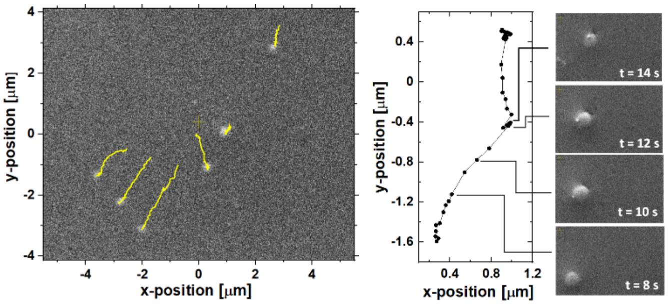


FIGURE 3. Time dependence of the average mean squared displacement for the silica particles imaged in Fig. 2. The dashed line corresponds to the expected two-dimensional Brownian motion.

The data collected for this assembly is summarized in Figure 3 by graphing the mean square displacement $\langle \Delta \vec{r}^2 \rangle$ of the collection of particles as a function of time. For the control silica particles system, the resulting dynamics is consistent with the expectations based on the Stokes-Einstein equation (shown in Figure 3, $D = \frac{k_B T}{6R}$) for thermal diffusion, where the diffusion constant D is calculated based on the particle hydrodynamic radius R = 890 [nm]/2 and the measured ionic liquid viscosity η at room temperature T. In the above analysis, the motion is assumed to be two-dimensional as the secondary electron signal used for imaging originates primarily from the top surface of the sample, and thus only the motion of particles moving along the ionic liquid – vacuum interface could be captured. This approach is consistent with other high-resolution studies of hard-sphere like particles suspended in ionic liquids [8].

A similar procedure was followed to obtain corresponding data sets for microgel samples. In contrast with the silica samples the microgels exhibit more complex behavior, which deviates from simple thermal motion and includes clustering, rotational diffusion, and drift. Figure 4a, shows the initial positions as well as the subsequent motion of several microgel particles. The four particles in the lower-left corner have convergent trajectories which in many instances leads to clustering, where particles become temporarily attached and undergo collective motions. This type of clustering is particularly pronounced in regions close to where the ionic liquid suspension is attached to the copper TEM grid, possibly due to the liquid layer being thicker near the grid.



(a) (b)

FIGURE 4. (a) Trajectories of microgels tracked over ~45 seconds; (b) High resolution snapshots of the translational and rotational motion of a single microgel particle and on left, trajectory of the particle imaged.

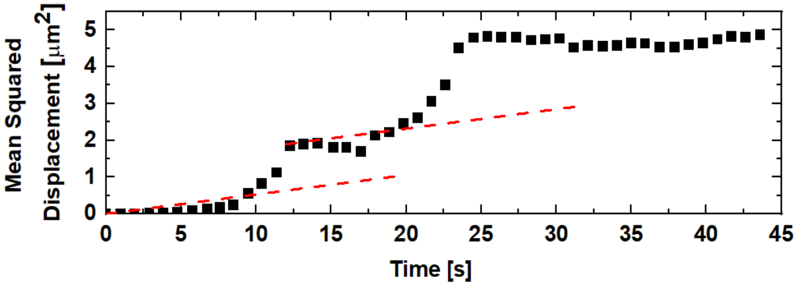


FIGURE 5. Mean squared displacement of the microgel tracked in Fig. 4b (the dashed lines correspond to the expected time dependence of the mean squared displacement for an assembly of thermally diffusing particles).

In another example of complex motion, Figure 4b shows a series of high-resolution snapshots of a single microgel particle. The morphological asymmetry of this particle allows for the observation of its rotational motion where the particle undergoes a ~90° rotation in the image plane over 4 seconds. This rotational motion is also accompanied by a complicated translational motion, in which the particle motion is localized over time scales on the order of 10 seconds, then rapidly drifts to another region, where the localized motion resumes. An analysis of the mean squared displacement, Figure 5, finds that the localized motion is consistent with thermal diffusion. The episodes of rapid drift sequences interrupting the thermal diffusion, indicate that the dynamics of this system is quite rich. This is possibly related with the complex microgel morphology and their more complicated interactions with the environment. The observed complex microgel dynamics made it impossible to deduce microgel translational diffusion coefficient via averaged mean-squared displacement approach used for silica particles. Additional data on particle-particle and particle-environment interactions is needed to fully understand microgel motion in ionic liquid.

CONCLUSIONS

We have demonstrated that high resolution imaging of particles dispersed in an ionic liquid can be a very powerful tool for studying their structure and dynamics. For silica systems tracked particle motions match well the theoretical assumptions of monodisperse noninteracting spherical particles. The results are consistent with motion dominated by thermal diffusion. On the other hand, microgel suspensions show significant deviations from simple Brownian motion, presumably related to their different morphology and non-trivial particle-particle and particle-environment interactions. Future work will focus on acquiring data to uncover these relationships, as well as to image microgel dynamics under changing environmental conditions, such as temperature.

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