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**XPCS Study of Silica Nano-particles in Glycerol**W.-R. Chen<sup>a</sup>, C.-W. Do<sup>a</sup>, Y. Shinohara<sup>b</sup> and T. Egami<sup>a,b</sup><sup>a</sup> Oak Ridge National Laboratory, <sup>b</sup> University of Tennessee

The rheology of suspensions of colloidal particles plays a critical role in many technological applications where it is essential to control the flow properties by tuning the shear viscosity. Theoretical calculations showed that introducing porosity into colloids gives an additional degree of freedom to tune their hydrodynamic properties. The goal of this project is to carry out an x-ray photon correlation spectroscopy (XPCS) study on such nano-particles to verify these theories, using nanoparticles of precisely controlled size and porosity which became available recently. To distinguish between prevailing theories we need to reach the high  $q$  plateau of the hydrodynamic function, where  $q$  denotes the momentum transfer in scattering.

Keywords: Nano-particles, colloids, XPCS

Porous silica particles suspended in glycerol were used to experimentally explore the concentration and porosity dependence of the collective diffusion coefficient  $D(q)$  and the short-time self-diffusion coefficient. To compare directly with theoretical predictions, samples containing 1wt%, 5wt%, 10wt%, 20wt%, 30wt%, 40wt% and 50wt% porous silica in glycerol were prepared. The samples were filled in capillaries and sealed before the measurement. The porous silica particles, shown in Figure 1, were synthesized at the Center of Nanophase Materials Sciences (CNMS), at the Oak Ridge National Laboratory (ORNL) according to the procedure described elsewhere [1]. The diameter of the nanoparticles and their pore size were 200nm and 4nm, respectively. Since the degree of porosity of the particles can be controlled precisely by the reaction temperature during the synthesis process, systems with 5 different degree of porosity (including the non-porous case) were tested.

We have investigated the dynamical properties of silica particles immersed in glycerol using eth XPCS at SPring-8 BL40XU beamline. The beam size used in this study was  $1\ \mu\text{m}$ . The energy of incident monochromatic x-ray was  $20\ \text{keV}$  and the pathlength of the cell is 0.1 mm. In this suspension the silica particles are highly charged. The volume fraction of the silica particles was 0.45 and preliminary rheological data shows the glassy nature of this sample. The non-ergodicity of this sample is clearly reflected by the split of the 2nd peak of structure factor  $S(q, 0)$  given in the left panel of Figure 2. We would also like to point out that the reliable data can only be collected up to the third peaks due to the limitation of the longitudinal coherency. It is our conjecture that the decays of the fourth and the fifth peaks below the value of 1 is due to the form factor  $P(q)$ . In comparison to its value  $P(0)=1$ , the intensity has dropped at least four orders of magnitudes around this  $q$  range.

Figure 2 gives the relaxation time extracted from the decays of the measured collective intermediate scattering function  $F_c(q, t)$  as a function of wavevector  $q$ .  $F_c(q, t)$  is defined as

$$F_c(q, t) = \frac{1}{N} \left\langle \sum_{i,j}^N \exp \left[ i\vec{q} \cdot \left( \vec{r}_i(t) - \vec{r}_j(0) \right) \right] \right\rangle, \quad (1)$$

We have found the disappearance of de Gennes narrowing around the  $q$  range of the first peak of  $S(q)$ . Whether this unexpected observation can be simply attributed to the undesirable radiation effect or it is due to the interplay of direct screened Coulombic interaction and indirect hydrodynamic interaction remains unclear at present. This uncertainty delayed the publication of our results. In order to resolve this issue we are planning to conduct a Stokesian simulation and investigate the relaxation in real space to identify its origin.

It is important to point out that that knowledge on short-time dynamic properties is critical for understanding of long-time dynamic properties, such as the static viscosity, which are relevant to their industrial applications. For example, the long-time transport properties of porous colloidal suspensions can be

calculated via several theoretical routes such as mode-coupling theory with the short-time transport coefficients as input [2]. Fundamental insights regarding the sort-time dynamics of porous particles within the relevant length and time scales is therefore of significant technological importance and scientific interest.

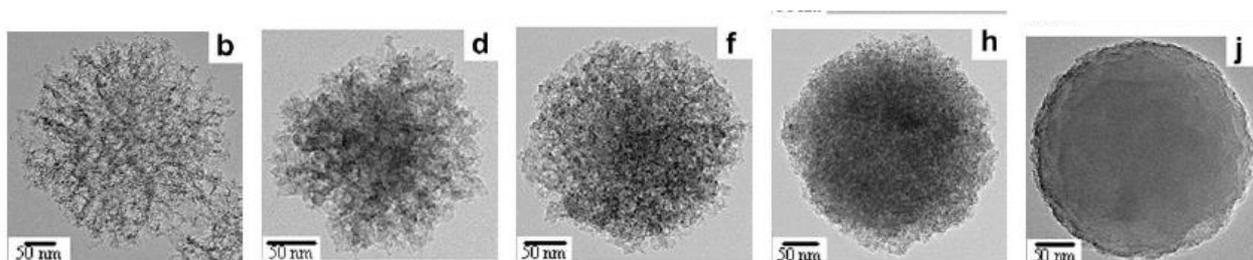


Fig. 1 TEM images of the silica nano-particles with various degrees of porosity. The particles were synthesized at CNMS ORNL via a procedure described in reference 1.

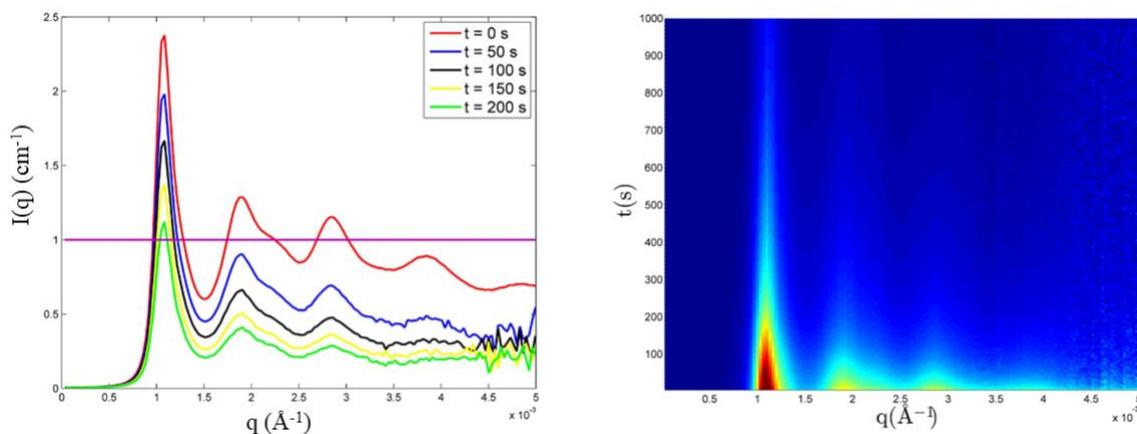


Fig. 2 The intermediate scattering function,  $Fc(q, t)$ , cuts at constant  $t$  (left) and the intensity map (right) of  $Fc(q, t)$  from which the decay time as a function of  $q$  was determined.

#### References:

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