

# Structural and Dynamical Studies of Concentrated Micrometer-Sized Colloidal Suspensions with Ultra-Small Angle X-ray Scattering Based X-ray Photon Correlation Spectroscopy

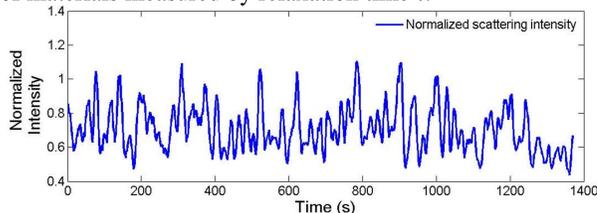
## Introduction

Interacting colloidal suspensions of spherical particles in a liquid are among the simplest of complex fluids. Much effort has been devoted to investigate the static structure and dynamic behavior of such suspensions. However, it remains a well-documented challenge to quantify the dynamic behavior of concentrated, optically opaque, micrometer-sized colloidal suspensions with laser scattering techniques, due to the complications introduced by multiple scattering events, or with pinhole camera based X-ray photon correlation spectroscopy (XPCS), due to its limited scattering  $q$  range.

In order to overcome these limits, we have developed an ultra-small angle X-ray scattering (USAXS) based XPCS technique to probe the equilibrium dynamics of such materials. With this technique and with regular USAXS, we have tracked the structural and dynamical properties of concentrated monodisperse suspensions of different sized polystyrene (PS) microspheres in glycerol. For these PS suspensions, we found their static structures display a hard-sphere like behavior. Furthermore, by analyzing the intensity autocorrelation functions, we found these autocorrelation functions can only be described by a form of stretched exponential decay function with exponent greater than 1. The inverse of the effective diffusion coefficients displays a peak with respect to the scattering vector that resembles the peak in the static structure factor, a signature of de-Gennes narrowing. All this evidence suggests a collective motion of the PS microspheres.

## XPCS

- Interference pattern originates from coherent scattering of the illuminated scattering volume by short wavelength ( $\lambda$ ) X-rays.
- Using entrance slits to define a small (10 - 20  $\mu\text{m}$ ) beam from an APS undulator source, up to  $\beta \sim 15\%$  maximum beam coherence is achievable.
- Temporal coherent scattering patterns are related to dynamics of materials measured by relaxation time  $\tau$ .



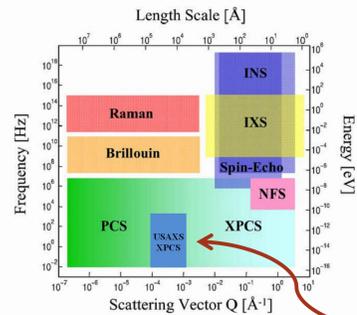
Temporal Intensity Autocorrelation Function

$$g_2(q, t) = \frac{\langle I(q, 0)I(q, t) \rangle}{\langle I \rangle^2}$$

$$= 1 + \beta \frac{S(q, t)^2}{S(q, 0)^2}$$

$q = (4\pi/\lambda)\sin(\phi/2)$ , here  $\phi$  = scattering angle  $\lambda$  = wavelength.

## USAXS-XPCS Bridges the Gap between XPCS and DLS



Grubel & Zontone, *J. Alloys Comp.*, 362, 3-11, 2004 (modified).

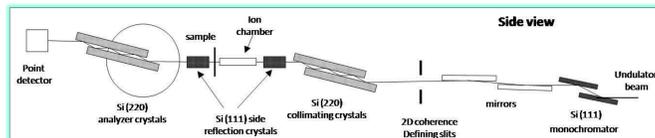
XPCS: great success but limited to  $\approx 500\text{\AA}$

Dynamical light scattering (DLS):  $\approx 2000\text{\AA}$  possible but suffers from multiple scattering and lack of penetration power.

**Dynamics in this "blue area" can be probed with USAXS-based XPCS.**

## Experimental Setup

### USAXS/USAXS-XPCS



### Operational Parameters:

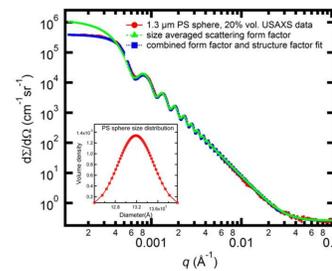
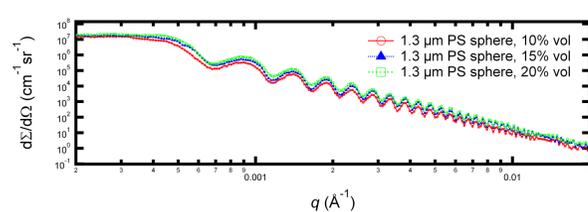
- Intensity at ultra-small scattering angles is measured as the analyzer crystals are rotated.
- For USAXS, slits are set at 1.5 mm  $\times$  0.1mm. USAXS data are acquired by point-scanning the analyzer crystals over a wide  $q$  range ( $\sim 1 \times 10^{-4}\text{\AA}^{-1}$  to  $1\text{\AA}^{-1}$ ).
- For USAXS-XPCS, coherence-defining 2D slits set at 15  $\mu\text{m}$   $\times$  15  $\mu\text{m}$ , or similar. USAXS-XPCS data are acquired by setting the analyzer crystals at a fixed  $q$  and counting continuously.
- Detector time resolution for USAXS-XPCS: 0.1 s for photodiode detector, 1 ms for autocorrelation scintillating detector.

### Materials

- 1.0  $\mu\text{m}$ , 1.3  $\mu\text{m}$ , and 1.5  $\mu\text{m}$  diameter polystyrene (PS) microsphere dispersions in glycerol at 5  $^{\circ}\text{C}$
- PS microspheres have very narrow size distribution ( $< 2\%$ )
- Very stable suspensions at 10%, 15%, and 20% volume fraction, i.e., equilibrium dynamics.

## Static Structure

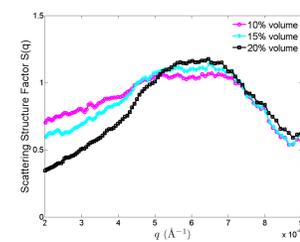
### Typical USAXS Data



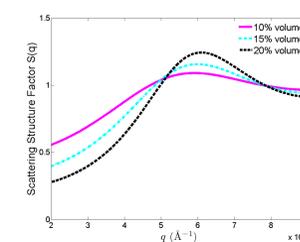
- Analysis of the Bessel oscillations between  $1 \times 10^{-3}\text{\AA}^{-1}$  and  $1 \times 10^{-2}\text{\AA}^{-1}$  leads to the size distribution of the particles ( $< 3\%$  in all cases).
- Structure factors are acquired by dividing the USAXS curves of the concentrated suspensions by their scattering form factors.

## Structure Factors

### Experimental structure factor



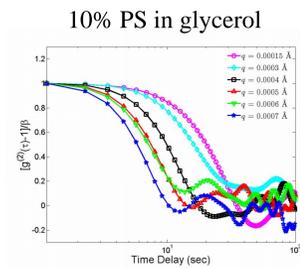
### Percus-Yeivick



Although the PS microspheres are highly charged, their Debye lengths are at least two orders of magnitude smaller than the microsphere size. Beyond the Debye layer, the charges are screened, and the structure factor of these PS spheres resembles that of the hard spheres.

## Dynamic Behavior

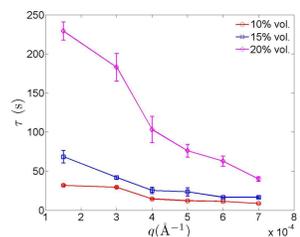
### Autocorrelation Functions



Kohlrausch-Williams-Watts (KWW) function

$$g_2(t) = \beta \exp\left(-\left(\frac{t}{\tau}\right)^\gamma\right) + 1$$

**Dynamics cannot be described by simple diffusion.**



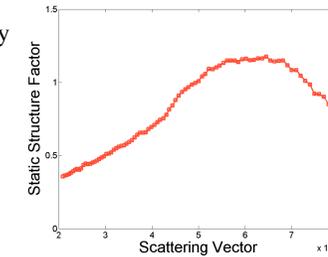
Relaxation time shows monotonic decrease with increasing  $q$ , which suggests that the short-range, local fluctuations (large  $q$ ) occur more rapidly than long-range fluctuations (small  $q$ ) in interacting colloidal suspensions.

**In all cases,  $\gamma > 1$ , which suggests hyperdiffusive behavior of the colloidal particles. It also signifies that the motion of the PS microspheres is at least partially collective in nature.**

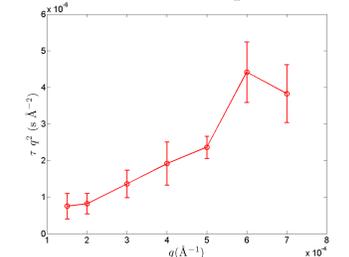
## de-Gennes Narrowing

- Relaxation rate of a concentrated suspension with collective motion can be described by  $\Gamma = q^2 D(q)$
- $D_0/D(q) \sim q^2 \tau$ , with  $\tau = \Gamma^{-1}$ .

### Static Structure Factor



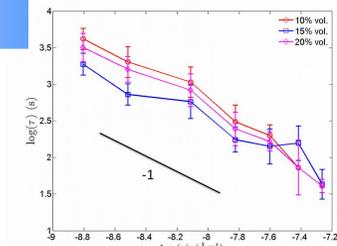
### Inverse of D(q)



- The static structure factor shows the configuration of the lowest equilibrium free energy state in reciprocal space.
- The effective diffusion constant quantifies the speed of particle motion in these concentrated suspensions.

**The observed proportionality suggests that the lowest free-energy configuration in the static case also has a long life-time, as illustrated by the peak in the inverse of the effective diffusion coefficient.**

## Scaling Behavior



- Our results show that, in all cases, the logarithm of  $\tau$  is approximately linearly related to the logarithm of  $q$ , with the slope being  $-1.06 \pm 0.22$ , i.e.,  $\tau \sim q^{-1.06 \pm 0.22}$ .

- This  $\tau \sim q^{-1}$  relationship indicates underlying dynamics of the particles are associated with relaxations under the effect of relaxation of heterogeneous local stress.

**A collective motion of the particles and their neighboring particles again emerges.**

- **In concentrated PS microsphere suspensions, the microspheres move collectively.**
- **USAXS-XPCS connects structure and dynamics in a new space-time regime.**

### References:

- [1] F. Zhang, A.J. Allen, L.E. Levine, J. Ilavsky, A.R. Sandy, and G.G. Long, "Development of X-ray Photon Correlation Spectroscopy in the Ultra-Small-Angle Scattering Regime", *J. Appl. Cryst.*, **44**, 200-212, 2011.
- [2] F. Zhang, A.J. Allen, L.E. Levine, J. Ilavsky, and G. G. Long, "Ultra-Small-Angle X-ray Scattering—X-ray Photon Correlation Spectroscopy: A New Measurement Technique for in-situ Studies of Equilibrium and Nonequilibrium Dynamics", *Mater. Mater. Trans. A*, **43A**, 1445-1453, 2012.
- [3] F. Zhang, A.J. Allen, L.E. Levine, J. Ilavsky, and G. G. Long., "Structure and Dynamics Studies of Concentrated Micrometer-Sized Colloidal Suspensions", *Langmuir*, **29**, 1379-1387, 2013.