ESRF	**Experiment title:** **Using coherence to measure microscopic dynamics in shear flow**	**Experiment number**: MI-789
Beamline: ID10A	**Date of experiment**: from: 15/09/2005 to: 20/09/2005	**Date of report**: 01/03/2006
Shifts: 15	**Local contact(s)**: Andrei Fluerasu	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Peter Falus*, ILL
Andrei Fluerasu*, ESRF
Abdellatif Moussaïd*, ESRF
Anders Madsen*, ESRF

This work presents a new experimental method that combines X-ray Photon Correlation Spectroscopy (XPCS) and microfluidics and allows the direct measurement of the slow (10^{-3}-10^{2} s) mesoscale (~10-1000 Å) dynamics of various soft condensed matter systems (i.e. colloids, polymers, biological molecules like proteins, RNA, etc.) under shear flow. This method allows the study of various samples that are sensitive to the X-ray beam, the risk of having beam-induced damage of the sample being significantly reduced by the flow. It also allows time-resolved studies of various processes taking place in mixing flowcells. The main problem associated with this method is the possible coupling between the intensity fluctuations of the speckles that measure the internal dynamics of the sample, with their flow-induced motion. Theoretical predictions and experimental evidence from dynamic light scattering experiments [1] show not only that this coupling is present, but also that it is dependent on the scattering geometry.

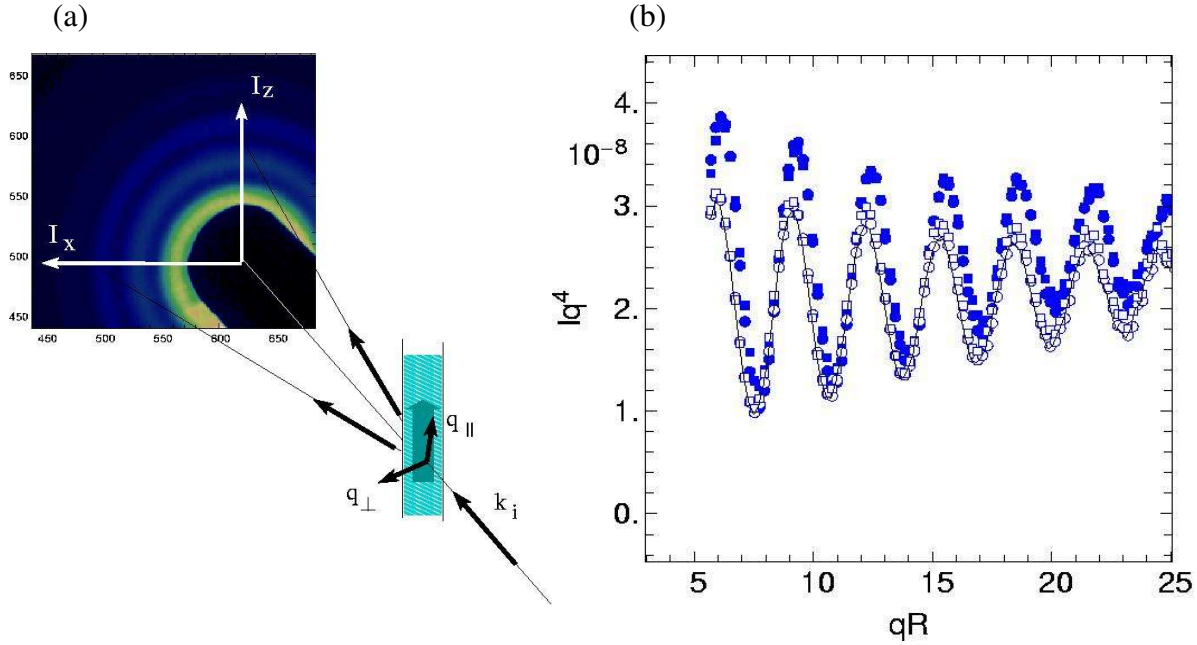

Fig. 1: (a) Scattering geometry used to perform "transverse" and "longitudinal" scans. (b) Static scattering from the suspension of colloidal PMMA particles and the Schultz fit (solid line). Filled symbols show data from longitudinal scans and empty symbols show the data from transverse scans. The circles show data taken at zero shear (flow) rate while the squares were recorded at an average volume flow velocity of 117 µm/s, corresponding to a shear rate of 0.35 s^{-1}.

In the experiments reported here, we have used a colloidal suspension of sterically-stabilized PMMA particles in cis-decalin, and studied their Brownian dynamics while flown through an in-house made flowcell. Static and dynamic measurements were performed at different flow rates, for two different

scattering geometries (Fig. 1a): "transverse" scans with the scattering vector **q** perpendicular to the direction of flow were obtained by scanning with a point detector in the Ox direction, and "longitudinal" scans, with **q** (quasi-)parallel to the direction of flow were obtained by doing scans along the Oz direction (see Fig. 1a)
The static data (Fig. 1b) shows that within the range of scattering vectors that were available in these experiments, the scattering from the PMMA colloidal suspension is well described by the form factor of hard spheres with a radius of R=255nm. Fits with a Schultz distribution function indicate a polydispersity of 5.6%. While some shear-induced differences in the structure factor may be observed at lower values of q, for the wave vectors probed here, the static data was independent of the flow (shear) rate.
Theoretical predictions for the Brownian dynamics in shear flow [1,2] indicate that the diffusion of the colloidal particles in the two directions probed here is described by:

$$\langle x^2(t)\rangle = 2Dt \qquad (1)$$
$$\langle z^2(t)\rangle = 2Dt + 2/3\gamma^2 t^3.$$

Here Ox is the direction perpendicular to the direction of flow and Oz the direction parallel to the flow, γ is the shear rate and D is the diffusion constant which in the case of hard spheres is given by the Einstein-Stokes relationship, $D=k_BT/6R\pi\eta$, where R is the radius of the particles and η is the viscosity of the solvent.
Our experimental results agree with these theoretical predictions and show that for a transverse scattering geometry, and in the low-shear limit, the diffusive (Brownian) dynamics of the PMMA particles is decoupled from the convective, flow-induced response in the intensity fluctuation correlation functions (Fig. 2a). The "Kratky plots" (τq^2 vs. qR) have been used to emphasize the $\tau \sim q^{-2}$ dependence of the correlation times, in agreement with the free diffusion of colloidal particles. For different scattering geometries, such is the "longitudinal" one also probed by our experiments this result does not apply. The intensity autocorrelation functions $g_2(q,t)$, measure a coupling between the diffusive dynamics of the colloidal particles and a flow-induced convective component (Fig. 2b). A more detailed study of this coupling is currently under way.
In conclusion, this new experimental method, of XPCS-microfluidics can be used to study the dynamics in a large variety of beam-sensitive liquid samples. In order to avoid a coupling between the flow and the diffusive dynamics a transverse scattering geometry must be used.

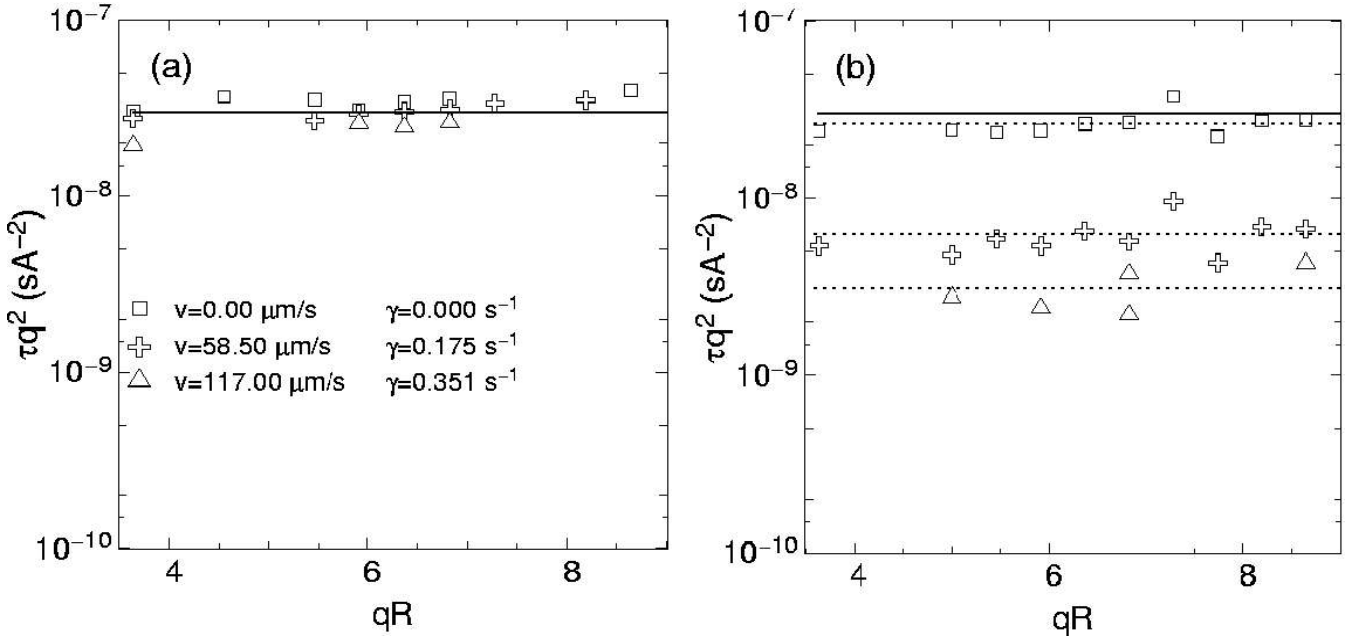

Fig. 2: "Kratky plots" for the fitted correlation times of the intensity autocorrelation functions $g_2(q,t)$ as a function of q, for three different flow rates and for the two scattering geometries probed here: (a) transverse scans and (b) longitudinal scans. The solid lines were calculated using the Einstein-Stokes relationship for the diffusion coefficient.

References

[1] B.J. Ackerson, and N.A. Clark, J.Physique **42**, 929-936 (1981)

[2] Yoshishige Katayama and Ryutaro Terauti, Eur. J. Phys. **17**, 136-140 (1996).