

# Supporting Information

## Microrheology with Fluorescence Correlation Spectroscopy

Silke Rathgeber<sup>1,2,\*</sup>, Hans-Josef Beauvisage<sup>1</sup>, Hubert Chevreau<sup>1,3</sup>, Norbert Willenbacher<sup>4</sup>,  
Claude Oelschlaeger<sup>4</sup>

<sup>1</sup>Max Planck-Institute for Polymer Research, Polymer Physics, 55128 Mainz, Germany.

<sup>2</sup>Johannes Gutenberg-University Mainz, Institute for Physics, 55099 Mainz, Germany.

<sup>3</sup>Ecole Polytechnique Universitaire de Lille, 59655 Villeuneuve D'Ascq Cedex, France.

<sup>4</sup>Technical University Karlsruhe, 76131 Karlsruhe, Germany.

## Dynamic Light Scattering

### Experimental Setup

In order to determine the diffusion coefficients of the tracer particles by an independent measurement dynamic light scattering experiment were carried out using a home-made apparatus equipped with a near-infrared diode laser from Schäfer und Kirchoff (SuK) company. The laser provides vertically polarized light at a wavelength of 831.5 nm with a power output of 80 mW (maximum of 60 mW on the sample). This laser wavelength lies far outside of the absorption bands of the tracer particles. Two avalanche diodes, SPCM-AQR-15 model from Perkin-Elmer company were used as detectors operated in the pseudo cross-correlation mode to suppress electronic artifact originating from the single detectors. The intensity correlation function  $g_2(q, t)$  was calculated using a 5000/E/ALV hardware correlator. Here,  $q$  denotes the scattering vector and  $t$  the lag time covering a range from 0.2 ms up to 300 s. The experimental coherence factor,  $f=0.96$ , was determined using PS latex spheres ( $d=155$  nm) in water (Duke Scientific). Using a circulating temperature bath the temperature at the sample position was kept fixed to  $293.2 \pm 0.1$  K. Samples with solid concentration from  $6.7 \cdot 10^{-3}$  wt% down to  $4.6 \cdot 10^{-4}$  wt% were measured in round Hellma cuvettes with a diameter of 20 mm. Samples were prepared by dilution from the stock solution of FluoSpheres® (FSP) provided by Molecular Probes, Inc.. The water used for dilution was filtered through a  $0.2 \mu\text{m}$  Millex®-HA filter (Millipore) beforehand. The refractive index  $n_w=1.332$  and the viscosity  $\eta_w=1.0015$  mPas of water at 293 K were taken from literature. Dynamic light scattering (DLS) spectra were taken

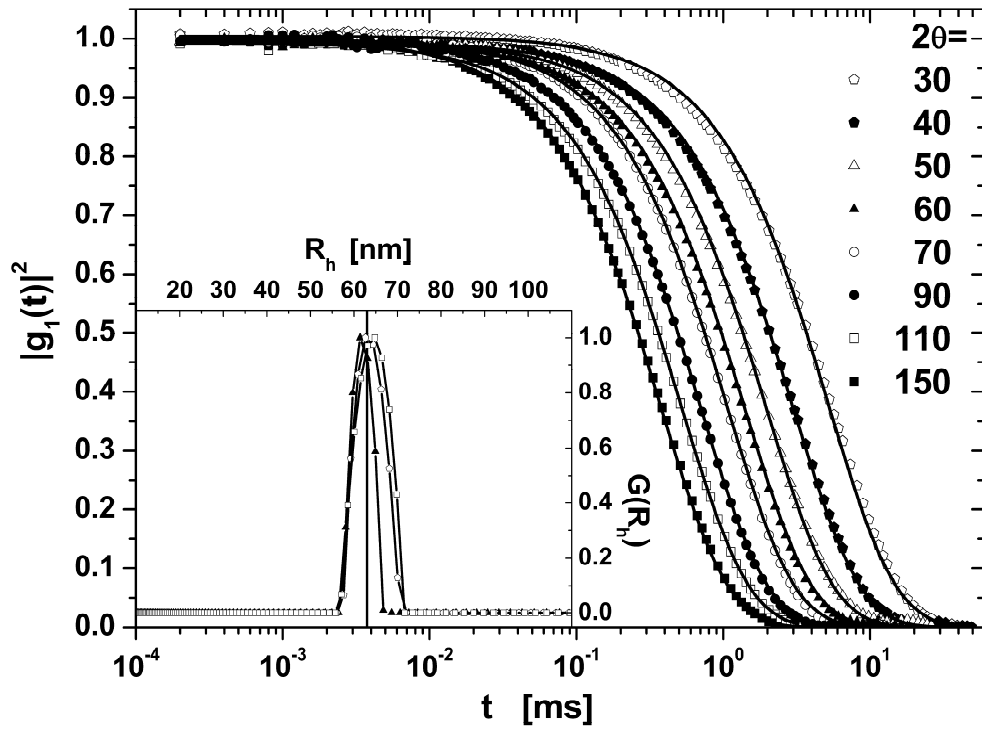
in 10° steps for scattering angles between  $\theta=30^\circ$  and  $150^\circ$ . Thus a scattering vector range from  $q=0.5210 \cdot 10^{-3} \text{ nm}^{-1}$  to  $1.944 \cdot 10^{-3} \text{ nm}^{-1}$  is covered.

## Data Evaluation

The Siegert relation  $g_2(q, t) = 1 + f |g_1(q, t)|^2$  connects the intensity correlation function  $g_2(q, t)$  to the electric field correlation function  $g_1(q, t)$ . The latter is directly related to the dynamic structure factor  $S(q, t)$  normalized to its value at  $t=0$ :  $g_1(q, t) = S(q, t)/S(q, t=0)$ . The z-averaged diffusion coefficient  $\langle D \rangle$ , the average bead hydrodynamic radius  $\langle R_h \rangle$  and the width of the distributions,  $\Delta D$  and  $\Delta R_h$ , respectively, as a measure the polydispersity were determined using two different approaches: (1) CONTIN analysis [S1] and (2) cumulant method, which expands  $\ln[g_1(q, t)]$  in a power series in  $t$ :  $\ln[g_1(q, t)] = -K_1 \cdot t + (K_2/2) \cdot t^2 - \dots$  [S2]. The first cumulant  $K_1$  is related to the z-averaged diffusion coefficient by  $K_1 = q^2 \langle D \rangle$ . The second cumulant  $K_2 = q^4 \langle \Delta D^2 \rangle$  measures the variance  $\Delta D^2 = \langle (D - \langle D \rangle)^2 \rangle$  of the  $D$  distribution. The hydrodynamic radius  $\langle R_h \rangle$  can be calculated using the Stokes-Einstein relation  $\langle R_h \rangle = k_B T / (6\pi\eta_w \langle D \rangle)$ , where  $k_B$  = Boltzmann constant and  $T$  = temperature. The width  $\langle \Delta R_h \rangle$  of the  $R_h$  distribution is given by  $\Delta R_h / R_h = \Delta D / D = \sqrt{K_2} / K_1$ . In Figure S1 the measured correlation functions are plotted as a function of time for some representative scattering angles. The solid lines show the result of a simultaneous fit of all spectra using the cumulant method with  $\langle D \rangle$  and  $\langle \Delta D^2 \rangle$  as only adjustable parameters. The  $q^2$ -dependence expected for free diffusion is well preserved. Furthermore no dependence of the result on the particle concentration is observed. We obtain  $\langle D \rangle = (3.4 \pm 0.2) \cdot 10^{-12} \text{ m}^2/\text{s}$  and  $\Delta D / \langle D \rangle = 9\%$  which corresponds to a hydrodynamic radius of 3nm. In the insert of Figure S1 the  $R_h$  distribution obtained from the CONTIN analysis is shown for comparison. The result  $\langle R_h \rangle = 64 \text{ nm}$  with a half-width-of-half-maximum of 11% corresponds well to the result obtained using the cumulant analysis.

## References

- S1. Provencher, S.W. a) *Comput. Phys. Commun.* **1982**, 27, 213-227. b) *Comput. Phys. Commun.* **1982**, 27, 229-242.
- S2. Schärftl, W. *Light Scattering from Polymer Solutions and Nanoparticle Dispersions*; Springer: Berlin, 2007.



**Figure S1:** Correlation functions measured dynamic light scattering for the tracer beads in water for representative scattering angles (markers). The solid lines show the result of a simultaneous fit of all spectra using the cumulant analysis. For comparison the inset presents the distributions obtained for the hydrodynamic radius by applying the CONTIN method to the data taken at  $2\theta=30^\circ, 60^\circ, 90^\circ, 110^\circ$ .