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Polymer and Colloid Highlights

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Optical Microrheology

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Thermal motion of small particles in a liquid was initially described by Brown in 1827 and explained much later by Einstein and Smoluchowski. They showed that the particle diffusion coefficient D is directly related to the thermal energy $k_B T$. Using the friction coefficient of a sphere leads to the famous Stokes-Einstein relation $D = k_B T/6\pi\eta R$. Nowadays, many sensitive tools to monitor such microscopic particle motion exist. One of the most powerful methods is photon correlation spectroscopy (PCS). A variant of PCS applied to turbid 'white' systems is called diffusing wave spectroscopy (DWS). DWS allows the measurement of particle mean square displacements $\Delta r^2(t)$ on time scales from nanoseconds to minutes and can resolve motion on lengths scales smaller than a nanometer.

The Stokes-Einstein relation can be generalized to complex fluids such that from the measured particle mean square displacement $\Delta r^2(t)$ the frequency dependent complex shear modulus of the fluid $G^*(\omega) = G'(\omega)+i\,G''(\omega)$ can be deduced.[1] This optical 'microrheology' has emerged as one of the most important new techniques to study and characterize rheological properties of complex fluids. The method can be applied both using tracer particles in transparent fluids as well for the study of naturally opaque systems, for example dairy products.

One of the many advantages of DWS-based microrheology is the enormous range of times scales, or frequencies, that can be accessed in a single experiment. Recently, we have carried out a detailed DWS tracer experiment in viscoelastic surfactant solutions.[2] One of the aims was to compare ultra high frequency mechanical measurements with DWS. Although classical rheometry is usually limited to frequencies well below 1000 rad/s there exist very specific tools, such as mechanical resonators, that operate at and above 10^5 rad/s.

In our experiments we added a small amount of micron sized polystyrene tracer particles to the solution and then determine the mean square displacement $\Delta r^2(t)$ with DWS as shown in Fig. 1. Excellent agreement was found between optical and mechanical measurements up to frequencies of 10^6 rad/s. Since the high frequency viscoelasticity is intimately related to the local dynamics it is possible for example to extract the persistence length of the elongated surfactant micelles from such measurements.

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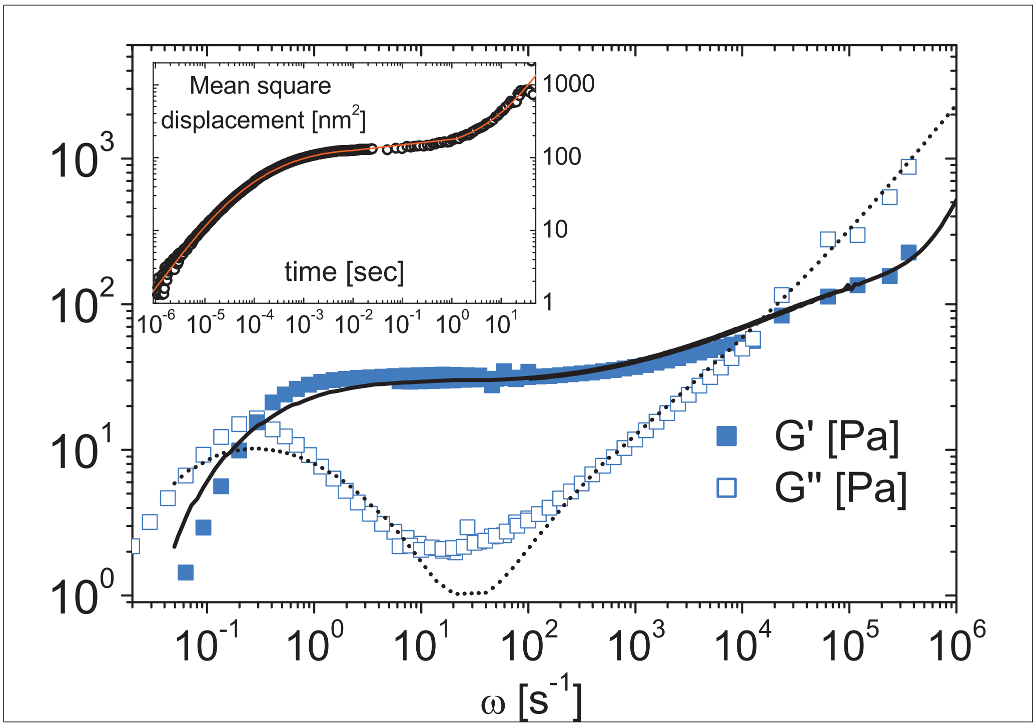

Fig. 1. Shear moduli G'(ω) and G''(ω) of an aqueous solution of 100 mM CPyCl and 60 mM NaSal at T = 20 °C obtained from DWS (lines) and various mechanical rheometers (symbols). Inset: Particle mean square displacement of the polystyrene d = 720 nm tracer particles added to the surfactant solution.

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