

Microrheology of giant-micelle solutions

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Abstract. – Optical tracer-microrheology has been applied to study the rheological properties of a concentrated surfactant solution. Under the chosen conditions these surfactants self-assemble to form giant polymer-like micelles, resulting in a strongly viscoelastic liquid. A novel approach to the analysis of the local dynamic properties of tracer particles is presented, based on a combination of single- and multi-speckle diffusing wave spectroscopy (DWS). With this technique we could significantly extend the accessible frequency range to the key rheological properties as given by the loss and storage modulus, $G''(\omega)$ and $G'(\omega)$. A study of the high-frequency range, not accessible to standard techniques, shows good overall agreement with conventional models. However, we find a distinct temperature dependence of the characteristic modulus G_0 incompatible with the simple picture of a single relaxation process.

Introduction. – In recent years significant progress has been made in the development of modern optical techniques to study and characterize the rheological properties of complex fluids. These techniques have been first applied in fundamental research on complex systems from colloids and emulsions to biopolymers [1–3]. More recently they have become available to both industrial and applied researchers. For example, it has been shown that optical microrheology can be successfully used to characterize ceramic slurries and green bodies as well as colloidal suspensions and biopolymer gels, such as yogurt [4–7]. The underlying concept is to study small (colloidal) particles embedded in the system under study. In this case the particles can either be artificially introduced, which is then called *tracer-microrheology*, or can be part of the system itself, *e.g.*, as in the case of colloidal gels. By analyzing the thermal motion of the particles it is possible to obtain quantitative information about the loss and storage moduli, $G''(\omega)$ and $G'(\omega)$, over an extended range of frequencies, not accessible to standard rheometers [1, 2].

One of the most popular techniques to study the motion of the particles is diffusing wave spectroscopy (DWS), an extension of standard photon correlation spectroscopy (PCS) to turbid media. Here the analysis of (multiply) scattered laser light is used to determine the time evolution of the probe particle mean-square displacement [1–3, 8]. DWS allows access to a broad range of time scales which results in a very large frequency range, typically 1 to 10^6 Hz, as we will show later in the text. Despite the broad use of DWS-based tracer-microrheology (see ref. [2]) there is still a lack of quantitative information about the validity of the fundamental assumptions of the microrheology approach itself, which is based on an *ad hoc* assumption

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relating the particle mean-square displacement to the complex modulus [1]:

$$\tilde{G}(s) = \frac{s}{6\pi a} \left[\frac{6k_B T}{s^2 \langle \Delta \tilde{r}^2(s) \rangle} \right]. \quad (1)$$

Recently, a theoretical justification (albeit certain constraints) for eq. (1) has been reported [9]. On the experimental side there are however few studies on well-defined model systems where such theoretical models could be verified.

In this letter we present a study of DWS-based microrheology on giant micelle solutions. What makes our systems unique is the fact that the size of surfactant molecules and the typical length scales of the structures formed are of nanoscopic size, hence always much smaller than the tracer particle (typically 0.3–3 μm). Furthermore, these *living* structures assemble and break up rapidly leading to a perfectly homogeneous (on mesoscopic scales) and ergodic system. This stands in sharp contrast to a number of previous studies where interactions between tracer particle and viscoelastic matrix have been complicated by inhomogeneities, which led to irreproducible or erroneous results (some examples are discussed in refs. [2, 3, 10]). Another problem present in many microrheology studies is the fact that the particles in thermal motion themselves give a significant or even dominant contribution to the sample viscoelasticity, leading to the breakdown of the concept of a probe (or tracer) particle. Results obtained on such system are either *approximate at best* or require a detailed model for the structure and dynamics of the system under study, *e.g.*, as has been reported in the case of colloidal gels [5, 11, 12].

Polymer-like micelles. – The material we want to study is a concentrated aqueous solution of the surfactant molecule hexa-ethylene glycol mono *n*-hexadecyl ether (C_{16}E_6). Under the chosen conditions these molecules (typical size = 3 nm) self-assemble to form large elongated aggregates, having much in common with flexible polymers in a good solvent [13, 14]. Apart from being a convenient model system in polymer science, these giant micellar systems display a number of highly interesting properties on their own. One of the most prominent differences to polymers is the fact that the micelles are in thermal equilibrium with single monomers. Since they break and reform continuously the micelles are also called *living* or *equilibrium polymers*. Much interest has been dedicated to these systems over the last decade and significant progress has been made in the understanding of the structural and dynamic properties [15–17]. Far above the overlap concentration c^* (in our case $c = 100 \text{ mg/ml} \gg c^* = 2 \text{ mg/ml}$) a surprisingly strong viscoelastic material is obtained.

In contrast to cross-linked gels, polymer-like entanglements in semi-dilute or concentrated solutions are only temporary and therefore on sufficiently long time scales the system always exhibits liquid-like behavior (even in the case of very long chains). For classical polymers above the overlap concentration c^* , molecules relax on a characteristic time scale τ_{rep} by a curvilinear diffusion along an imaginary tube, called *reptation* [18]. The reptation model has been extended by Cates to the case of equilibrium polymers by taking into account the equilibrium molecular-weight distribution and the finite lifetime of the micelles. The reversible scission of the micelles has to be considered as an additional relaxation process, characterized by τ_{break} . It represents the time taken for a micelle of the average length L to break into two pieces, as well as the lifetime of a micellar end before a recombination event occurs. In general, the rheological behavior of living polymers is governed by both τ_{rep} and τ_{break} [17]. In the fast-breaking limit $\tau_{\text{break}} \ll \tau_{\text{rep}}$, chain breakage and recombination occur often before the chain reptates out of its tube segment. This means that before a given tube segment relaxes, the chain will undergo many breaking and fusing reactions, so that there is no memory of the initial length and position of the chain in the tube. The stress relaxation function $\sigma(t, \gamma)$, which is

proportional to the relaxation modulus $G(t, \gamma)$, then decays as a single exponential with a new terminal relaxation time τ_r given by $\tau_r = (\tau_{\text{break}}\tau_{\text{rep}})^{1/2}$. This regime is thus characterized by a purely Maxwellian behavior at low frequencies. This means that the complex elastic modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$ approaches the form [19]

$$G^*(\omega) = G_0 \left(\frac{(\omega\tau_r)^2}{1 + (\omega\tau_r)^2} + i \frac{\omega\tau_r}{1 + (\omega\tau_r)^2} \right), \quad (2)$$

with a single relation time τ_r . Deviations from this idealized behavior are expected if the above-mentioned condition does not apply. At high frequencies the model eventually breaks down due to the finite viscosity η_{sv} of the solvent itself ($G''(\omega) \rightarrow \eta_{\text{sv}}\omega$). Moreover, in the high frequency regime we expect additional relaxation processes to become important. The model of Cates has been extended [20] in order to include the short-time-scale relaxation processes and theoretical predictions were obtained from computer simulations [21]. If τ_{break} is reduced, one enters a regime where tube length fluctuations or “breathing” are the dominant motion on the time scale of τ_{break} . At still smaller values of τ_{break} , a further regime arises where the dominant motion on the chemical time scale is unentangled. The relaxation no longer depends on the length or configuration of the micellar chains. It corresponds to Rouse modes, associated with molecular motions of pieces of chains of order the entanglement length l_e . These additional modes strongly affect the high-frequency behavior. However, experimentally it is very difficult to obtain detailed information about the viscoelastic behavior of these materials due to the limited frequency range covered by classical rheometers. Attempts to do so usually need to compare a number of different data sets using a time-temperature-concentration superposition scheme (for details see refs. [19, 22]). However, for micellar solutions this is problematic due to the equilibrium nature of the micellar size distribution, which leads to a strong dependence of the micellar contour length on concentration and temperature.

We have prepared mixtures of concentrated surfactant solutions and aqueous solutions of charge-stabilized polystyrene spheres at a salt concentration of 0.005 M NaCl with a final surfactant concentration of 100 mg/ml (particle volume fraction $< 4\%$). Two different tracer particles, with diameter $d = 0.72 \mu\text{m}$ and $1.5 \mu\text{m}$, were used. No visible heterogeneities were observed and the mixtures are found stable over the measurement time (typically less than 30 minutes). We note, however, that after several hours the mixtures start to macroscopically phase separate, indicating some surfactant-mediated attraction between the particles (which we did not further investigate). With a classical rheometer, MCR300 from PHYSICA, in cone-plate geometry the loss and storage modulus have been determined over the frequency range accessible to the instrument ($\omega < 10^3$ rad/s). Measurements with and without tracer particles show no detectable differences, hence confirming that the tracer particles have only a negligible influence on the rheological properties of the system.

Single- and multi-speckle diffusing wave spectroscopy. – Our aim is to analyze the local motion of tracer particles (sulfate polystyrene latex spheres from IDC) in an otherwise transparent giant micellar matrix with diffusing wave spectroscopy (DWS) (see fig. 1). DWS extends *conventional* dynamic light scattering (DLS) to media with strong multiple scattering, treating the transport of light as a diffusion process. Analogous to DLS it is possible to express the measured intensity autocorrelation function $g_2(\tau) = \langle I(0)I(\tau) \rangle / \langle I(0) \rangle^2$ in terms of the mean-square displacement of the scattering particle: $g_2(\tau) - 1 = \left\{ \int_0^\infty ds \cdot P(s) \cdot \exp\left[-\frac{1}{3}k_0^2 \langle \Delta r^2(\tau) \rangle \frac{s}{l^*}\right] \right\}^2$, where we have used the Siegert relation between the field and the intensity correlation function $g_1(\tau)^2 = g_2(\tau) - 1$ [8]. $k_0 = 2\pi n/\lambda$ is the wave number of light in a medium with refractive index n . $P(s)$ is the distribution of photon trajectories of length s in a sample of thickness L , and can be calculated within the diffusion model.

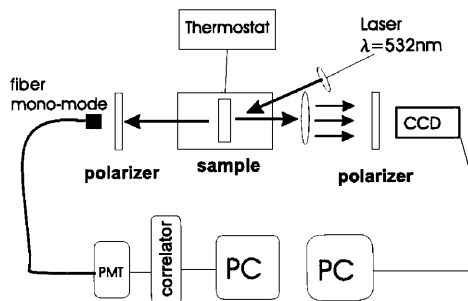


Fig. 1 – DWS setup: An intense laser beam (Verdi from Coherent) is scattered from a turbid sample contained in a temperature-controlled water bath. The scattered light is detected in transmission or backscattering with a single-mode fiber or a CCD camera and subsequently analyzed digitally (correlator and PC).

The transport mean free path l^* characterizes the typical step length of the photon random walk, given by the individual particles scattering properties and particle concentration [8]. l^* can be determined independently and enters the analysis as a constant parameter. Using this expression it is possible to numerically calculate the particle mean-square displacement $\langle \Delta r^2(\tau) \rangle$ from the measured autocorrelation function $g_2(t)$. In transmission we analyze the intensity-autocorrelation function, fig. 2a), using a traditional fiber optic based DWS setup. Figure 2b) displays the mean-square displacement obtained by inverting $g_2(t)$ using the appropriate boundary conditions (plane-wave limit for an extended incident beam, for details see ref. [8]).

Instead of analyzing the fluctuations of the intensity at a single spatial position (one-speckle spot) a large area of the intensity pattern (hence multi-speckle) of the scattered light can be analyzed using a CCD camera [23, 24]. The main advantage of this setup in DWS-based microrheology is the significantly reduced data acquisition time, since a large number of DWS-scattering experiments is performed simultaneously [6]. Furthermore, since

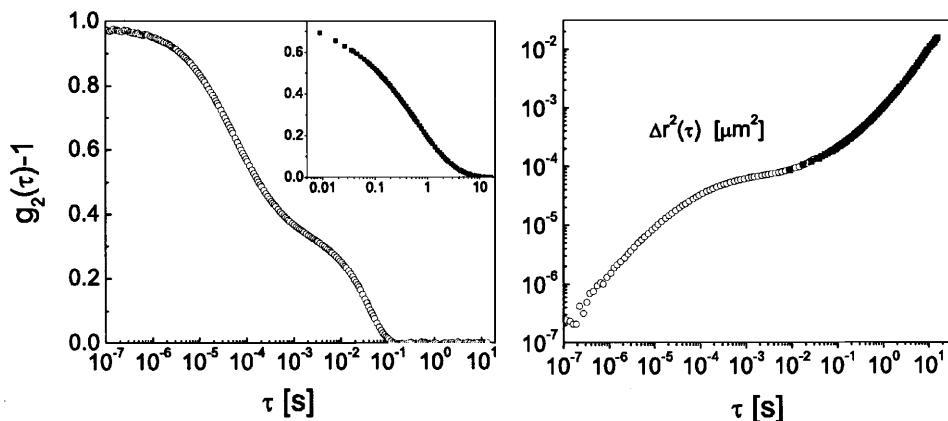


Fig. 2 – DWS analysis of the tracer particle motion ($d = 720$ nm) in a 100 mg/ml surfactant solution at $T = 28$ °C. a) Intensity autocorrelation function $g_2(t) - 1$ in transmission geometry ($L = 2$ mm, $l^* = 0.149$ mm). Inset: CCD-camera-based multi-speckle DWS in backscattering geometry ($L = 5$ mm, $l^* = 0.149$ mm). b) Mean-square displacement determined from the data shown in a) (same symbols correspond to the same scattering geometry).

different configurations of the sample are probed simultaneously, the measured correlation function never suffers the problems of nonergodicity and can hence also be used in the case of viscoelastic solids (*i.e.* systems with a finite storage modulus $G'(0) > 0$). The backscattering geometry provides access to slow relaxation processes since the distribution of multiple scattering paths is broad ($P(s) \propto s^{-3/2}$). The inset in fig. 2 shows the correlation function obtained for the 100 mg/ml sample [25]. A quantitative description of the intensity-autocorrelation function, as measured in backscattering geometry, is given by the following expression: $g_2(\tau) - 1 = \exp \left[-2\gamma\sqrt{k_0^2 \langle \Delta r^2(\tau) \rangle + a} + 2\gamma\sqrt{a} \right]$ [8]. Introducing a constant γ value allows to quantify low-order scattering, *i.e.* the coupling of the incident light to the turbid media, in our case $\gamma = 1.9 \pm 0.05$. The parameter a characterizes deviations from the idealized semi-infinite slab geometry, *i.e.* photon loss along the multiple-scattering paths. For the non-absorbing samples used in this study a depends only on the cell geometry and on the optical density of the sample (L/l^*). In principle all DWS parameters (l^*, γ, a) can be determined independently using a reference sample with identical optical properties and known $\langle \Delta r^2(\tau) \rangle$. However, due to unavoidable experimental errors this will always result in a slight mismatch between the two sets of data (transmission and backscattering) complicating the following microrheology analysis. Instead, we fit the value of a to obtain a smooth curve over the whole time-range [26]. Figure 2b) displays the $\Delta r^2(\tau)$ -data obtained for a 100 mg/ml surfactant solution at $T = 28^\circ\text{C}$ with a concentration of 1.7% of tracer particles ($d = 720$ nm). As can be seen from fig. 2, the combination of traditional and CCD-based DWS extends the accessible range of microrheology by several orders of magnitude [27]. We also note that DWS of virtually any nonergodic medium now becomes straightforward if our approach is combined with the recently introduced (fiber-based) two-cell technique [5]. Within the experimental error (mainly given by an uncertainty in the l^* value of ca. 5–10%) no systematic dependence on size and concentration of the tracer particles has been observed. To exclude any size dependence it would however be necessary to cover a broader range of particle sizes, which will be the subject of future investigations.

Results and discussion. – Based on the microrheology approach suggested by Mason and Weitz, the frequency-dependent loss and storage modulus $G'(\omega)$, $G''(\omega)$ can be calculated directly from $\langle \Delta r^2(\tau) \rangle$. A generalized Stokes-Einstein relation connects the complex modulus to the mean-square displacement as described by eq. (1) (for details see ref. [1]). A comparison of the results from classical rheometry and DWS-based microrheology, fig. 3a), shows that the latter technique covers a dramatically increased frequency range. It allows in particular for measurements at very high frequencies, where classical techniques fail. Moreover, the method measures in the linear regime only as it is probing thermal fluctuations of the system, and thus no problems arise due to the application of external shear fields.

We have used optical microrheology for an investigation of the temperature dependence of the viscoelastic properties from $T = 28^\circ\text{C}$ to $T = 36^\circ\text{C}$, fig. 3b). Two key rheological parameters can be directly obtained by a comparison to the simple Maxwell model, eq. (2). From the first crossing point $G'(\omega) = G''(\omega)|_{\omega=1/\tau_r}$ there follow both the typical relaxation time τ_r and the (Maxwell) plateau modulus $G_0 = 2G'(\omega_r) = 2G''(\omega_r)$. We find that the relaxation time shows an Arrhenius-type decay, $\ln \tau_r \propto -T$, as displayed in the inset of fig. 3b) characteristic of a temperature-activated relaxation process. A similar temperature dependence of τ_r has been reported previously (see [22] and references therein). Clear deviations to what is expected for a single relaxation process are found however for the Maxwell plateau which is not well established and rather shows a long stretching. This behavior becomes even more pronounced with increasing temperature. Furthermore, the values of $G_0/2$, circles in fig. 3b), show a temperature dependence that is much more pronounced than previously found

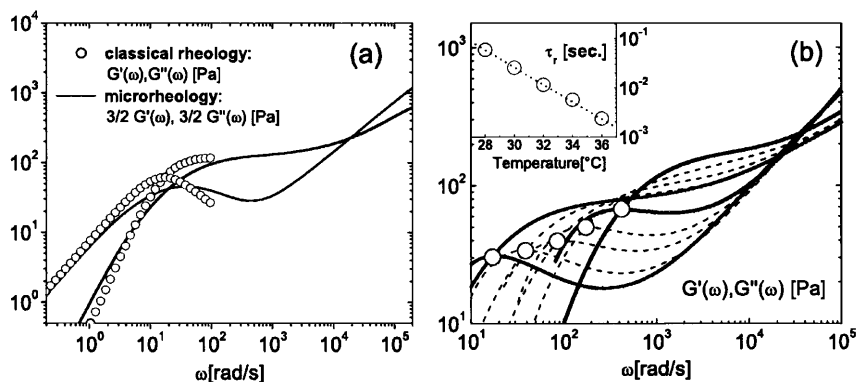


Fig. 3 – a) Classical rheometry and optical microrheology of giant micellar solutions ($c = 100$ mg/ml) at $T = 28$ °C. The microrheology results are based on $\langle \Delta r^2(\tau) \rangle$ -data averaged over two tracer sizes and different particle concentrations ($< 4\%$) thereby reducing statistical errors. Microrheology data were multiplied by a scaling factor of $3/2$, as discussed in the text. b) Temperature dependence of the viscoelastic moduli obtained from microrheology: $G'(\omega)$ and $G''(\omega)$ for $T = 28, 30, 32, 34, 36$ °C (from left to right). In the Maxwell model the first intersection of $G' = G'' = G_0/2$ determines both G_0 and $\omega_r = 1/\tau_r$ (open symbols). Inset: Relaxation time τ_r .

in ref. [22] for another system forming polymer-like micelles. A detailed comparison with existing theoretical models of both the concentration and temperature dependence of $G'(\omega)$ and $G''(\omega)$ is currently under way and will be the subject of future articles.

Another interesting finding is the scaling (or correction) factor of approximately 1.5-2, necessary in order to obtain quantitative agreement between tracer microrheology and classical rheometry, as can be seen in fig. 3. Currently, we do not have a detailed understanding about the origin of this scaling factor, which appears to be independent of tracer size and concentration. If eq. (1) holds quantitatively, our results imply that the particles influence their immediate surrounding leading to a modified coupling of the tracer sphere to the medium. However, the fact that no distinct tracer size and concentration dependence is observed may also indicate that eq. (1) does not fully describe our system. In this context it is interesting to note that the classical Stokes-Einstein relation differs by a very similar factor of $3/2$ depending on the choice of the boundary conditions on the particle surface (stick or slip) [28]. Further experimental and theoretical efforts are necessary to obtain a complete picture of tracer microrheology and its range of validity. We think that our results on these simple self-assembling and homogeneous structures may be very well suited to stimulate further progress in this field.

In conclusion, we have demonstrated the application of optical tracer microrheology to concentrated surfactant solutions. A combination of single- and multi-speckle DWS has been introduced, extending the range of frequencies accessible to microrheology by several orders of magnitudes. This new technique can play an important role in future experiments since the use of a CCD-camera gives access to the low-frequency range of $G'(\omega)$ and $G''(\omega)$, thus providing significant overlap with mechanical measurements. Furthermore, both single- and multi-speckle DWS can be carried out simultaneously, which adds important practical use since the rheometric study of time-dependent phenomena, such as gelation or aging, becomes straightforward.

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