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Current Opinion in Colloid & Interface Science 12 (2007) 43 – 49

Current Opinion in COLLOID and INTERFACE SCIENCE

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Dynamics and structure of complex fluids from high frequency mechanical and optical rheometry

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Abstract

High frequency rheometry here defined as measurement of dynamic shear moduli in the frequency range beyond that accessible by conventional rotational rheometry ($f > 10^2$ Hz) provides insight into microstructure and local dynamics of complex fluids. We review the mechanical devices as well as the optical and other microrheological techniques available today, discussing especially the frequency and modulus range the different methods cover. We also emphasise on the comparison between optical and mechanical methods and finally, on the microscopic structural and dynamic information extracted from high frequency rheology on complex fluids like polymers, surfactants, biomaterials and colloidal dispersions.

Keywords: High frequency rheology; Microrheology; Viscoelasticity; Polymers; Surfactants; Colloidal dispersions

1. Introduction

The dynamics of complex fluids, such as colloidal suspensions, emulsions, gels or solutions of synthetic polymers, polyelectrolytes, surfactants or biopolymers and proteins extends across several orders of magnitude on the time ranging from microseconds to tens of seconds or even hours and days, thus reflecting the diversity of relaxation processes occurring in such fluids. High frequency rheology particularly provides insight into microstructure, interactions and local dynamics of complex fluids. This is of great interest both for pure and applied research. In the case of concentrated colloidal suspensions e.g. the high frequency modulus probes thermodynamic particle interactions and can be directly related to suspension stability. For polymer or surfactant solutions the hierarchical relaxation of structural elements results in characteristic scaling regimes for the high frequency moduli which can be related to microscopic features like chain stiffness, molecular architecture or solvent–polymer interactions. The location of the high frequency regime on an absolute scale of course strongly depends on the characteristic features of the respective fluid and typically extends from 10 to 10^6 Hz. Conventional rotational rheometers are usually limited to frequencies $< 10^2$ Hz and for complex fluids time–temperature superposition is generally not suitable to extend this frequency range. In the past few years both mechanical and optical techniques have become increasingly available, covering the frequency range beyond 10^2 Hz. These techniques are now robust and accurate enough to study a wide variety of fluids from dilute (bio) polymer solutions to entangled networks and concentrated colloidal suspensions.

2. Mechanical devices

2.1. Piezo-driven shear and squeeze flow rheometer

Various piezo-driven oscillatory shear rheometers have been built to cover the frequency range from about 0.1 Hz to almost 10 kHz. Generation of flow as well as detection of sample response are handled by piezoelectric transducers. Frequency can be varied continuously and the applied strain amplitudes γ_0 are on the order of 10^{-4}–10^{-3}. Moreover, the required sample volume is very small, typically < 100 μl. Instruments operating in simple either linear [1] or torsional [2] shear flow are suitable for fluids with moduli $G^* > 10^2$ Pa.

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doi:10.1016/j.cocis.2007.03.004

Piezo-rheometers operating in the squeeze flow mode have been introduced by Pechhold and co-workers [3] and Palierne [4]. For small deformations the complex squeeze stiffness K^* of such a set-up is related to the shear modulus G^* and compressibility κ^* of the fluid

$$\frac{1}{K^*} = \frac{2d^3}{3\pi R^4}\left(\frac{1}{G^*} + \frac{3R^2}{2d^2}\cdot\kappa^*\right) \tag{1}$$

where R and d are the gap radius and height, respectively. In principle, this allows for simultaneous determination of G^* and κ^* through variation of the gap height, but for dilute polymer or surfactant solutions the compressibility term is negligibly small. Shear moduli G^* down to 10^{-3} Pa are accessible. Recently, such devices have been used to study polymer and surfactant solutions, as well as colloidal suspensions and concentrated emulsions [3–5•]. A linear shear flow rheometer has been placed into a magnetic field and combined with a light scattering device in order to study the structure and rheology of magnetic particles in polymeric matrices [6].

2.2. Torsional resonators

Torsional resonators provide access to the frequency range from about one to a few hundred kHz. Immersion of the resonator into a fluid results in a shift of the resonance frequency Δf and a broadening of the resonance curve ΔD compared to its behavior in air. The shear modulus G^* of the surrounding fluid is directly related to ΔD and Δf. First introduced about 60 years ago [7], various experimental designs have been employed [8,9] facilitating measurements at one or multiple frequencies. Resonators with different geometries (cylinder, tube, plate) as well as driving and detecting modes (piezo, electromagnetic, magnetostrictive) with high quality factors are available now [10], the required sample volume is typically >10 ml. Piezo-driven devices operate at strain amplitudes $\gamma_0 < 10^{-3}$. Such small strain amplitudes are mandatory to access the linear viscoelastic response regime e.g. in the case of concentrated colloidal suspensions. Moduli $G^* > 10$ Pa are accessible with the set-up used by Willenbacher and co-workers, but careful calibration is necessary [11••]. Robust, electromagnetically driven resonators have been introduced recently by Romoscanu et al. [10,12]. Operating at $\gamma_0 > 10^{-2}$ reasonable results for Newtonian fluids and weakly viscoelastic polymer solutions with $G^* > 100$ Pa were obtained without calibration using only the mechanical specifications of the resonator set-up.

2.3. Ultrasonic shear rheometers

Piezoelectric crystal resonators oscillating in thickness-shear mode at frequencies in the MHz range are also used to obtain rheological information of complex fluids. Analogous to the torsional resonator technique described above, the mechanical impedance of the quartz crystal is coupled to the viscoelastic properties of the fluid in contact with its surface [13]. The penetration depth δ of the shear wave is related to its frequency f as well as the density ρ and dynamic shear modulus $G^* = G' + iG''$ of the surrounding fluid:

$$\delta = \frac{|G^*|}{2\pi f}\sqrt{\frac{2}{\rho}\cdot\frac{1}{|G^*| - G'}}. \tag{2}$$

Accordingly the penetration depth in the MHz range is often below 1 μm and the required sample volume is only a few microliters, but it has to be checked carefully, whether bulk properties are probed. Shear amplitudes are again around 10^{-3} and moduli $G^* > 10^4$ Pa are accessible. The technique has recently been used to study protein–protein interactions in concentrated protein solutions [14,15] or gelation in dairy products [16•]. Alig et al. have set up an ultrasonic rheometer operating in the reflection mode. The shear modulus of a fluid film applied to the quartz block is inferred from the amplitude and the phase shift of the ultrasonic pulse reflected at the interface between quartz and fluid using special ultrasonic shearwave transmitters. This technique is less sensitive than the resonator method and moduli $10^6\ \text{Pa} < G^* < 10^9$ Pa are detectable, but it allows for characterization of thin fluid layers with one free surface. Recently, it has been used to study film formation from solutions and suspensions also in combination with spectroscopic methods [17].

2.4. Atomic force microscopy (AFM)

AFM is more and more used as a tool for nanorheology and -tribology, providing information about viscoelastic properties with high spatial resolution, stress–strain measurements are performed even with single polymer molecules [18]. The method requires only small sample volumes (≪1 μl), it is fast and thus especially suitable for high throughput screening. Naturally, AFM is a surface characterization method and it is widely used to characterize viscoelastic properties of polymer films or even biological cells [19]. Extracting absolute values for bulk rheological quantities of non-Newtonian fluids is still a challenge due to the complex and often poorly reproducible flow field around the cantilever tip. An AFM-based oscillatory strain microrheometer has been used to extract the dynamic tensile modulus E^* of polyacrylamide gels and biological cells based on a generalized Hertz model [20]. Analysis of the power spectral density of thermally-induced cantilever deflections is a different route to AFM-based dynamic mechanical spectroscopy and gives access to frequencies in the kHz range. So far, this has been used for viscosity measurements on simple liquids [21].

3. Optical techniques

Optical and other microrheological techniques including magnetic tweezers and AFM have rapidly developed within the last 10–15 years, consequently the state of the art has been summarized in various review articles [19,22–24••,25]. We focus on the high frequency aspect here.