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Hao Zhang, Benjamin Gorin, Hamid Kellay, Abdelhamid Maali. Viscoelastic rheology of polymer solution probed by resonant thermal capillary fluctuation. 2023. hal-04048325

HAL Id: hal-04048325

<https://hal.science/hal-04048325>

Preprint submitted on 27 Mar 2023

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Viscoelastic rheology of polymer solution probed by resonant thermal capillary fluctuation

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We present a measurement of the viscoelastic properties of polymer solutions using the resonant thermal capillary fluctuations (RTCF) of the surface of a polymer solution droplet. The instantaneous deflection of a cantilever in contact with the drop surface allows for measuring the nanoscale thermal fluctuations of the interface. From the power spectral density of the measured fluctuations, we determine the two components of the rheological response of the fluid. Our experimental results were compared with rheological measurements using a classical commercial rheometer. We find a good agreement between the two measurements. Additionally, our experiments allow to extend the range for dynamical measurements of the rheological properties of the solutions up to 20000 s^{-1} .

I. INTRODUCTION

Viscosity is an important property that governs the behavior of fluid flow, and it is a key issue in several industrial applications, such as printing, painting, food processing, material processing, cosmetics, and lubrication which prevent friction and wear [1,2]. The rheology of fluids such as polymer solutions, polymer melts, colloidal solutions, and emulsions is complex and generally depends on the deformation rate imposed on the fluids. The rheology of complex fluids is mainly performed with commercial rheometers based on the measurement of the torque needed when the fluid is sheared between a moving member and a fixed one. Different geometries are used such as cone-plate, parallel plates, concentric cylinder, or double gap cylinder geometry [3,4]. The imposed shear is produced either by pure rotational motion or in an oscillatory one and thus the properties are measured versus the imposed shear rate and provide the viscoelastic response at different time scales. However, most devices are limited by rheometer inertia to low frequencies [4].

New methods have been developed to overcome these frequency limitations. The image tracking of the Brownian motion of micro-particles in the fluids is one of the promising methods, but requires high speed imaging and image processing which are time consuming [5,6]. Methods based on the use of microelectromechanical systems (MEMS) immersed in fluids have also been developed to extract the rheology of fluids [7-10]. Microfluidic rheometry has gained significant interest due to its ability to measure fluid properties using a small volume [11]. Optical coherence viscosimetry [12], surface light scattering on fluid interfaces [13-16] and drop oscillations [17-19] were also used to probe the rheology of liquids and polymer solutions.

Recently we have shown that a soft atomic force microscopy (AFM) cantilever in contact with an air bubble is a powerful tool to probe the thermal fluctuations of the air-water interface. The instantaneous deflection of the cantilever reflects directly the nanoscale thermal fluctuations of the interfaces. The power spectral density (PSD) of the fluctuations presents sharp resonance peaks that correspond to specific frequencies for which the thermal fluctuations of the interface are much more important than for other frequencies. Our measurements allow to probe the surface rheology due to the presence of surfactant [20] and to measure the additional damping due to the presence of minute amounts of contaminants [21].

II. METHOD AND EXPERIMENT

Here in this work, we will present a measurement of the rheological properties of polymer solutions using the resonant thermal capillary fluctuations (RTCF) of the interface between air and a polymer solution droplet. From the PSD of the RTCF, we determined the two components of the rheological response of the fluids. We have also performed measurements of the rheology of the same solutions using a classical cone-plate rheometer in oscillating mode and imposed shear rate mode. The results obtained by RTCF are in good agreement with the measurements obtained using the classical rheometer. The RTCF experiment allows extending the range of frequency for the study of the dynamic rheological properties of polymer solutions up to 20000 s^{-1} .

The sketch of the experiment is shown in *Fig. 1*. A thin layer (thickness 100 nm and roughness 0.2 nm) of Polystyrene (PS) was spin coated on a glass surface. A micro-drop (10 μL) of the polymer solution is deposited on the PS surface (to obtain a contact angle around 90°). An AFM cantilever was utilized to contact the drop surface and probe its time-dependent fluctuations, as a result, the PSD of the capillary fluctuations of the air-liquid interface was determined.

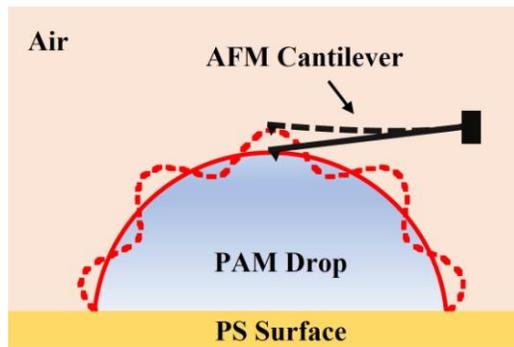


Figure 1: Schematic illustration of the experiment: a drop of the polymer solution is deposited on a PS surface. The AFM cantilever is in contact with the north pole of the drop surface. The instantaneous deflection of the cantilever directly reflects the nanoscale thermal fluctuations of the drop surface.

Polyacrylamide (PAM, Polysciences) with a high molecular weight of 1.8×10^7 ua, is dissolved in 10 mM NaCl solution at concentrations ranging from 0 to 1000 ppm (parts per million by weight). The rheological properties of the PAM solutions were measured with our RTCF experiment, and with a commercial rheometer (AR1000 Advanced Rheometer, TA Instruments) in a cone-plate geometry (with a 60 mm diameter, 0.5° cone angle, and a truncation gap of 10 μm). The RTCF experiments were performed using an AFM (Dimension 3100, Bruker) equipped with a cantilever holder (DMFT-DD-HD) that allows operation in a liquid. The cantilevers used are purchased from NT-MDT (CSG01, stiffness $k_c = 0.12 \pm 0.02$ N/m). The distance between the cantilever and the drop was controlled by the AFM stepping motor stage allowing to bring the cantilever in contact with the north pole of the drop. Once the contact between the cantilever and the drop was established, the thermal vibrations of the drop drove the cantilever to deflect. The vertical deflection of the cantilever, due to these oscillations, was acquired by an A/D acquisition board (PCI-4462, National Instruments, USA). From the measured time-dependent cantilever deflection signal the PSD of the AFM cantilever vibrations was calculated.

III. RESULTS AND DISCUSSION

Figure 2 shows an example of the PSD of the RTCF of the interface measured with a solution of the PAM polymer at concentration of 400 ppm. We observe up to twelve well-defined resonance peaks corresponding to the resonance modes of the thermal fluctuations of the drop interface. Each peak was fitted separately using the PSD of the harmonic oscillator:

$$S(\omega) = \frac{k_B T}{\pi m_n} \frac{4\beta_n}{(\omega^2 - \omega_n^2)^2 + 4\beta_n^2 \omega^2} \quad (1)$$

where $k_B T$ is the thermal energy, m_n is the effective mass, β_n the damping coefficient, ω_n the resonance frequency, and n is the mode number [21].

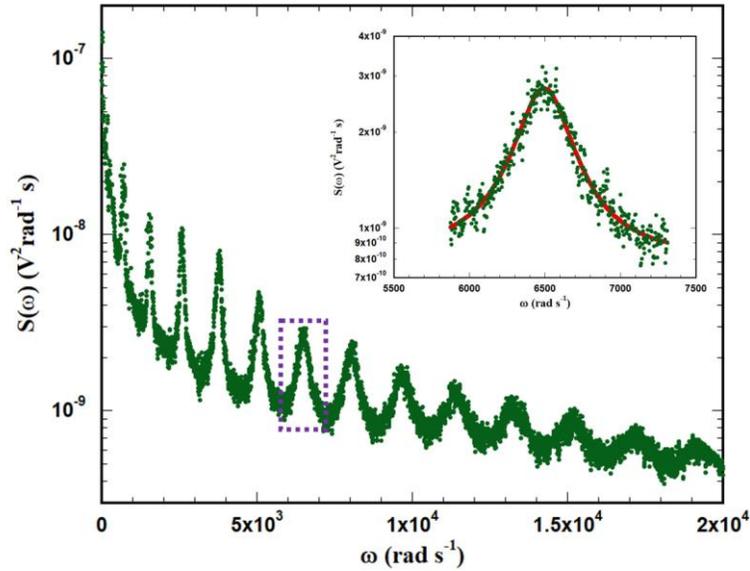


Figure 2: Example of the PSD of the RTCF of the drop surface measured with a solution of the PAM polymer at a concentration of 400 ppm. The insert shows a zoom of the marked region, the sixth peak and the fitting curve (solid line) using Eq. (1).

Figure 3(a) shows the effect of the polymer concentration on the resonance frequency which turns out to be small in accordance with what we can expect since the polymer action on the surface tension is minor as shown in the inset (surface tension versus the concentration of the polymer). Figure 3(b) shows the damping versus frequency for pure water and three different concentrations of the PAM solutions. We clearly observe that as the concentration increases the damping increases. This damping is also sensitive to the polymer concentration.

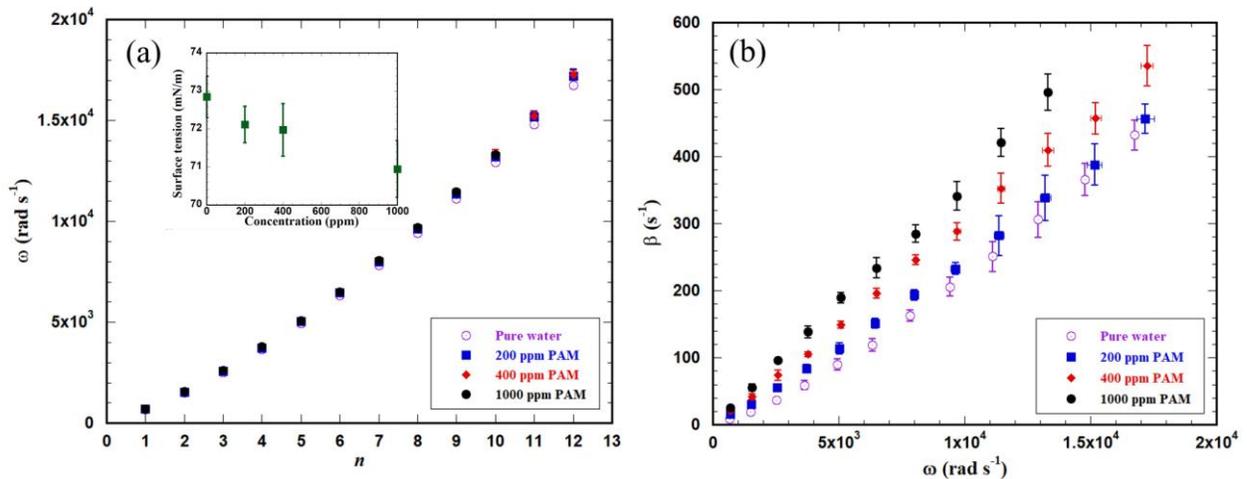


Figure 3: Experimental data being measured in pure water and polymer solutions at concentrations of 200 ppm, 400 ppm and 1000 ppm. (a) Measured resonance angular frequency versus the mode number. The insert shows the surface tension of the polymer solution for each concentration used in the experiments. (b) Damping coefficient versus the angular frequency.

The dispersion equation for capillary oscillations of an interface is given by [13-15,22-24]:

$$\omega_n^2 - \frac{\sigma k_n^3}{\rho} + 4 \frac{\eta^{*2} k_n^2}{\rho^2} m_n (k_n - m_n) = 0 \quad (2)$$

where σ is the surface tension, ρ the fluid density and η^* the fluid viscoelastic viscosity, $m_n^2 = k_n^2 + \frac{j\omega_n \rho}{\eta^*}$, j is the complex number and the wave vector $k_n = \frac{2\pi}{\lambda_n}$ associated with the wavelength λ_n .

The viscoelastic viscosity is usually frequency dependent, and it has two components ($\eta^* = \eta' + j\eta''$), the real part is the dynamic viscosity, and the imaginary part is the elastic viscosity. For inviscid liquids, the dispersion equation Eq. (2) becomes $\omega_n^2 - \frac{\sigma}{\rho} k_n^3 = 0$ and thus the frequency is given by:

$$\omega_n^0 = \sqrt{\frac{\sigma}{\rho} k_n^3} \quad (3)$$

For a viscoelastic liquid, assuming that the effect of the viscosity is a small correction, the frequency can be written as:

$$\omega_n = \omega_n^0 + \delta\omega_n \quad (4)$$

where $\delta\omega_n$ is a complex quantity where the real part $Re(\delta\omega_n)$ gives the frequency shift and the imaginary part gives the damping $\beta = -Im(\delta\omega_n)$.

Inserting Eq. (4) in Eq. (2) and keeping only low order terms, we get the expression for the frequency and damping of the fluctuations of the interface:

$$\omega_n \approx \omega_n^0 + \frac{2\eta''}{\frac{1}{\rho^{\frac{1}{3}}} \frac{2}{\sigma^{\frac{2}{3}}}} \omega_n^{\frac{4}{3}} \quad (5)$$

$$\beta_n = -Im(\delta\omega_n) \approx \frac{2\eta'}{\frac{1}{\rho^{\frac{1}{3}}}\sigma^{\frac{2}{3}}}\omega_n^{\frac{4}{3}} \quad (6)$$

In these equations the density is taken as the density of water and σ is the measured surface tension of the solution, β_n and ω_n are the measured damping and frequency values for the mode n . The unknown parameters in these equations are only the viscoelastic viscosities η' and η'' . To obtain the value of η' versus the frequency, we solve Eq. (6) for each of the set of measured values (β_n, ω_n). The value of η'' is obtained by combing the resonance frequencies measured in pure water ω_n^w and in the polymer solutions and using $\omega_n^0 = \sqrt{\frac{\sigma}{\sigma_w}}\omega_n^w$ where σ_w is the surface tension of pure water. Eq. (4) can then be rewritten as:

$$\omega_n \approx \sqrt{\frac{\sigma}{\sigma_w}}\omega_n^w + \frac{2\eta''}{\rho^{\frac{1}{3}}\sigma^{\frac{2}{3}}}\omega_n^{\frac{4}{3}} \quad (7)$$

Thus, the value of the elastic viscosity η'' is obtained from the expression:

$$\eta'' = \frac{\rho^{\frac{1}{3}}\sigma^{\frac{2}{3}}}{2\omega_n^{\frac{4}{3}}}\left(\omega_n - \sqrt{\frac{\sigma}{\sigma_w}}\omega_n^w\right) \quad (8)$$

The obtained values of the dynamic and elastic viscosity (η', η'') versus the angular frequency are shown in *Fig. 4a*. In the same figure we have also reported the values of η' and η'' measured with the cone-plate rheometer in oscillating mode. The dynamic commercial rheometer is limited to roughly 10 rad s⁻¹ while the RTCF experiment covers the angular frequency range of 20000 rad s⁻¹. To compare the dynamic viscosity obtained by the two methods with the viscosity obtained by the rheometer in constant rotation mode we use the Cox-Merz rule that stipulates:

$$|\eta^*| = \sqrt{\eta'^2 + \eta''^2} \quad (9)$$

and

$$\dot{\gamma} = \omega \quad (10)$$

where $\dot{\gamma}$ is the shear rate and ω is the angular frequency.

Figure 4(b) presents the modulus of the viscoelastic viscosity $|\eta^*| = \sqrt{\eta'^2 + \eta''^2}$ versus the angular frequency for the data obtained by the RTCF and the commercial rheometer in dynamic mode, and also the viscosity versus the shear rate obtained by the commercial rheometer in imposed shear flow mode. Our measurements using the RTCF are in good agreement with the data obtained by the commercial rheometer, and it allows to extend the range of the rheological study up to a shear rate of 20000 s^{-1} . Furthermore, our method requires only a small volume of liquid ($10 \text{ }\mu\text{L}$) to measure the viscosity and is thus suitable for the measurements on precious liquids.

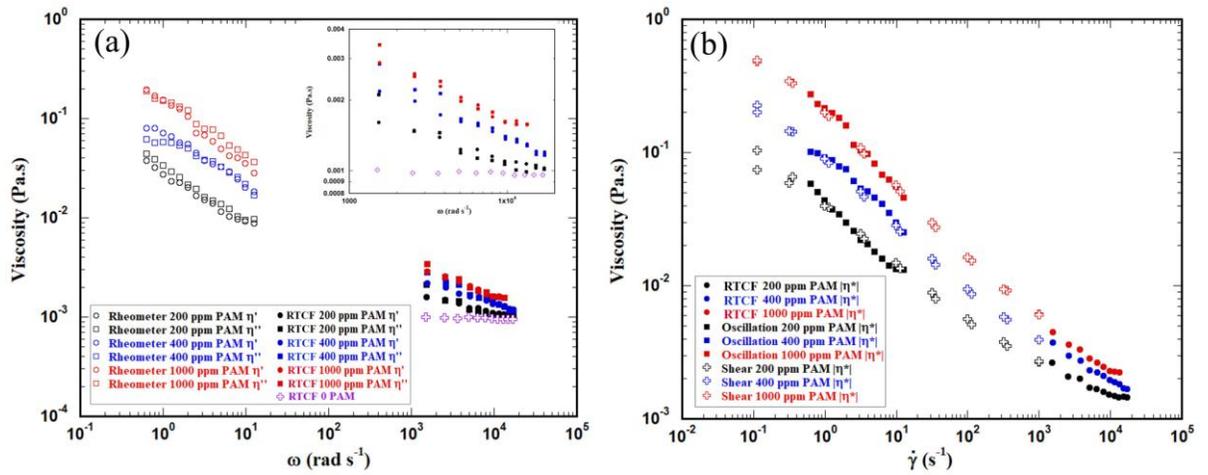


Figure 4: (a) The viscoelastic components of the viscosity η' and η'' versus the angular frequency for PAM solutions with concentrations of 200 ppm (black), 400 ppm (blue) and 1000 ppm (red) measured by the RTCF and commercial cone-plate rheometer in oscillating mode. The insert shows a zoom of the data obtained using the RTCF. (b) The modulus of the viscoelastic viscosity $|\eta^*|$ versus the angular frequency or shear rate measured by the RTCF and by the rheometer using both oscillation and shear modes.

IV. CONCLUSION

We have shown that an AFM cantilever in contact with a drop of polymer solution is a powerful tool for the measurement of the rheology of the solutions. The rheological properties of the fluids are determined by analyzing the PSD of the RTCF measured on the surface of the droplet. Our measurements are in good agreement with the results obtained using the classical

rheometer. Besides the fact that our method requires only a small volume of liquid, and it also allows to perform rheological measurements up to 20000 s^{-1} beyond the inertial limit of commercial rheometer.

ACKNOWLEDGMENTS

The authors would like to thank Zaicheng Zhang for fruitful discussions. The authors acknowledge the French National Research Agency through the supporting grant No. ANR-19-CE30-0012. Hao Zhang acknowledge the financial support by the China Scholarship Council.

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