

Oscillating Ferrofluid Droplet Microrheology of Liquid-Immersed Sessile Droplets

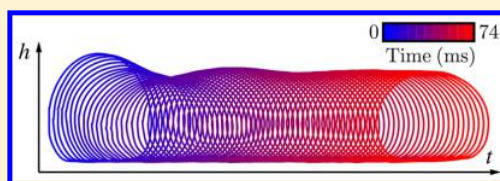
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Supporting Information

ABSTRACT: The damped oscillations of liquid-immersed ferrofluid sessile droplets were studied with high-speed imaging experiments and analytical modeling to develop a novel microrheology technique. Droplet oscillations were induced with an external magnetic field, thereby avoiding transients in the resulting vibrational response of the droplet. By following the droplet relaxation with a high-speed camera, the frequency and relaxation time of the damped harmonic oscillations were measured. We extend upon existing analytical theories to describe our liquid-immersed sessile droplet system, and directly quantify the droplet relaxation with the viscosity of the internal and external fluid as well as the interfacial tension between these. The easily controllable magnetic droplets make our oscillating ferrofluid droplet technique a potential candidate for high-throughput microrheology and tensiometry in the future.



INTRODUCTION

Measuring the rheological properties of tiny liquid samples is essential in, for example, biological systems, where the available sample volumes are on the microliter scale. Beautiful examples include probing protein unfolding,¹ DNA solutions,² and neonate blood samples.³ Conventional rheological tools, however, typically require sample sizes greater than several milliliters.⁴ To solve this problem, different microrheological approaches have been introduced,^{4–7} where the motion of colloidal particles inserted into the fluid sample is analyzed for information about the fluid viscosity. Also, various microfluidic approaches^{8–10} as well as nanorheological capillary leveling techniques^{11–13} have recently been developed to explore the possibilities of performing rheology with tiny liquid samples. The focus of this article is on the oscillating droplet microrheological technique, where the oscillation frequency and damping rate of a freely vibrating droplet are analyzed to give information about its surface tension and viscosity. Originally, the theoretical treatment of the system, assuming a levitating droplet, was provided by Lord Rayleigh¹⁴ and developed further by Chandrasekhar.¹⁵ Many levitating droplet studies have been performed to verify and further develop the technique,^{16–18} and the theory has been extended to also apply to the more practical pendant^{19,20} and sessile^{21–28} droplet geometries in air. The oscillating droplet technique provides a cheap, practical, and simple alternative to other microrheological tools.²⁸

All of the above-mentioned studies have focused on liquid droplets in air. However, in many biological systems, such as high-throughput cell screening experiments,²⁹ cell culture bioreactors,³⁰ and protein crystallization studies,³¹ there is often a need to prevent droplet evaporation during long

experiments. This can be done by immersing the droplets in another fluid. Furthermore, in many interfacial tension studies, a liquid–liquid system would be of greater interest than the liquid–air alternative. The theoretical treatment by Lamb³² describes the vibrations of a levitating, inviscid droplet oscillating in an inviscid fluid, resulting in a solution very similar to that in the liquid–air model. For viscous droplets immersed in a viscous fluid, the bulk damping of the inner and outer fluids as well as the boundary layer damping at the liquid–liquid interface need to be included.³³ Theoretical work relating the droplet relaxation time and oscillation frequency to the physical properties (droplet radius, interfacial tension, and fluid viscosities and densities) of a levitating low-viscosity droplet oscillating in a low-viscosity fluid has been developed by Miller and Scriven³³ and later refined by Marston³⁴ and Prosperetti³⁵ independently. Experimental work has partially confirmed the refined theory³⁶ but has also shed light on the limitations of the analytical model,^{37,38} which breaks down especially for smaller droplets and fluids with large viscosity differences. Using an exact numerical solution, Basaran et al. explained the observed discrepancies between the analytical model and experiments by finite-amplitude oscillations, gradients in the interfacial tension, and variations of physical properties other than the interfacial tension.³⁸ From a practical point of view, developing a rheological technique requiring levitating droplets is not ideal because the necessary levitation technologies, such as the elegant acoustic¹⁷ or electromagnetic¹⁸ approaches, overly complicate the experimental

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setup.²² To the best of our knowledge, no work has been done on the oscillations of substrate-supported droplets immersed in another fluid, although such a system has great potential for an actual technique.

Here, we investigate the low-amplitude oscillations of low-viscosity sessile droplets immersed in low-viscosity liquids. We introduce a novel way to create droplet vibrations by using a ferrofluid as the inner (droplet) phase. The droplets can thus easily be elongated by an external magnetic field in a well-controlled manner, and by quickly turning off the field, the droplets will perform damped harmonic oscillations back to their original equilibrium shapes. We follow the droplet oscillations with a high-speed camera and measure the oscillation frequency and relaxation time of the droplets. By not applying any mechanical impulses to the system to induce droplet vibrations, we avoid problematic transients in the vibrational response of the droplet, where a signature of the mechanical disturbance would be mixed with the actual relaxation signal of the droplet. Furthermore, by locally affecting only the fluid of the droplet, no additional flow patterns are created in the external fluid during the droplet elongation. The initial droplet elongation (oscillation amplitude) can easily be controlled by tuning the external magnetic field strength or the saturation magnetization (concentration) of the ferrofluid. In this work, we expand upon existing theoretical models to describe our liquid-immersed sessile droplet system. We investigate the effect of the surrounding fluid viscosity on the oscillations of ferrofluid droplets with different sizes and find that our oscillating ferrofluid droplet technique is well suited for probing the viscosity of either the ferrofluid or the fluid surrounding the droplet.

EXPERIMENT

Oscillating Ferrofluid Droplet Microrheology Setup. A schematic illustration of the experimental setup is shown in Figure 1a. A polystyrene (PS) box ($25 \times 25 \times 16 \text{ mm}^3$) was used as a chamber. The box had a flat, smooth bottom and flat, transparent side walls, allowing for high-quality optical imaging. For the droplet oscillation experiment, the chamber was first filled with silicone oil (Sigma-Aldrich). In this work, we investigated the effect of three different kinematic viscosities of the surrounding oil phase (5, 20, and 50 cSt, as given by Sigma). An aqueous ferrofluid droplet with a volume in the range of $0.3\text{--}5 \mu\text{L}$ was pipetted into the oil-filled chamber, where it was completely immersed in the oil. The droplet was placed far enough from the chamber walls (at a distance on the order of 10 droplet radii from the side walls) to avoid damping from these. When using PS as the chamber material, a lubricating oil film was found to be stable between the ferrofluid droplet and the plastic substrate. The droplet thus did not wet the plastic, and a high contact angle ($\theta \approx 140^\circ$) could be achieved. Also, poly(methyl methacrylate) was tested (not shown here), but in this case, no lubricating oil layer was present and the resulting contact angle was less than 90° .

The chamber was placed on top of a pull solenoid (G-1250, 24VDC, SP-elektronikka), which was connected to a power supply (Mastech Single-Output dc power supply HY3005D, 31 V/1.6 A). The maximum magnetic field strength, measured in the center of the coil at the surface of the coil, was $13.1 \pm 0.2 \text{ mT}$. At a 2 mm distance above the coil, where the droplets were located, the field strength was $9.8 \pm 0.2 \text{ mT}$. To elongate the droplets in only the vertical direction and not tilted to one side, a single droplet was placed above the center of the solenoid, where the magnetic field was vertical. To quickly turn off the magnetic field, a switch was installed in series with the power supply, the coil, and a resistor ($3.28 \pm 0.01 \text{ k}\Omega$), which was connected in series to the power supply and in parallel to the coil. Using an oscilloscope (SO-X 2004A, InfiniiVision), the relaxation time of the electric current flowing in the circuit after the switch was turned off

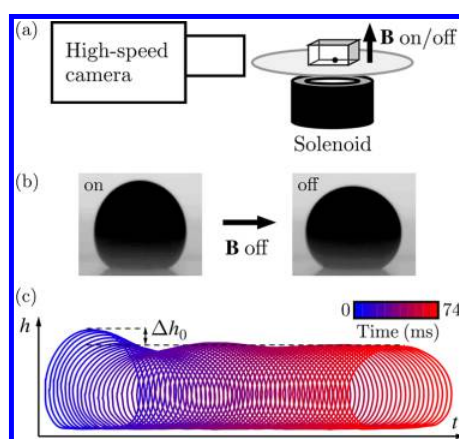


Figure 1. (a) Schematic illustration of the oscillating ferrofluid droplet microrheology setup. A ferrofluid droplet is immersed in oil in a polystyrene box, which is placed on top of a solenoid. The droplet is monitored from the side with a high-speed camera. (b) Examples of optical images from the experiment (droplet radius $R = 860 \pm 20 \mu\text{m}$). By turning on the magnetic field, the droplet is slightly elongated (left), after which the field is quickly turned off. By following the droplet oscillations as it relaxes back to equilibrium (right), information about the fluid viscosities of the system can be gained. (c) The height (h) oscillations of an $R = 1040 \pm 20 \mu\text{m}$ droplet as a function of time, where the droplet outline (as seen from the side) has been manually shifted to the right for each frame (0.11 ms time steps) to better visualize the oscillation. The initial elongation of the droplet is defined as Δh_0 and is $330 \mu\text{m}$ in this example, where a very large relative initial elongation ($\Delta h_0/2R = 0.16$) was used to better highlight the oscillations. The relative initial elongations used in the actual experiments were much smaller than this (on the order of $\Delta h_0/2R = 0.06$), as shown in (b).

was determined to be $3 \mu\text{s}$. Because the typical viscous relaxation times of the ferrofluid droplets were on the order of milliseconds, the zeroing of the magnetic field was deemed fast enough for our system.

The droplet oscillations were followed using a Phantom V1610 high-speed camera at a frame rate of 10 000–30 000 fps. A macro lens (Canon MP-E 65 mm f/2.8 1–5 \times Macro Photo) was used at its highest magnification ($\sim 5.6 \mu\text{m}/\text{pixel}$) to maximize the spatial resolution. (See examples of optical images in Figure 1b.) The experimental results were analyzed using Matlab, where the droplet size was determined and the droplet height change was monitored as a function of time. The contact angle was found to be constant at $\theta = (140 \pm 5)^\circ$ for all droplet sizes and oil viscosities used in this work. (See the Supporting Information for more details.) In Figure 1c, the time-resolved droplet relaxation is visualized by showing the outline of the droplet as a function of time during a typical droplet oscillation experiment.

Ferrofluid Synthesis and Properties. To synthesize the aqueous ferrofluid, iron oxide nanocrystals were produced using the coprecipitation method³⁹ and stabilized with citric acid near pH 7 in water.^{40,41} The final density of the ferrofluid was $\rho_{\text{FF}} = 1824 \pm 1 \text{ kg}/\text{m}^3$, and its volumetric iron oxide nanocrystal concentration was around 20%. The ferrofluid was characterized in the liquid state with a vibrating sample magnetometer (Physical Property Measurement System Dynacool, Quantum Design) equipped with a 9 T magnet. The ferrofluid showed saturation magnetization of $70.7 \pm 0.5 \text{ kA}/\text{m}$ with no magnetic hysteresis, as expected for superparamagnetic nanoparticles. The average particle diameter $d = 5.9 \pm 2.8 \text{ nm}$ was measured from transmission electron micrographs taken with an FEI Tecnai 12 Bio Twin TEM using 120 kV voltage.

Many studies have investigated the effect of an external magnetic field on the rheological properties of various ferrofluids.^{42,43} However, because the total magnetic relaxation time^{44,45} of our ferrofluid is

much shorter than the viscous relaxation times of our droplets, the ferrofluid will be assumed to behave as a nonmagnetic, isotropic Newtonian fluid after the external field has been turned off and the droplet has started to oscillate.

Parallel Plate Rheology. Conventional plate-on-plate rheology (Physica MCR 300, Anton Paar) was performed at 22 °C. The rheometer was equipped with a Peltier element to ensure that the temperature was controlled as accurately as possible. An aluminum plate (25 mm in diameter) with 1 mm spacing from the stainless steel base was used. When measuring the viscosity of the ferrofluid, care was taken to perform the measurements quickly to avoid drying of the fluid, which would otherwise lead to an increase in the viscosity. No external magnetic field from the equipment could be detected. A steady-shear test was performed at shear rates between 10 and 100 s⁻¹. (See the Supporting Information for more details.) These shear rates cover the frequency range used in our oscillation droplet experiments. The dynamic viscosity of our ferrofluid was determined to be $\eta_{\text{FF}} = 21.5 \pm 0.4$ mPa·s.

The dynamic viscosities of the 5, 20, and 50 cSt silicone oils (Sigma-Aldrich, kinematic viscosities given by the company) were measured at 22 °C in the same way as described above and were determined to be $\eta_{0,5} = 5.2 \pm 0.4$ mPa·s, $\eta_{0,20} = 23.5 \pm 1.6$ mPa·s, and $\eta_{0,50} = 56 \pm 0.3$ mPa·s, respectively (See the Supporting Information for more details.) The oil densities were measured to be $\rho_{0,5} = 910.1 \pm 0.6$ kg/m³, $\rho_{0,20} = 947.1 \pm 0.7$ kg/m³, and $\rho_{0,50} = 957.9 \pm 0.1$ kg/m³, respectively.

Pendant Droplet Tensiometry. The interfacial tensions between the ferrofluid and the 5, 20, and 50 cSt silicone oils were determined to be $\sigma_5 = 36.7 \pm 0.3$ mN/m, $\sigma_{20} = 35.9 \pm 0.3$ mN/m, and $\sigma_{50} = 36.9 \pm 0.4$ mN/m, respectively, using the pendant drop method (Attension Theta optical tensiometer; see the Supporting Information for more details).

THEORY

To describe our system theoretically, the droplet oscillations were quantified by the change in droplet height (Δh) as a function of time and modeled as a damped harmonic oscillation

$$\Delta h(t) = A \exp\left(-\frac{t}{\tau}\right) \cos(2\pi ft + \phi) \quad (1)$$

where A is the amplitude, τ is the relaxation time, f is the oscillation frequency, and ϕ is the phase shift. For all of the models presented in this article to be valid, the initial droplet elongation ($A \approx \Delta h_0$, as defined in Figure 1c) needs to be sufficiently small as compared to the droplet size.³³ In Figure 2a, the relative initial droplet elongation ($\Delta h_0/2R$) is plotted as a function of droplet radius (R) for all experiments performed in this work. Because the relative initial droplet elongation was $\Delta h_0/2R \approx 0.04\text{--}0.07 < 0.1$, the following droplet vibrations were classified as small-amplitude oscillations, as demanded for the theory to remain linear.

As illustrated schematically in the inset of Figure 2a, our system consists of a droplet of radius R , dynamic viscosity η_i , and density ρ_i , fully immersed in an immiscible fluid of viscosity η_o and density ρ_o . The density difference and interfacial tension between the two fluids are denoted as $\Delta\rho = \rho_i - \rho_o > 0$ and σ , respectively, and the contact angle at the three-phase contact line is θ . All fluids in our system are considered incompressible and Newtonian, and only droplets with radii less than the capillary length ($R < l_c = \sqrt{\sigma/g\Delta\rho} \approx 2$ mm) will be considered to avoid the effect of gravity. Below, we will first briefly review the existing theoretical oscillating droplet models for a levitating droplet in a surrounding fluid as well as a sessile droplet in air. We will then combine these two systems in order to introduce our own model for a low-viscosity sessile droplet oscillating in a low-viscosity fluid.

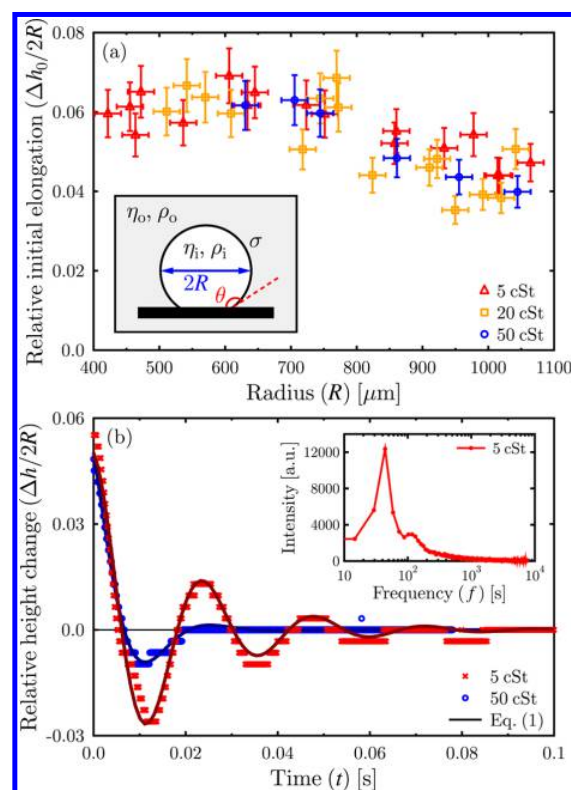


Figure 2. (a) Relative initial elongation (initial height change normalized by the droplet diameter) as a function of droplet radius for ferrofluid droplets in three different viscosity silicone oils. The initial height change Δh_0 is defined in Figure 1c. All droplets have been elongated by a vertical external magnetic field of 9.8 ± 0.2 mT. The inset shows the variables of our liquid-immersed, sessile droplet system. (b) Relative height change as a function of time for similarly sized ferrofluid droplets ($R = 860 \pm 20$ μm) oscillating in 5 and 50 cSt silicone oil. The oscillations are highly underdamped in the low-viscosity medium, whereas the higher-viscosity oil damps the droplet motion more strongly. The solid lines are harmonic oscillation fits to eq 1 to the data. The inset shows an FFT of the 5 cSt data, with a clear main peak corresponding to the $l = 2$ vibrational mode and a small shoulder that could be the signature of the $l = 3$ vibrational mode.

For the case of a levitating, inviscid droplet oscillating in an inviscid fluid, Lamb³² has derived an expression for the angular oscillation frequency

$$\omega_L = 2\pi f_L = \left[\frac{\sigma l(l+1)(l-1)(l+2)}{R^3 \Gamma} \right]^{1/2} \quad (2)$$

where $\Gamma = \rho_o l + \rho_i(l+1)$ and l is an integer corresponding to the vibrational mode number ($l = 2, 3, \dots$). Miller and Scriven³³ extended upon this work to also take into account the case of fluids with what they call low viscosities, and they derived a nonlinear dispersion relation, giving

$$\omega_\eta = 2\pi f_\eta = \omega_L - \frac{1}{2} \kappa \sqrt{\omega_L} \quad (3)$$

where

$$\kappa = \frac{(2l+1)^2 (\eta_i \eta_o \rho_i \rho_o)^{1/2}}{\sqrt{2} R \Gamma [(\eta_i \rho_i)^{1/2} + (\eta_o \rho_o)^{1/2}]} \quad (4)$$

Miller and Scriven also formulated a model for the damping rate in such a low-viscosity system. Marston³⁴ and Prosperetti³⁵ later independently corrected the prediction by Miller and Scriven. The final theoretical model for the relaxation time of a levitated, low-viscosity droplet oscillating in a low-viscosity fluid is

$$\tau_{\eta}^{-1} = \frac{1}{2}\kappa\sqrt{\omega_L} + \frac{1}{2}\gamma - \frac{1}{2}\kappa^2 \quad (5)$$

where

$$\gamma = \frac{(2l+1)[2(l^2-1)\eta_i^2\rho_i + 2l(l+2)\eta_o^2\rho_o + \eta_o\eta_i(\rho_i(l+2) - \rho_o(l-1))]}{R^2\Gamma[(\eta_i\rho_i)^{1/2} + (\eta_o\rho_o)^{1/2}]^2} \quad (6)$$

The first term on the right-hand side of eq 5 represents the damping in the boundary layer on either side of the liquid–liquid interface, whereas the second term can be described as the bulk damping in both of the fluids far away from the liquid–liquid interface.³³ The third term was omitted by Miller and Scriven, but because both Marston and Prosperetti independently determined the magnitude of κ^2 to be similar to that of γ , the κ^2 term was retained in the final solution.^{34,35}

The validity of eq 5 has been experimentally verified by Trinh et al.³⁶ for the case of small-amplitude oscillations of levitated droplets. In our experimental system, however, the droplets are not freely levitating but rest on a nonwetting substrate. Extensive work has been performed by others for the case of oscillating sessile droplets in air.^{21,23–28} Noblin et al.²¹ approached the sessile droplet system by first deriving the frequency of capillary waves on the surface of a liquid with a finite depth (as described in Landau and Lifshitz⁴⁶). They then made the assumption that, under the conditions of resonant vibrations, the droplet profile length (L) will contain a half-integer number of wavelengths (λ) so that $L = 2R\theta = l\lambda/2$, where θ is the contact angle (CA) in radians ($\theta = \pi\theta_m/180$, where θ_m is the CA measured in degrees). This approach gives an expression for the oscillation frequency of oscillating sessile droplets in air

$$f_{CA} = \alpha\sqrt{\frac{\pi\sigma l^3}{32\Delta\rho R^3\theta^3}} \quad (7)$$

where α is a constant needed to correct for the simplifying assumptions made in the derivation of the model. Sharp et al.²⁵ have experimentally determined $\alpha \approx 0.81$ for sessile droplets with different contact angles in air.

To the best of our knowledge, no theory exists for low-viscosity sessile droplets vibrating in a low-viscosity fluid. To include the effects of both the surrounding fluid and the substrate on the oscillation frequency of the droplets in our system, we will make the first-order assumption that the surrounding fluid influences a sessile droplet in the same manner as if it were levitating. We thus combine eqs 3 and 7 in the following way

$$f_{CA,\eta} = f_{CA} - \frac{1}{4\pi}\kappa\sqrt{2\pi f_{CA}} \quad (8)$$

This equation is simply the Miller and Scriven correction (eq 3) to the Lamb frequency, but where the Lamb frequency (derived for levitating inviscid droplets in inviscid fluids) has been substituted by the contact-angle-dependent frequency (derived for sessile droplets in air). Similarly, we will make the

same frequency substitution in eq 5 to make an estimate of the relaxation time in our system

$$\tau_{CA,\eta}^{-1} = \frac{1}{2}\kappa\sqrt{2\pi f_{CA}} + \frac{1}{2}\gamma - \frac{1}{2}\kappa^2 \quad (9)$$

In the following section, we will study how these theoretical models capture the data from our oscillating ferrofluid droplet experiments.

RESULTS AND DISCUSSION

Experiments were performed with droplets of the same ferrofluid in silicone oils with three different viscosities. The fluid viscosities, densities, and interfacial tensions were measured as described in the Experiment section above. Droplets of different sizes (all much smaller than the capillary length $R < l_c \approx 2$ mm) were used. In Figure 2b, the normalized height change is plotted as a function of time for two similarly sized droplets in 5 and 50 cSt silicone oil. (See Supporting Information Movies SM1.avi and SM2.avi for movies from these experiments.) As expected, the higher-viscosity oil causes a more strongly damped droplet oscillation. Both data sets are successfully modeled as underdamped harmonic oscillators, as shown by the solid lines that are fits of eq 1 to the data. The fits were made with the amplitude, relaxation time, frequency, and phase shift as free-fitting parameters. An interesting feature for large droplets in the 5 cSt oil can be seen in the raw data right before the first dip ($t \approx 0.007$ s), where a small shoulder appears. We believe that this shoulder is caused by fluid waves being reflected upward by the substrate. These reflected, up-going waves then interfere with the down-going bulk motion of the rest of the droplet fluid (Supporting Information Movie SM1.avi), causing the shoulder in the height-change data. This kind of shoulder was not detectable in any of the more viscous oils.

In the inset of Figure 2b, a fast Fourier transform (FFT) of the 5 cSt data of the main graph is shown. One clear, main peak occurs, within error, at the same frequency as derived using the harmonic oscillation fit to the raw oscillation data. This peak corresponds to the $l = 2$ vibrational mode of the droplet. A small shoulder can also be seen in the FFT at a frequency 2–3 times higher than that of the main peak. We believe that this is a sign of the $l = 3$ vibrational mode, which is expected to arise at lower viscosities and larger droplet sizes.²⁴ The intensity of the second peak decreases as a function of decreasing droplet size (not shown here) and is not detectable for any of the higher oil viscosities used in this work. Because of the indistinctness of the second peak, we will not include it in any further analysis.

In Figure 3a, the droplet oscillation frequency is plotted as a function of droplet radius for the 5 cSt case. The frequency decreases strongly with increasing droplet size and spans the range between 100 and 30 Hz. The analytical predictions of Lamb (eq 2) as well as Miller and Scriven (eq 3) are plotted as solid and dashed blue lines, respectively. Both of these levitating droplet models overpredict the oscillation frequency by almost a factor of 2, indicating the importance of the substrate in our sessile droplet system. Our new model (eq 8, containing no free parameters) is shown by the solid red line in Figure 3a. The theory is in excellent agreement with the experimental data for droplets larger than $R > 600$ μm but deviates slightly from the data as the droplets become smaller. Similar findings have been reported for levitating droplets,^{33,38} where the theories have been shown to break down for smaller droplets. The discrepancy between theory and experiments could also be

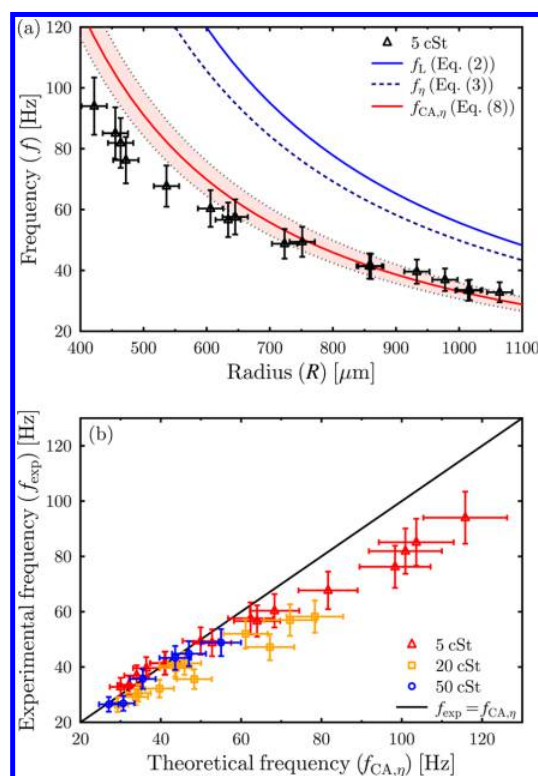


Figure 3. (a) Experimental oscillation frequency of ferrofluid sessile droplets in 5 cSt silicone oil as a function of droplet radius. The blue lines show the theoretical predictions of Lamb (eq 2, solid line) and Miller and Scriven (eq 3, dashed line), derived for levitating droplets. The solid red line shows the prediction of our analytical liquid-immersed sessile droplet model (eq 8). The shaded area shows the uncertainty in our model, as calculated from the propagation of error of all variables (R , θ , σ , ρ_p , ρ_w , η_p , η_w). (b) Experimental oscillation frequency of differently sized ferrofluid droplets in three different viscosity oils plotted as a function of our theoretical prediction for low-viscosity sessile droplets in low-viscosity fluids (eq 8). The solid black line has a slope of unity and denotes perfect agreement between experiments and theory.

due to the damping from the solid substrate, which was evident in the raw oscillation data (Figure 2b). No solid–liquid interactions are taken into account in our current model, and a more advanced theoretical treatment would thus be required to fully capture the complete physics behind our system. In Figure 3b, the experimental oscillation frequency measured in all of the viscosities studied in this work is plotted as a function of the prediction of our new theoretical model (eq 8). The solid black line in the graph denotes the perfect agreement between theory and experiments. The theory is in excellent agreement with the 50 cSt data, whereas it slightly overpredicts the frequency for the 20 cSt case.

In Figure 4, the experimentally measured relaxation time is plotted as a function of our theoretical model of eq 9 for all experiments performed in this work. The solid line has a slope of unity and denotes perfect agreement between theory and experiments. For the 20 cSt silicone oil, the experimental relaxation times are in excellent agreement with our new theoretical model. For the 5 and 50 cSt silicone oils, however, the data deviates from the theoretical model by factors of 1.2 ± 0.1 and 1.3 ± 0.15 , respectively. The 20 cSt oil viscosity was

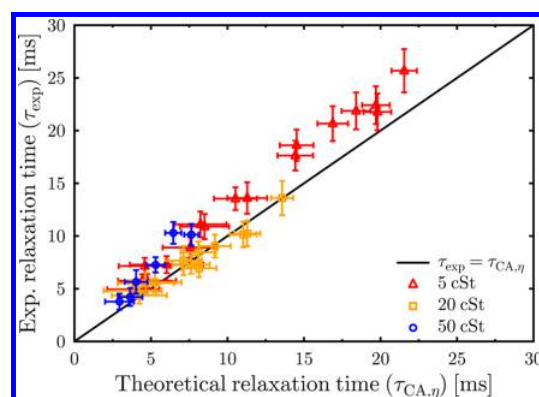


Figure 4. Experimental relaxation time of differently sized ferrofluid droplets in three different viscosity oils plotted as a function of our theoretical prediction for low-viscosity sessile droplets in low-viscosity fluids (eq 9). The solid black line has a slope of unity and denotes perfect agreement between experiments and theory.

very close to that of the ferrofluid ($\eta_{FF}/\eta_{o,20} = 0.91 \pm 0.06$), and these findings are also in agreement with the simulation results of Basaran et al.,³⁸ where existing levitating droplet theories were shown to work best for fluids with similar viscosities. Another factor that could influence the results is a possible residual structure still present in the ferrofluid at the beginning of the experiment, when the nanoparticles might not have fully relaxed to their isotropic and nonmagnetic final state. In such a case, a slightly longer experimental relaxation would be expected because the magnetic relaxation time of the ferrofluid would contribute to the total relaxation time that we measure. As was the case for the oscillation frequency, the effect of the substrate could also contribute to the measured relaxation times. Test experiments performed in a 100 cSt silicone oil (results not included here) showed a very strong disagreement between theory and experiments, indicating the upper viscosity limit of the low-viscosity theory.

In summary, the oscillating ferrofluid droplet technique is a potential candidate for determining the viscosity of either the ferrofluid or the surrounding fluid or, alternatively, even the interfacial tension between these. On the experimental side, the technique can be used with droplet volumes down to $0.3 \mu\text{L}$, where the limiting factor is the temporal and spatial resolution needed to accurately detect the small-amplitude oscillations of the droplets. In our experiments, we were limited by the magnification of the camera. Some improvements could be made by, for example, using an optical microscope or by using the experimental approach by Sharp et al., where the refraction of a laser beam through a droplet was used to detect its oscillations.²³ By using an array of several tiny droplets in a uniform magnetic field, high-throughput measurements of the droplet viscosities could be performed in parallel. The viscosity measurement of the external liquid surely has a wider range of practical, including biological, applications than measuring the properties of a ferrofluid. The ferrofluid droplet would then be used as a viscosity probe. A sample volume as small as $\sim 100 \mu\text{L}$ of the surrounding fluid would be possible in a small-enough chamber (with side lengths shorter than $\sim 5 \text{ mm}$) and by using small-enough droplets ($R \approx 0.5 \text{ mm}$). Here, either aqueous or oil-based ferrofluids could be used, allowing for the viscosity measurements of both oil-based and aqueous liquid samples. Similar to the ferrofluid viscosity measurements, an array of

several tiny chambers with different fluid samples could be probed simultaneously, providing a novel high-throughput technique.

CONCLUSIONS

Here we present an oscillating droplet microrheology technique using liquid-immersed ferrofluid sessile droplets. The magnetic droplets were slightly elongated with an external magnetic field, and by quickly turning off the field, the droplets were left to relax back to their equilibrium shapes. The subsequent underdamped harmonic droplet oscillations were followed using a high-speed camera, and the relaxation times and frequencies of the oscillations were determined. By inducing the droplet oscillations in a nonmechanical way, the creation of transients in the vibrational response of the droplet was avoided. Experiments were performed with differently sized ferrofluid droplets oscillating in silicone oils with three different viscosities. We have extended upon existing analytical oscillating droplet theories to model the contributions of both the substrate and the surrounding fluid on the oscillations of the droplets in our system. Our new theoretical model was shown to be well suited to describe both the relaxation times and frequencies of the low-viscosity sessile droplets oscillating in a low-viscosity fluid.

Our oscillating ferrofluid droplet microrheology technique provides a potential candidate for viscosity measurements of either ferrofluid droplets or the fluid surrounding them or, alternatively, even the interfacial tension between these. As a future avenue, our technique has the potential to be extended to perform parallel high-throughput microrheology and tensiometry measurements by using an array of many tiny droplets and/or chambers. Such simultaneous measurements could, for example, probe the viscosity or interfacial tension change caused by a chemical reaction, thereby providing an interesting screening tool for different biological systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b01327.

Contact angle measurements, parallel plate rheology of the ferrofluid and silicone oils, pendant drop measurements (PDF)

Movie of a droplet oscillating in 5 cSt silicone oil (AVI)

Movie of a droplet oscillating in 50 cSt silicone oil (AVI)

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The authors declare no competing financial interest.

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made use of the Aalto University Nanomicroscopy Center premises.

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