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Rheological Properties of Viscoelastic Drops on Superamphiphobic Substrates

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Abstract

The rheological properties of microlitre sized drops of polymer solutions were investigated using measurements of their mechanical vibrational response. Drops were suspended on superamphiphobic substrates and vibrated by the application of a short mechanical impulse. Surface vibrations were monitored by refracting laser light through the drops and focussing the refracted light on to the surface of a photodiode. Time dependent variations in the photodiode output were Fourier transformed to obtain the frequency and spectral width of the mechanical resonances of the drops. These quantities were related to the frequency dependent shear storage and loss moduli (G' and G" respectively) using a simple theoretical model. The resulting rheological properties were found to be in agreement with microrheology measurements of the same solutions. Drop vibration therefore provides a fast and accurate method of quantifying the rheological properties of single drops.

Introduction

Mechanical vibrations of viscoelastic drops hold significant potential as a method of determining the frequency dependent flow (or rheological) behaviour of microlitre volumes of non-Newtonian fluids such as polymer solutions. High molecular weight polymer and biopolymer additives have a dramatic effect on the surface and rheological properties of small liquid drops. These properties influence phenomena such as the wetting, spreading and dewetting behaviour of the fluids.[1–4] The surface and rheological properties of drops also significantly influence their performance in applications such as drop atomisation, ink jet printing, fuel injection,[5] microscale mixing/demixing,[6,7] and during drop impact and rebound phenomena.[4,8] Viscoelastic properties can also be used to understand the dynamics of atomic nuclear vibrations,[9] crustal deformation of planets[10,11] and energy relaxation mechanisms in neutron stars.[12]

Drop vibration has already been demonstrated as a viable approach to the measurement of simple liquid properties such as surface tension and viscosity in levitated,[13–15] sessile[16–18] and pendant[19,20] geometries. Theories have been developed to relate the frequencies and spectral widths (full width at half maximum, hereafter referred to as the width) of vibrational peaks to these quantities.[6,16,18,21–23] This method is not only fast when compared to other methods, such as the drop volume technique,[24] but allows the use of significantly smaller volumes of material.

Measurements of the frequency and width of mechanical vibrational peaks are also capable of providing information about the frequency dependent shear storage and loss moduli (G' and G" respectively) of viscoelastic solutions such as polymer, biopolymer and protein solutions. If the vibrating drop is considered as a damped harmonic oscillator, then the frequency of vibration should be related to its effective spring constant and hence the storage modulus and surface tension of the material. At the same time, the width of the resonance provides information about viscous damping in the drop which is determined by the loss modulus. Moreover, the existence of multiple peaks in the vibrational spectrum of drops with low damping allows a single measurement to be used to extract these properties over a range of frequencies. Varying the drop size can also be used to probe the mechanical response at different frequencies.

Previous studies have considered how the properties of viscoelastic drops can be related to their vibrational response.[25,26] These studies have largely focussed on levitated drops and on extracting properties such as the relaxation and retardation times of viscoelastic fluids. The use of these particular physical quantities is somewhat limited and whilst the technology for levitating small drops using electromagnetic[15] and acoustic[14] techniques exists, these measurements can be quite expensive and difficult to implement. A more attractive method would involve vibrating substrate supported drops and extracting frequency dependent rheological properties such as G' and G".

However, recent work on simple liquids has demonstrated that the presence of a substrate introduces additional damping mechanisms which complicate the analysis of drop vibration data.[18] One way to mitigate these effects is to use substrates on which drops will have three phase contact angles close to 180^o. This approach was used by McHale and coworkers[27] who showed that liquid marbles (droplets coated by hydrophobic particles) on non-wetting surfaces exhibited vibrational properties similar to those of levitated drops. However, the properties of these liquid marbles tend to be dominated by the hydrophobic particles and the sample volumes can be quite large. Our recent success in extracting the rheological properties of levitated viscoelastic drops[28] has motivated us to use a similar approach to McHale and coworkers in an attempt to try to extract the rheological properties of microlitre sessile viscoelastic drops supported on high contact angle surfaces. On a superamphiphobic surface water or oil drops rest on the top faces of asperities, separated from the substrate by an air cushion.[29] This greatly reduces the lateral adhesion force and the drop-solid contact area. In supporting drops on superamphiphobic substrates we hope to simplify the experimental setup being used, while retaining a similar theoretical approach to that used for levitated drops.

A key advantage of using drop vibration (rather than conventional rheometry) is that it provides access to higher frequencies for weakly viscoelastic materials. In conventional rheometry, inertial effects tend to dominate the measurements at high frequencies and it becomes difficult to extract G' and G". Although higher frequencies can be accessed using techniques such as microrheology[30] and piezorheometry,[31] the low cost, low sample volume, portability and ease of implementation of the drop vibration technique make it much more attractive.

Here we demonstrate that the frequencies and widths of the mechanical vibrations of viscoelastic drops supported on superamphiphobic substrates can be used to extract values of the frequency-dependent storage and loss moduli. This study is the first combined experimental and theoretical study of the vibration of sessile viscoelastic drops. As such, it represents a significant step forward in our understanding of the drop vibration phenomenon and our ability to measure the rheological properties in small sample volumes ($\sim \mu l$ to ml) - as is often the case with biological samples.

Experimental Section

Solutions of poly(acrylamide-co-acrylic acid) (PAA, M_w=15 MDa, Sigma, UK) were prepared in deionised water (ELGA) and made up to concentrations of 1.1, 2 and 3 wt% respectively. The overlap concentration for this polymer[32] is $\sim 0.1wt\%$ and as such all of the polymer solutions studied will contain overlapping chains. Microlitre drops of these solutions were placed individually on to superamphiphobic substrates that were prepared in a similar way to that described by Deng *et. al.*[33] Briefly, glass microscope slides were annealed in the flame of a parrafin candle until a black soot developed. The soot was then exposed to a combination of tetraethoxysilane (TEOS, Sigma-Aldrich, 98%) and ammonia vapour (VWR, 28%) for 72 hours at room temperature. The resulting substrates were then annealed at 1000 ^oC for 3 hours to calcify the soot and form a fractal-like silica network on the surface (see

Figure 1(a) and Supplementary Information Figure S1). These substrates were then exposed to a second chemical vapour deposition of the semi-flourinated silane, (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane (Sigma, 97%)[33] for 3 hours, 25 mbar at room temperature, resulting in an advancing contact angle of 180 ± 2^o, a receding angle of 166 ± 2^o and a roll-off angle of less than 2^o (Supplementary Information, Figures S1 and S2).

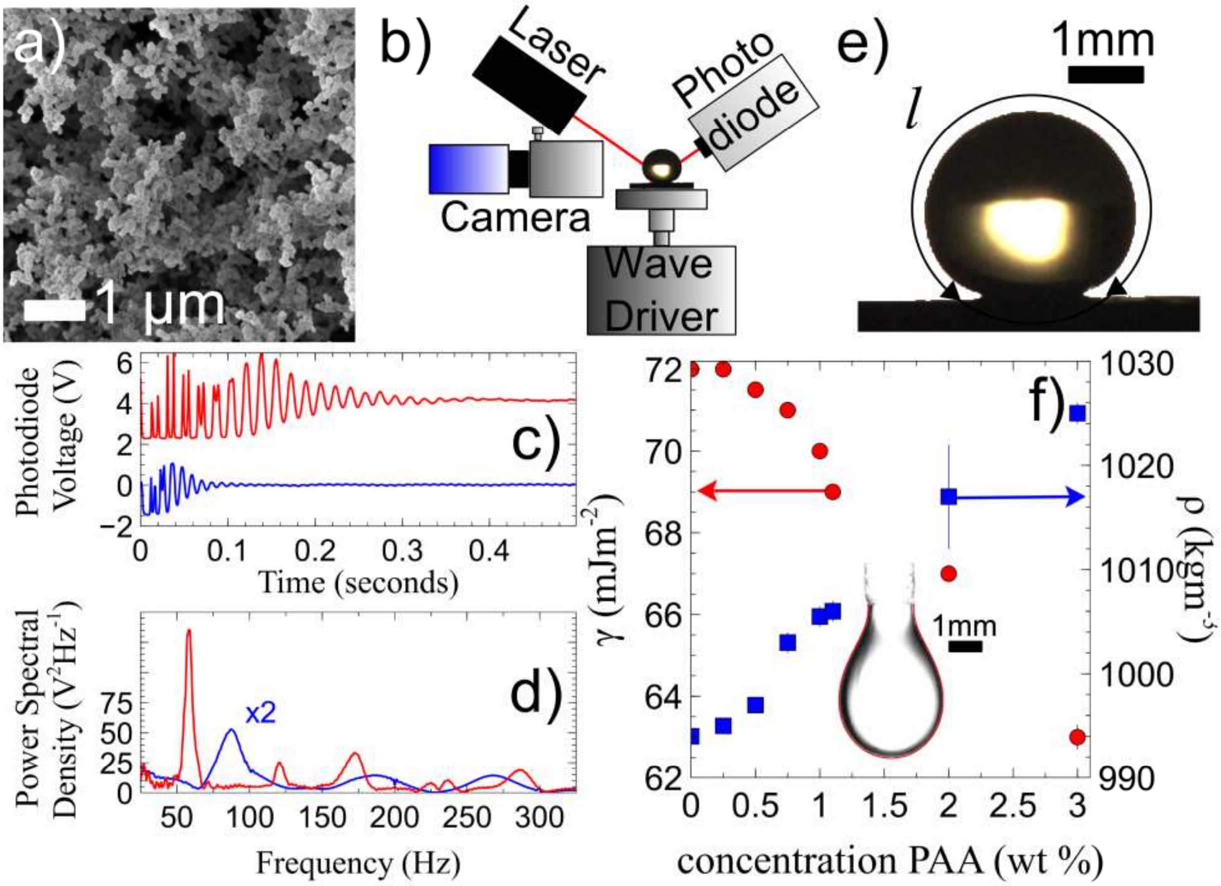

Figure 1: Vibrations of sessile viscoelastic drops on superamphiphobic surfaces. **a)** A scanning electron microscope image of the surface of a superamphiphobic substrate. **b)** A diagram of the light scattering setup. **c)** The vibrational response as measured by the photodiode for drops of 1.1wt% (top plot, red) and 2wt% (bottom plot, blue) of similar size ($l \sim 6.5mm$). **d)** The corresponding power spectra of the curves in panel c). **e)** An image of 1.1 wt% PAA drop supported on a superamphiphobic substrate with a roll off angle $< 2^o$. The definition of the drop profile length, l, is also shown. **f)** Concentration dependence of the surface tension (red circles) and density (blue squares) of the viscoelastic solutions. The inset shows an image of a pendant drop that was used to determine the surface tension of the viscoelastic fluids using axisymmetric drop analysis.[34] The line on this image is the fit obtained when extracting the surface tension.

Vibrations were excited in PAA drops supported on superamphiphobic substrates[33] (Figure 1a) by applying a short ($\sim 5ms$) mechanical impulse from below the substrate using a SF-9324 mechanical wave driver (Pasco Scientific, Figure 1(b)). As the drop vibrated, a laser beam (1mW, 633nm, Edmund Optics) was refracted through it and allowed to fall on the surface of a photodiode. Vibrations of the free surface of the drops resulted in small oscillations of the laser spot on the photodiode and gave rise to intensity variations similar to those shown in Figure 1(c). These intensity variations were recorded at a sampling rate of 1kHz over a 2-3 second period using a USB-6211 data acquisition card, connected to a computer running LabView Software (National Instruments).

At time, $t = 0$, the mechanical pulse was initiated and a rapid change was observed in the intensity measured by the photodiode (see figure 1c) as the drops started to vibrate. High frequency oscillations were observed to be damped more quickly and the droplets eventually settled down into their lowest frequency mode of vibration. Prior to $t = 0$, the intensity signals remained constant (data not shown). Fourier transformation of the entire intensity signal from $t = 0$ onwards produced a series of peaks corresponding to the mechanical vibrational spectrum of the drops (Fig 1(d)). These spectra contained peaks at different frequencies which correspond to the different modes of vibration. The resonant frequencies and widths of the different modes were found to depend on the size of the drops and their physical/mechanical properties.

An image of each drop was collected after vibration using a HC640 camera (Teledyne Dalsa). These images were used to extract the physical dimensions of the drops - in particular their profile lengths, l (Figure 1(e)). For the droplets studied here, $l \sim 2\pi R$ (i.e. the drop circumference), where R is the droplet radius. The analysis described here could therefore be performed using R or the mass of the drop as the parameter which quantifies the size of the drop.[17,18,20] However, the profile length, l, was chosen for this work because its relationship to the drop radius mentioned above only holds for contact angles close to 180^o. Use of the profile length allows for any deviations in the contact angle away from 180^o.

Measurements of the density, ρ, of the PAA solutions were obtained by weighing known volumes of the solutions. Pendant drops of the same solutions were suspended from the end of a pipette and photographs used to extract the surface tension,γ, using the axisymmetric pendant drop technique[34] (see inset, Figure 1(f)). The surface tension decreased with increasing PAA concentration while the density of the solution increased by up to 3% for the concentrations studied (Figure 1(f)).

Results and Discussion

Figure 2 shows plots of the frequency and width of the lowest vibrational peak obtained in the drop vibration experiments. These data are shown as a function of the drop profile length for PAA solutions with concentrations in the range 1.1-3 wt% , corresponding to drop volumes ranging from 1 to 20 μl. As the polymer concentration is increased, both the frequency and width of all the vibrational peaks increases. This is consistent with an increase in stiffness and a greater viscous damping in the drops with increasing polymer concentration.

In order to interpret the data shown in Figure 2 in a more quantitative manner, it is necessary to relate the frequency, f, and width, Δf, of vibrational peaks to the drop size and the frequency dependent shear and loss moduli ($G'(f)$ and $G"(f)$). A simple model of viscoelastic drop vibration can be derived using the dispersion relation for capillary waves on the surface of a semi-infinite viscoelastic medium derived by Pleiner and Pincus[35]

$$4\pi^2\rho\left(f+i\Delta f\right)^2=\frac{4i\left(f+i\Delta f\right)\left(G"(f)-iG'(f)\right)k^2}{f}+\gamma k^3. \tag{1}$$

where k is a wavevector magnitude.

The effects of the spherical geometry of the drops are introduced by assuming that the resonant modes correspond to the case when a half integer number of wavelengths can fit around the periphery of the sessile drop. This gives the condition that $n\frac{\lambda}{2}=l$, where n is a mode number.[16,18,28] This condition results in the allowed wavevector magnitudes being

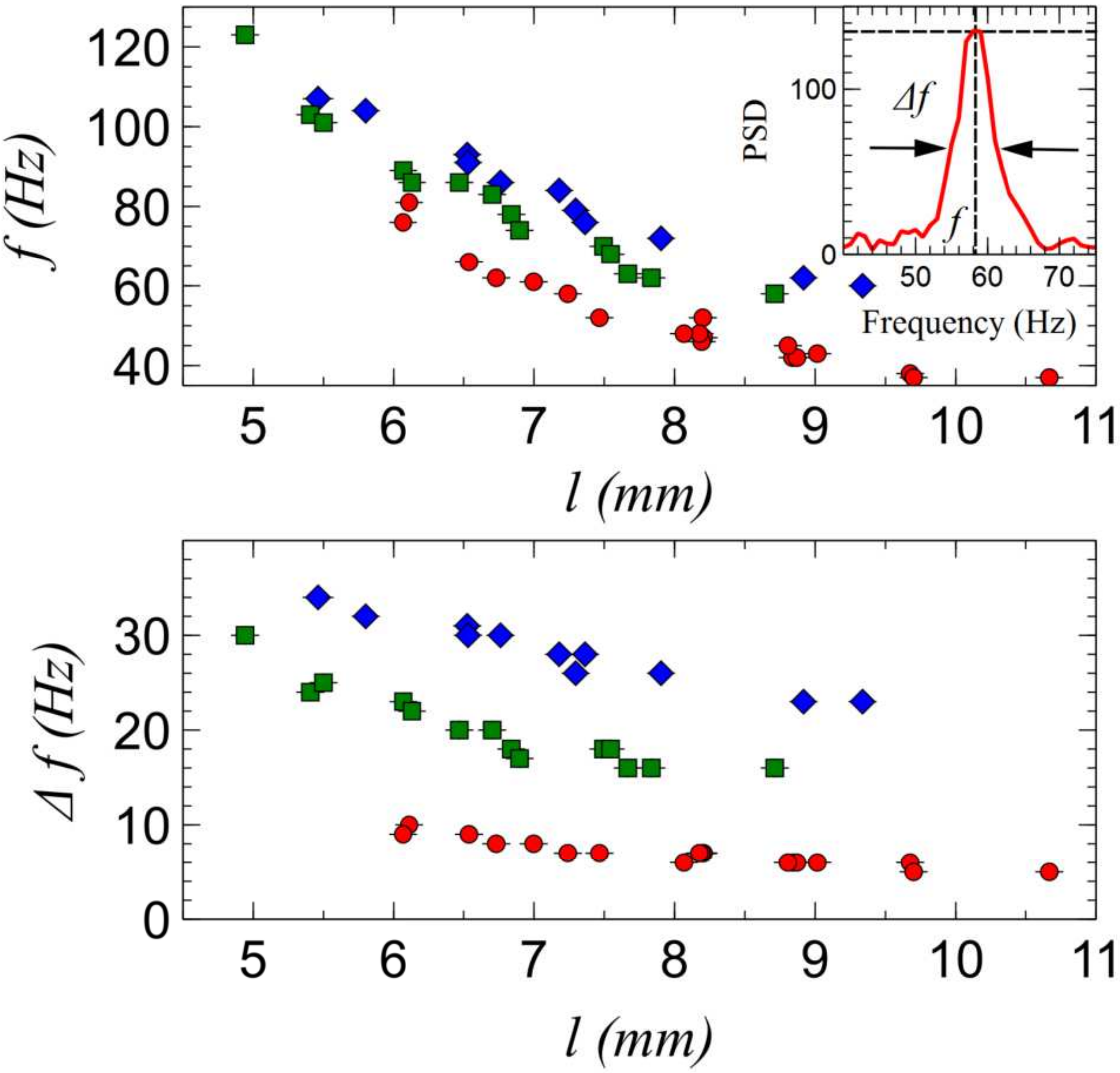

Figure 2: Vibrational response of sessile PAA loaded water drops. This figure shows plots of the vibrational frequency, (f) and spectral width (Δf) as a function of the drop profile length, l. Data are shown for the lowest vibrational mode of drops of 1.1 wt% (red circles), 2 wt% (green squares) and 3 wt% (blue diamonds) PAA in water. The inset in the top panel shows how f and Δf are defined.

$k = \frac{2\pi}{\lambda} = \frac{n\pi}{l}$. Inserting this result into equation 1 and equating real and imaginary parts gives the following expressions for the storage and loss moduli of the viscoelastic solutions

$$G' = \frac{\rho f^2 l^2}{n^2}\left(1 - \frac{\pi\gamma n^3}{4\rho l^3\left(\Delta f^2 + f^2\right)}\right) \tag{2}$$

$$G\text{”} = \frac{\rho f \Delta f l^2}{n^2}\left(1 + \frac{\pi\gamma n^3}{4\rho l^3\left(\Delta f^2 + f^2\right)}\right) \tag{3}$$

Figure 3 shows plots of the values of G' and G” obtained from the drop vibration data using these expressions - the G' and G” values are plotted against the vibrational frequencies of the drops (symbols) as this sets the frequency of the measurement probe. In assigning the mode number, values of $n = 2, 3, 4, ...$ were used. The justification for choosing $n = 2$ as the lowest vibrational mode is well established for sessile drops with pinned contact lines and is discussed in detail elsewhere.[16,18,20] No motion of the contact line was observed during the vibration experiments.

Calculation of the uncertainties/error bars associated with G' and G” shown in Figure 3 was performed by adding the fractional errors of the measured quantities in equations 2 and 3 in quadrature. Inserting typical values of $f = 50 \pm 0.1$ Hz, $\Delta f = 20 \pm 0.1$ Hz, $l = 8 \pm 0.1$ mm, $\gamma = 70 \pm 0.2$ mJm^{-2} and $\rho = 1010 \pm 5$ kgm^{-3} we obtain values for the fractional errors of 0.002, 0.005, 0.0125, 0.003 and 0.005 respectively. As each of the terms is squared during the calculation of the uncertainties in G' and G” the contribution due to uncertainties in the profile length, l, dominates the uncertainties. The full calculation (see supplementary information) shows that the fractional uncertainties in G' and G”, are such that $\frac{\Delta G'}{G'} = \frac{\Delta G\text{”}}{G\text{”}} \sim \sqrt{13}\frac{\Delta l}{l}$, where $\Delta G'$, ΔG” and Δl are the uncertainties in G', G” and l respectively. This simplified form of the uncertainty was used to calculate the size of the error bars shown in Figure 3.

Microrheology measurements of the same PAA solutions used in the drop vibration experiments were collected on a Malvern Zetasizer dynamic light scattering apparatus using polystyrene particles with a range of sizes (100-300 nm diameter) and the data analysed using the approach described by Mason.[36] In brief, intensity autocorrelation functions obtained from the light scattering data were used to calculate the mean square displacement of the particles. The time dependence of the mean square displacement was approximated using a power law expansion. This was then inserted into the generalised Stokes-Einstein equation to obtain the frequency dependent complex shear modulus ($\tilde{G}$). Real and imaginary parts of $\tilde{G}$ were used to determine the values of G' and G" respectively.[36]

The microrheology measurements (solid lines in Figure 3) were used to obtain an independent measure of the G' and G" values over the same frequency range used in the drop vibration experiments (10-300 Hz)- a range that is not accessible for these weakly viscoelastic solutions using conventional rheological techniques. In each case, the G' and G" values were found to agree for each particle size studied. The G' and G" values obtained using different particle sizes were averaged to obtain the final values for each PAA concentration.

The plots in Figure 3 demonstrate agreement between the drop vibration technique and microrheology. The values obtained are also in agreement with previous results obtained from levitated drop studies of PAA solutions similar to those described by Temperton *et. al*[28] (see Figure 3). However, despite the level of agreement, it is worth stressing that the model applied to describe the drop vibration phenomenon is oversimplified as curvature and the finite size of the drop may modify the dispersion relation used to describe drop vibration. The oversimplified nature of model may account for the small differences between the drop vibration data and microrheology in e.g. the slope of the G" data for the 1.1wt% PAA data in Figure 3.

The use of the semi-infinite medium assumption can, in part, be justified because the radius of the drops was typically an order of magnitude larger than the observed amplitudes of vibration. Also, the fact that very little of the interfacial area is in contact with the substrate means that the near spherical drops experience little substrate damping.[18] For larger amplitude vibrations (approaching the size of the drops) and or shallower three phase

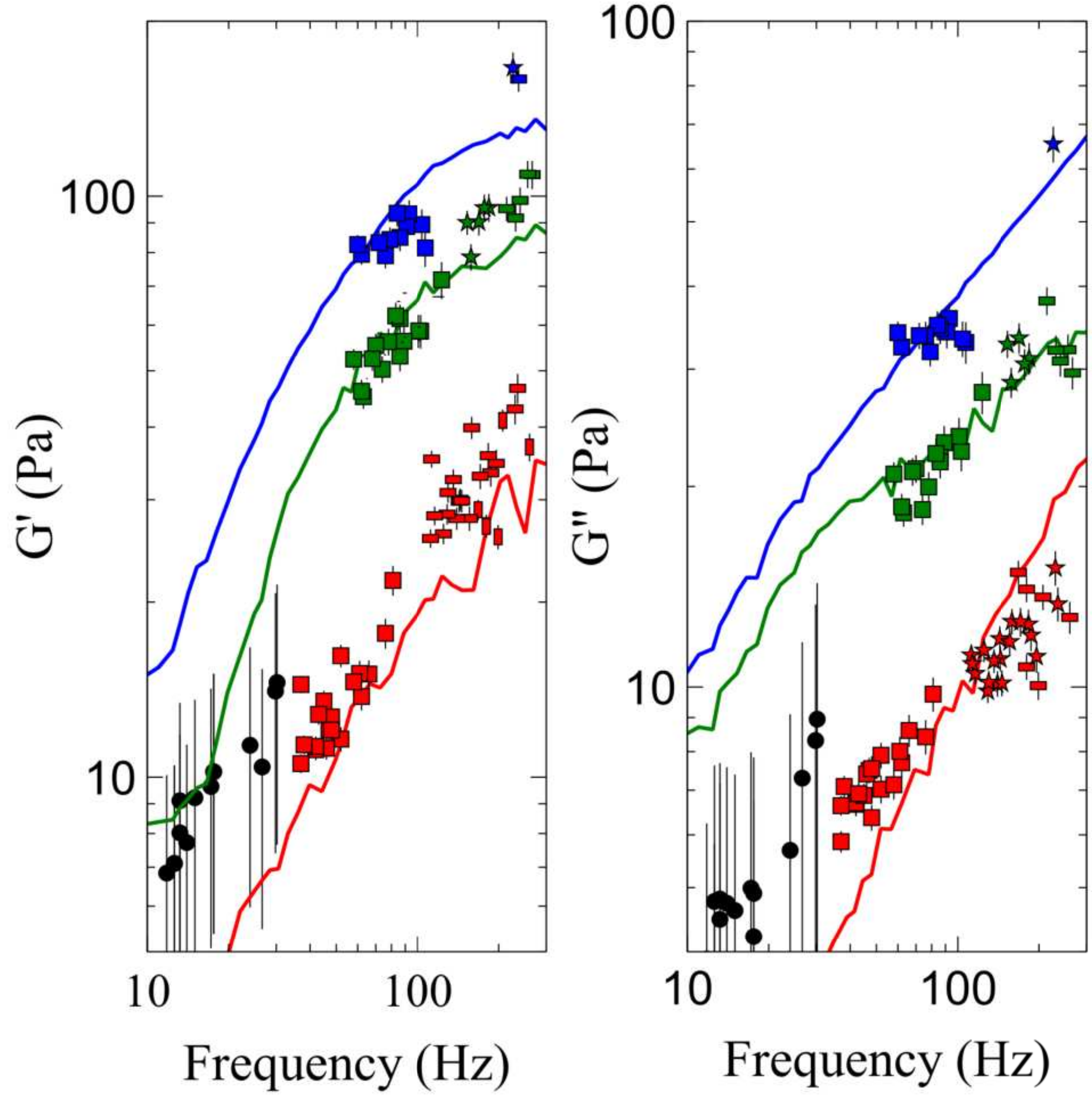

Figure 3: Rheological properties of vibrating drops. Values of G' (left panel) and G" (right panel) were calculated by inserting measured values of f,Δf, ρ and γ in equations 2 and 3. The values of G' and G" are plotted against the vibrational frequency for $\sim 10-12$ drops per concentration. Data are shown for 1.1 wt% (red), 2 wt% (green) and 3 wt% (blue) PAA in water and represent the average of 2-3 measurements per drop. The different modes of vibration are plotted as separate symbols. These are n=2 (squares), 3 (stars), 4 (horizontal bars) and 5 (vertical bars). The black circles show results obtained from magnetically levitated drops of 1.1wt% PAA similar to those described by Temperton *et. al.*[28] The solid lines are the results obtained from microrheology studies of the PAA solutions.

contact angles, the validity of this approximation is likely to break down. A rigorous theory of drop vibration would require correct expansion of the spherical harmonics of the drop and the application of appropriate boundary conditions associated with the presence of the drop interfaces.

The theory described above is also valid for droplets with radii that are smaller than the capillary length $l_c = \sqrt{\frac{\gamma}{\rho g}}$ ($\sim$ 2.7 mm for the solutions studied here, where g is the acceleration due to gravity). For drops larger than l_c an additional term of the form $\rho g k$ would need to be added the right hand side of equation 1 to account for the effects of gravity on the drops.[16] In addition, there are limits on the values of G' and G" that can be measured with this technique. As both G' and G" depend upon f, Δf and l, there is some scope for choosing an appropriate drop size that will enable these quantities to be determined. However, practical considerations mean that there are limits on the sampling frequency that can be used to measure the drop vibrations, the smallest drop size that can be measured and the level of damping that can be present in the drops before the oscillations become critically damped.

For the experimental setup used here, the highest frequency of vibration that could be measured is around 500-1000 Hz depending on the sampling frequency used. Assuming that the drop has the largest radius possible before gravitational effects start to become important i.e. $R = l_c$, we have a profile length of $l \sim 2\pi l_c$. This gives an upper limit for G' of order $\sim$ 70 kPa for fluids of this kind according to equation 2. However, this could be extended further if higher sampling rates and larger drops were used while accounting for the effects of gravity as discussed above.

In the case of G", the limiting factor is the droplet damping as it becomes difficult to measure the width of the resonant peaks when damping becomes too large. Larger drops tend to give better results as small drops tend to have larger spectral widths (shorter damping times) - a result that is consistent with measurements of the dynamics of liquid air interface oscillations in microbubbles[37] and simple liquids.[17,18,20]

In obtaining an approximation to the upper limit for G" we set the width of the peak to be comparable to the vibration frequency of the drop i.e. $f \sim \Delta f$ such that the peak becomes very broad and almost indistinguishable as a peak. According to equations 2 and 3, this should give a similar theoretical upper limit for G" $\sim$ 70 kPa to that obtained for G' when using the setup described here. However, strict caution must be exercised when analysing data from very broad vibrational peaks, as both G' and G" may vary strongly over the range of frequencies spanned by such peaks and the simple dependence described by equations 2 and 3 will therefore be invalid.

Previous measurements of drop vibration in glycerol/water mixtures[18] and other simple liquids[20] have been used to extract viscosities between 1 mPas $< \eta <$ 1 Pas with relative ease at frequencies up to 100 Hz ($G" = 2\pi f\eta \sim$ 0.63-630 Pa). Hence the upper limiting value of G" is expected to lie somewhere in the range 1-70 kPa for the experimental setup described here.

Conclusions

In the absence of a complete theory of viscoelastic drop vibration, the heuristic approach adopted here provides a reasonable description of the rheological properties of viscoelastic solutions; even for μL sized droplets. The fast, simple and non-invasive technique described lends itself to the measurement of liquid and viscoelastic properties in a range of different environments (ambient, high pressure, ultrahigh vacuum e.g. ionic liquids) and avoids the need for complex, bulky levitation apparatus.

Acknowledgement

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Supporting Information Available

The following files are available free of charge.

- supplementaryinfo.doc: Description of the procedure used during the preparation of superamphiphobic substrates and details of the procedure used to calculate uncertainties.

This material is available free of charge via the Internet at `http://pubs.acs.org/`.

References

(1) Bergeron, V.; Bonn, D.; Martin, J.Y.; Vovelle, L. Controlling droplet deposition with polymer additives. *Nature*, **2000**, 405, 772-775.

(2) Bartolo, D.; Boudaoud, A.; Narcy, G.; Bonn, D. Dynamics of Non-Newtonian Droplets. *Phys. Rev. Lett.*, **2007**, 99, 174502.

(3) B. Qian, B.; Loureiro, M.; Gagnon, D.A.; Tripathi, A.; Breuer, K.S. Micron-scale droplet deposition on a hydrophobic surface using a retreating syringe. *Phys. Rev. Lett.*, **2009**, 102 164502.

(4) Smith, M.I.; Bertola, V. Effect of Polymer Additives on the Wetting of Impacting Droplets. *Phys. Rev. Lett.*, **2010**, 104, 154502.

(5) Vukasinovic, B.; Smith M.K.; Glezer, A. Dynamics of a sessile drop in forced vibration. *J. Fluid Mech.*, **2007**, 587, 395-423.

(6) Wilkes E.D.; Basaran, O.A. Forced-oscillations of pendant (sessile) drops. *Phys. Fluids*, **1997**, 9(6), 1512-1528.

(7) Mugele, F.; Baret J.C.; Steinhauser, D.; Microfluidic mixing through electrowetting-induced droplet oscillations. *Appl. Phys. Lett.*, **2006**, 88, 204106.

(8) de Ruiter, J.; Lagraauw, R.; van den Ende, D.; Mugele, F. Wettability-independent bouncing on flat surfaces mediated by thin air films. *Nature Physics*, **2015**, 11, 48-53.

(9) Wong, C-Y.; Azziz, N. Dynamics of nuclear fluid 6. Nuclear giant-resonances as elastic vibrations. *Phys. Rev. C*, **1981**, 24(5), 2290-2310.

(10) Pollitz, F.F., Gravitational viscoelastic postseismic relaxation on a layered spherical earth. *J. Geophys. Res.*, **1997**, 102(B8), 17921-17,941.

(11) Tromp, J.; Mitrovica, J.X. Surface loading of a viscoelastic earth-I. General theory *Geophys. J. Int.*,**1999**, 137, 847-855.

(12) Bastrukov, S.I.; Weber, F.; Podgainy, D.V. On the stability of global non-radial pulsations of neutron stars. *J. Phys. G.:Nucl.Part. Phys.*,**1999**, 25, 107-127.

(13) Egry, I.; Lohöfer, G.; Seyhan, I.; Schneider, S.; Feuerbacher, B. Viscosity of eutectic $Pd_{78}Cu_6Si_{16}$ measured by the oscillating drop technique in microgravity. *Appl. Phys. Lett.*, **1998**, 73(4), 462–463.

(14) Shen, C.L.; Xie, W.J.; Wei, B. Parametrically excited sectorial oscillation of liquid drops floating in ultrasound. *Phys. Rev. E*, **2010**, 81, 046305.

(15) Hill, R.J.A.; Eaves, L. Vibrations of a diamagnetically levitated water droplet. *Phys. Rev. E*, **2010**, 81, 056312.

(16) Noblin, X.; Buguin, A.; Brochard-Wyart, F. Vibrations of sessile drops. *Eur. Phys. J. Special Topics*, **2009**, 166, 7–10.

(17) Sharp, J.S. Contact angle dependence of the resonant frequency of sessile water droplets. *Langmuir*, **2011**, 27,9367–9371.

(18) Sharp, J.S. Resonant properties of sessile droplets; contact angle dependence of the resonant frequency and width in glycerol/water mixtures. *Soft Matter*, **2012**, 8, 399–407.

(19) Meier, W.; Gruene, G.; Meyboon, A.; Hofmann, K.P. Surface tension and viscosity of surfactant from the resonance of an oscillating drop. *Eur. Biophys. J.*,**2000**, 29, 113–124.

(20) Temperton, R.H.; Smith, M.I.; Sharp, J.S. Mechanical vibrations of pendant liquid droplets. *Eur. Phys. J. E* ,**2015**, 38, 79–86.

(21) Rayleigh, R.W.S. On the capillary phenomena of jets. *Proc. R. Soc. London*, **1879**, 29, 71-97.

(22) Chandrasekhar, S. The oscillations of a viscous liquid globe. *Proc. London Math. Soc.*, **1959**, 3(9), 141-149.

(23) Milne, A.J.B.; Defez, B.; Cabrerizo-Vílchez, M. ; Amirfazli, A. Understanding (sessile/constrained) bubble and drop oscillations. *Adv. Coll. Int. Sci.*,**2014**, 203, 22–36.

(24) Miller, R.; Hofmann, A.; Haartmann, R.; Schano, K-H.; Halbig, A. Measuring dynamic surface and interfacial tensions. *Adv. Mat.*, **1992**, 4(5), 370-374.

(25) Khismatullin, D.B.; Nadim, A. Shape oscillations of a viscoelastic drop. *Phys. Rev. E*, **2001**, 63, 061508.

(26) Chrispell, J.C.; Cortez, R.; Khismatullin, D.B.; Fauci, L.J. Shape oscillations of a droplet in an Oldroyd-B fluid. *Physica D*, **2011**, 240(20), 1593-1601.

(27) McHale, G.; Elliot, S.J.; Newton, M.I.; Herbertson, D.L.; Esmer, K. Levitation-free vibrated droplets: resonant oscillations of liquid marbles *Langmuir*,**2009**, 25, 529–533.

(28) Temperton, R.H.; Hill, R.J.A.; Sharp, J.S. Mechanical vibrations of magnetically levitated viscoelastic droplets. *Soft Matter*, **2014**, 10, 5375–5379.

(29) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J.M.; Mazzella, S.A.; Rutledge, G.C.; McKinley, G.H.; Cohen, R.E. Designing superoleophobic surfaces. *Science*, **2007**, 318, 1618-1622.

(30) Mason, T.G.; Weitz, D.A. Optical measurements of frequency-dependent linear viscoelastic moduli of complex fluids. *Phys. Rev. Lett.*,**1995**, 74, 1250.

(31) Roth, M.; D'Acunzi, M.; Vollmer, D.; Auernhammer, G.K.; *J. Chem. Phys.*, **2010**, 132, 124702.

(32) de Gennes, P.G. Scaling Concepts in Polymer Physics; Cornell University, 1979.

(33) Deng, X.; Mammen, L.; Butt, H-J.; Vollmer, D. Candle soot as a template for a transparent robust superamphiphobic coating. *Science*, **2012**, 335, 67–70.

(34) del Rio, O.I.; Neumann, A.W. Axisymmetric drop shape analysis: Computational methods for the measurement of interfacial properties from the shape and dimensions of pendant and sessile drops. *J. Colloid Int. Sci.*, **1997**, 196, 136-147.

(35) Pleiner, H.; Harden, J.L.; Pincus, P. Surface-modes on a viscoelastic medium. *Europhys. Lett.*, **1988**, 7(5), 383-387.

(36) Mason, T.G. Estimating the viscoelastic moduli of complex fluids using the generalized Stokes-Einstein equation. *Rheo. Acta*, **2000**, 39, 371-378.

(37) Vakarelski, I.U.; Manica, R.; Tang, X.; O'Shea, S.J.; Stevens, G.W.; Grieser, F.; Dagastine, R.R.; Chan, D.Y.C. Dynamic interaction between microbubbles in water. *PNAS*, **2010**, 107(25), 11177-11182.

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