


Piezoelectric excitation and acoustic detection of thin film polymer membrane vibrationsNathaniel M. Roberts  and James S. Sharp ^{*}*School of Physics and Astronomy, University of Nottingham, Nottingham, NG7 2RD, United Kingdom* (Received 17 July 2023; revised 2 October 2023; accepted 8 January 2024; published 24 January 2024)

A simple method of measuring the vibrational response of a thin film membrane was developed. Piezoelectric excitation and acoustic detection (using a microphone) allowed the vibrational spectra of thin membranes to be measured in the kHz range. Vibrational frequencies were used to determine Young's modulus in thin (μm) solvent tensioned films of polydimethylsiloxane and to measure tension in ultrathin polystyrene films. Simulations of membrane motion generated vibrational spectra that agreed with the results of experiments for different membrane shapes.

DOI: [10.1103/PhysRevE.109.014802](https://doi.org/10.1103/PhysRevE.109.014802)**I. INTRODUCTION**

Measurements of material properties in thin films are becoming increasingly important as components and devices become smaller and coatings become thinner. Increasing demands are placed upon the materials that comprise thin films and the material properties are often influenced by confinement of individual molecules and/or interfacial effects [1]. Moreover, the stresses that are introduced into coatings as a result of manufacturing processes (e.g., stretching, solvent evaporation, thermal stress) become increasingly important as devices and coatings become thinner. Excessive in-plane stresses can result in the failure of the coating, giving rise to buckling and or delamination when the stored strain energy becomes comparable to the bending energy or adhesion energy of the film, respectively [2]. Occasionally these processes are desirable in the drive to create nano and microstructured surfaces [3]. However, more often than not these failure mechanisms need to be prevented in order to create a stable film or multilayer structure.

In the specific case of polymers, researchers have measured the mechanical properties using a range of techniques including wrinkling [4,5], extensional measurements of free-standing membranes [6], and films supported on liquid surfaces [7]. Bubble inflation methods have also been used to measure the mechanical properties of thin films [8]. A number of these techniques require the films to be supported on a solid or liquid substrate, meaning that extracting detailed information about the mechanical properties and/or stresses can be complicated by the influence of the supporting substrate and any forces (e.g., elastic, surface tension) that it may exert on the film. Other techniques require the use of relatively

specialized surface science techniques such as the atomic force microscopy [8] or bespoke pieces of equipment such as the thin film tensile tester developed by Bay and Crosby [6].

Here we present a simple method of determining the mechanical properties of thin free-standing membranes by exciting and measuring their vibrational modes. The physics of vibration of membranes of different shapes is well established. Among these, perhaps the most iconic—the circular membrane (or drumskin)—has been well studied and the frequencies and shapes of the associated vibrational modes can be derived analytically. A key factor in determining the frequency response of an arbitrarily shaped membrane is the magnitude of the tension, T , within it. For example, in the limit where the thickness, h , is much smaller than its radius (i.e., $h \ll a$), the vibrational frequencies of a circular membrane are [9]

$$f = \frac{\alpha}{2\pi a} \sqrt{\frac{T}{\rho h}}, \quad (1)$$

where ρ is the density of the membrane material and α is a constant which depends upon the mode of vibration [9]. If the strain in the membrane can be controlled (or is otherwise known) then the locations of the vibrational peaks can, in principle, be used to extract information about mechanical properties (e.g., Young's modulus).

Previous work has considered measurements of the vibration of gold nanoparticle membranes using laser interferometry [10], capacitive detection of Si membrane vibrations in vacuum [11] and metallic membranes [12], laser doppler vibrometry of SiC membranes [13], white light interferometry of gold and Inconel membranes [14], and the use of a laser deflection to measure the vibrations of micromechanical Si cantilever beams [15].

Here we describe how inexpensive piezoelectric buzzers can be hole punched and membranes prepared across the resulting holes. Electrical excitation of the piezo results in vibration of the membranes in the kHz regime. These vibrations can be detected using a simple microphone and amplifier

*james.sharp@nottingham.ac.uk

circuit, and the vibrational frequencies used to determine the tension in the membrane and/or the Young's modulus.

Measurements are performed on relatively thick films whose properties are well characterized—namely a commercially available cross-linked elastomer (Sylgard 184)—to confirm the validity of the approach. Although the majority of measurements are performed on ~ 50 μm thick films, we show that this technique can also be used to measure the vibrational response of ultrathin polymer films where interfacial effects have been shown to have a significant effect upon material properties, such as the glass transition temperature [16].

II. EXPERIMENTAL

Thin film membranes of polydimethylsiloxane (PDMS) elastomers were prepared by suspending them across holes in piezoelectric actuators. Briefly, thin layers of Carnauba wax (Sigma Aldrich, UK) were spin coated at 3000 rpm on to glass microscope slides from a 1wt% solution in chloroform (Sigma Aldrich, UK). These wax layers were used as a release layer and were coated with a layer of PDMS (Sylgard 184, Dow Corning) by spin coating. Three different ratios of the PDMS resin:crosslinker ratios of 5:1, 10:1, and 20:1 were used to vary the mechanical properties. Films were annealed in air at 110°C for 15 hours to crosslink the PDMS and allowed to cool to room temperature. After cooling, the films were scored and immersed in chloroform to remove the PDMS from the glass slides. Films were removed from the chloroform and allowed to dry/deswell before being placed in a bath containing a second pure solvent (e.g., acetone, ethanol, ethylacetate, chloroform, chlorobenzene, toluene). The second solvent was used to swell the films by a controlled amount [17]. The film dimensions were measured before and after immersion in the solvents, and the ratio of the solvent swollen and unswollen dimensions, S , was recorded for each film. Once equilibrated in the second solvent, the films were clamped between two circular washers, allowed to dry, and tensioned. The thickness, h , of the PDMS was determined by weighing a known area cut from an unused region of the same films that were used to create the tensioned membrane. Values of the thickness were determined to be 45 ± 5 μm . Solvent swelling/deswelling was used instead of direct application of mechanical forces because it creates an isotropic radial tension in the membranes once the solvent has been removed.

Piezoelectric buzzers (Murata 7BB-20-6L0, max frequency 6.3 kHz), each with a circular hole punched in it, were superglued to the tensioned PDMS membranes, allowed to dry, and placed in a custom built sample cell. Punching holes in the piezos was shown to result in little to no cracking in the remaining part of the buzzers when observed using an optical microscope.

A signal generator (Agilent 33521A) was used to drive vibrations in the piezo and PDMS membrane and a small condenser microphone was placed close to the sample (see diagram in Fig. 1). The output from the condenser microphone was high-pass filtered (cut off frequency 50 Hz) and amplified using an OP27 operational amplifier with a gain of ~ 100 . The amplified signal was then measured using a data acquisition card (National Instruments, USB-6021). We note that an alternative method of measuring the response of the

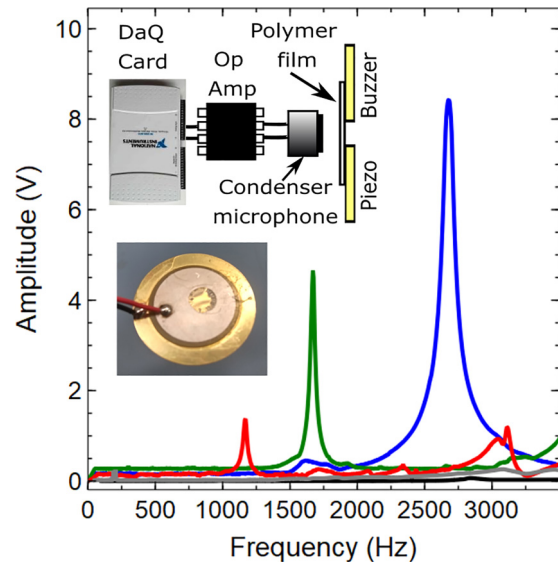


FIG. 1. Piezoelectric actuation and acoustic detection of thin film PDMS membranes. The main panel shows plots of three 45 ± 5 μm thick PDMS membranes tensioned with ethanol ($S = 1.04$, lowest tension, red line), acetone ($S = 1.10$, green line), and toluene ($S = 1.31$, highest tension, blue line), respectively. Each membrane had a diameter of $2a = 6$ mm. The black and gray lines show the background response of a piezo with a 6 mm diameter hole in it (with no film attached) and the response of a piezo having no hole and a 45 ± 5 μm thick PDMS membrane tensioned using chlorobenzene and glued to it, respectively. The insets show a diagram of the experimental setup and a photo of a tensioned PDMS film supported across a 6 mm diameter hole punched in a piezoelectric actuator.

membranes could involve using a laser and split photodiode. However, this method is considerably more expensive to implement and more difficult to align than placing a simple microphone close to the films.

The frequency response of the PDMS membranes was determined by driving the piezo with an amplitude of 5 V and sweeping a range of frequencies between 50 Hz and 3500 Hz (in steps of 5 Hz). This range of frequencies was used in order to avoid the main resonance of the piezo and prevent damage to the membranes. The root mean square (r.m.s.) of the signal obtained from the microphone over a period of one second was determined at each driving frequency and used to create the vibrational spectrum of the membrane. An alternative method of driving the films involved applying a short (100 μs , 10 V) pulse to the piezo and Fourier transforming the time-dependent signal obtained from the microphone over a 0.2 s period. This second method was faster than the sweeping method, but required the averaging of many pulse responses (typically 50). Both methods gave very similar results for the frequency response of the membranes. All measurements were performed at room temperature (20°C).

III. RESULTS AND DISCUSSION

The main panel in Fig. 1 shows plots of the vibrational spectra of PDMS membranes that have been tensioned by swelling in different solvents. This figure shows that as the tension in the PDMS increases, both the amplitude and

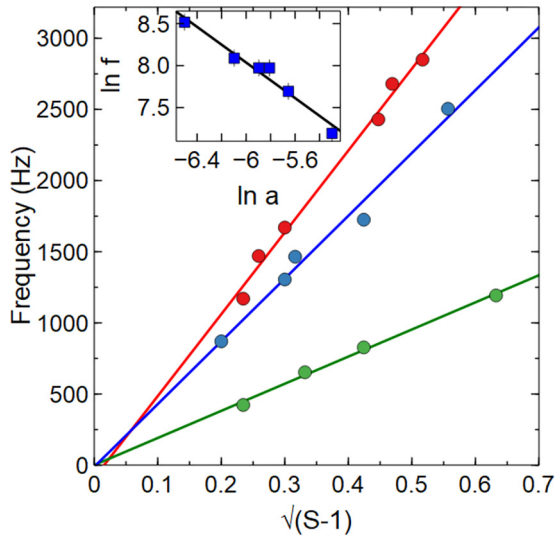


FIG. 2. Tension dependence of the fundamental frequency of vibration of PDMS membranes. The main panel shows the variation in the fundamental frequency of vibration of 6 mm diameter, 45 μm thick PDMS membranes as a function of $\sqrt{S-1}$ (see main text). Data are shown for PDMS membranes with resin:crosslinker ratios of 5:1 (red circles), 10:1 (blue circles), and 20:1 (green circles). The inset shows the hole size dependence of the vibrational frequency of PDMS membranes that were tensioned using chlorobenzene ($S = 1.22$). Solid lines in both plots are fits to Eq. (2).

frequency of the fundamental vibrational mode of the membranes increases. Also shown in this plot are the background response of a piezo with a hole in it and the response of a chlorobenzene tensioned PDMS film supported on piezo without a hole in it. These latter two plots show no features of interest in the frequency range studied and demonstrate that the peaks observed in samples where PDMS films were suspended across the holes are indeed due to the free-standing tensioned membranes.

In the limit that $h \ll a$, the fundamental frequency of a circular membrane can be rewritten in the form

$$f = \frac{\alpha}{2\pi a} \sqrt{\frac{E(S-1)}{(1-\nu)\rho}}. \quad (2)$$

Here the tension in the film is written as $T = \sigma h$ and the stress is given by $\sigma = \frac{E\epsilon}{(1-\nu)} = \frac{E(S-1)}{(1-\nu)}$. E and ν are the Young's modulus and Poisson ratio of the membrane, and $\epsilon = S - 1$ is the linear strain induced in the film during tensioning. A value of $\alpha = 2.40$ was used for the fundamental mode of a circular membrane [18].

Figure 2 shows a plot of the vibrational frequency of PDMS membranes with different resin:crosslinker ratios as a function of $\sqrt{S-1}$. Fits to Eq. (2) to the data in Fig. 2 yield values of the Young's modulus of $E = 1.05 \pm 0.02$ MPa, 0.62 ± 0.02 MPa, and 0.12 ± 0.02 MPa for PDMS membranes with 5:1, 10:1, and 20:1 resin:crosslinker ratios, respectively. Here we have assumed that the PDMS elastomers have $\rho = 1030 \text{ kgm}^{-3}$, $\nu = 0.5$, and $a = 3 \text{ mm}$. The values obtained for E are lower than, but of the same magnitude as, literature values for PDMS [19]. Rheometry measurements performed on 20 mm diameter, 2 mm thick

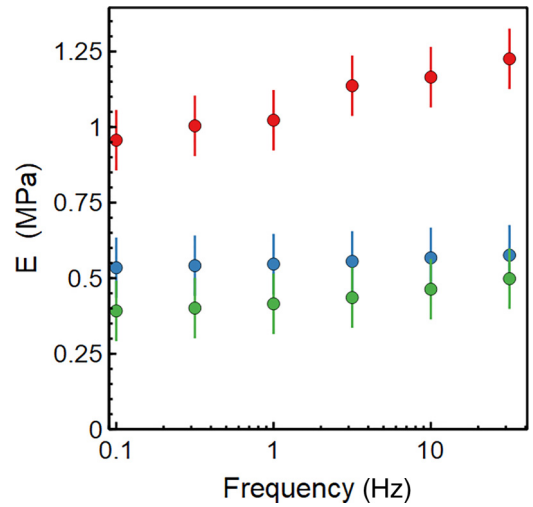


FIG. 3. Frequency dependent measurements of the Young's Modulus of 20 mm diameter, 2 mm thick PDMS disks. Data are shown for PDMS samples with resin:crosslinker ratios of 5:1 (red circles), 10:1 (blue circles), and 20:1 (green circles). All data were obtained at room temperature (20 $^{\circ}\text{C}$), using a strain of 0.5% and a normal force of $1N$.

PDMS disks using a Kinexus Pro KNX2100 rheometer (Malvern Instruments, UK) shown in Fig. 3 give values of E for the 5:1, 10:1, and 20:1 resin:crosslinker PDMS samples, respectively, that are in agreement with the values obtained using the membrane vibration technique for PDMS prepared in the same manner. The only exception is the data for the 20:1 PDMS where the thin membranes give a value for E which is a factor of ~ 4 smaller than the value obtained from rheometry measurements.

In each case, the values of E shown in Fig. 3 were obtained from measurements of the frequency dependent shear storage modulus, G , using the relation $E = 2G(1 + \nu)$. It is worth noting that the frequency range encompassed by the rheometry measurements is below the frequency scale of the probe used in the membrane vibration studies. While there is some frequency dependence of the Young's modulus in Fig. 3, it is relatively weak. Ideally, detailed temperature dependent studies should be used to measure the Young's modulus with both techniques. Time-temperature superposition would then be used to compare the values of E obtained more directly. However, the weak frequency dependence of the data shown for the 5:1 and 10:1 PDMS compositions suggests that this is not strictly necessary for the PDMS samples studied here. Direct comparison of the values of E obtained from the two techniques therefore seems to be an acceptable approach.

The level of agreement between membrane vibration and rheometry measurements for the 5:1 and 10:1 PDMS compositions suggests that contamination of the PDMS by the super (cyanoacrylate) glue or that significant amounts of leaching of small molecular weight components by the swelling solvent did not occur during sample preparation. Cyanoacrylate based glues can give off fumes that condense on nearby surfaces and this would be expected to result in increased values of E . The lack of contamination by the superglue observed here is potentially caused by the very low surface energy of PDMS

($\sim 20 \text{ mJm}^{-2}$ [20]) which prevents both water and cyanoacrylate vapour from condensing on it. Leaching of low molecular weight components (e.g., uncross-linked resin, residual cross linker) has also been shown to increase Young’s Modulus of Sylgard 184 when it is exposed to solvents [21].

The inset in Fig. 2 shows the hole size dependence of the fundamental frequency of a series of 10:1 PDMS membranes that were tensioned using the same solvent (chlorobenzene). A log-log plot of frequency versus hole radius gives a slope of -0.9 ± 0.3 , in agreement with hole size dependence predicted by Eq. (2). Another thing that is clear from this plot and Eq. (2) is that the hole size sets the frequency scale for the mechanical measurements that can be performed with the membrane vibration technique—with smaller hole sizes providing access to high frequencies. Membrane vibration easily provides access to frequencies $> 1 \text{ KHz}$ that are inaccessible to conventional rheometry techniques (typically less than a few hundred Hz). The use of thin films in the membrane vibration experiments also permits the use of significantly smaller sample volumes than are used in conventional rheometry measurements.

Numerical simulations were performed to model the frequency response of thin film membranes. A forward-time, center-space finite difference approach was used to solve the 2D wave equation

$$\frac{\partial^2 u}{\partial t^2} = c^2 \nabla^2 u, \tag{3}$$

where $c = \sqrt{\frac{T}{\rho h}}$ is the speed of sound in the membrane and $u(x, y, t)$ is the displacement of the membrane at position, (x, y) , and time, t . Software written in Python was used to simulate the response of both circular and square membranes superimposed on a cartesian grid. A sinusoidal time-dependent perturbation of fixed frequency and amplitude was applied around the periphery in a direction perpendicular to the plane of the membrane. The response of the membrane to this perturbation was simulated over 50 complete oscillations. This was repeated for a range of different frequencies and the r.m.s. displacement of the membranes was determined at each frequency of vibration.

Figure 4 shows both data and the results of simulations for the vibrational response of a circular and a square PDMS membrane, respectively. Both panels show that the simulations agree well with the results of experiments in terms of reproducing the positions and relative amplitudes of the peaks in the vibrational spectra. There are some small differences, which can be attributed to the simplicity of the simulation method used and the lack of damping therein. The insets in Fig. 4 show the membrane mode shapes that were generated by the simulations and the downward arrows indicate the expected locations of spectral features based upon analytical solutions to Eq. 3 [9]. In the case of the circular membrane [Fig. 4(a)] the peaks correspond to modes with radial symmetry and all azimuthal modes are suppressed. This is to be expected based upon the way in which the membranes are excited both in simulations and experiments, i.e., around their periphery.

Data and simulations for the square membrane [Fig. 4(b)] show that the relative positions of the peaks agree well with

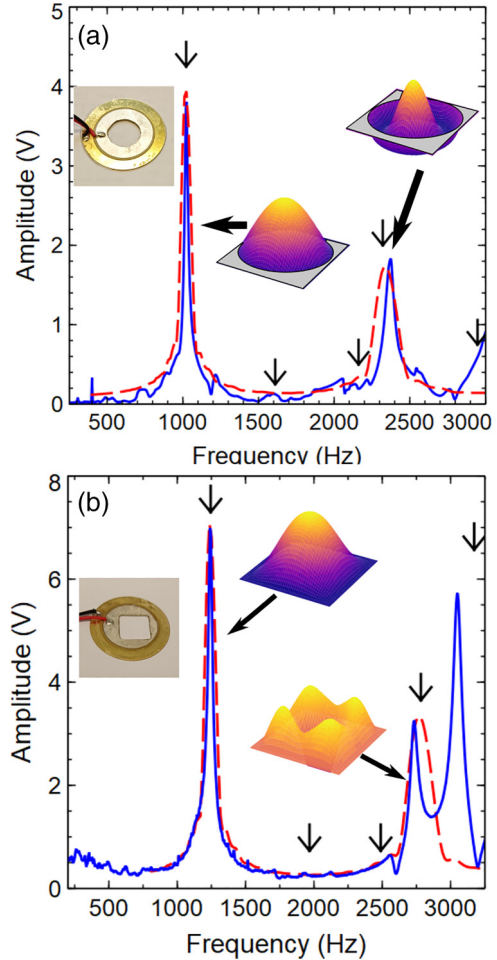


FIG. 4. Vibrational spectra of PDMS membranes. Panel (a) shows data for a 10 mm diameter circular membrane and panel (b) shows data for a square membrane of side length, $d = 10 \text{ mm}$ (blue lines). Both films were tensioned using acetone ($S = 1.10$). The red lines in both panels shows the results of simulations. Downward arrows mark the positions of the expected frequencies of the vibrational modes for circular and square membranes [9]. The insets show examples of the mode shapes that are associated with each peak as generated by the simulations. Images of the holes that were cut in the piezos are also shown as an inset.

analytical values for a square membrane [9],

$$f = \frac{c}{2d} \sqrt{n^2 + m^2}, \tag{4}$$

where n and m are mode numbers and d is the side length of the membrane. Once again, the simulations and measurements do not contain all of the possible vibrational modes of the square membrane, as noted by the locations of the downward arrows in Fig. 4(b). Vibrational modes with $n = m$ are present in both the measurement and simulations (see inset images in the same figure). Modes with $n \neq m$ are suppressed in the simulations because of the method used to drive the membranes. There is clearly one additional vibrational mode in the frequency range studied that is accessible in the experiments, but is not observed in the simulations. The reason for this is not entirely clear, but is likely related to the loss of radial symmetry caused by punching a square hole in a round piezo. The

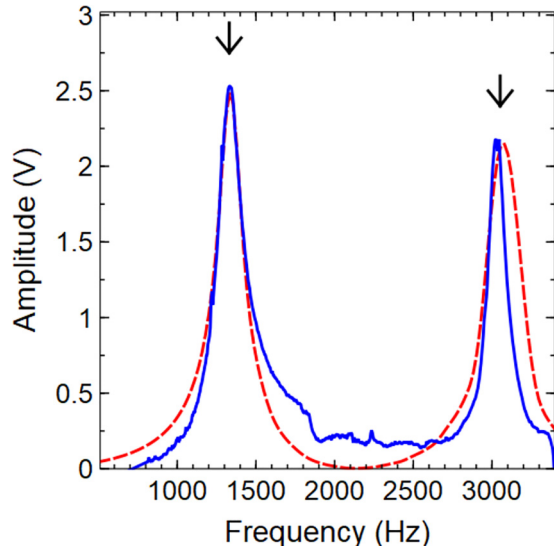


FIG. 5. Vibrational spectra of a 180 nm thick PS film suspended over a 10 mm hole (blue line). The downward arrows show the expected frequencies of vibration for a circular membrane [as derived from the 2D wave equation (3)] [9] and the red line shows the results of simulations. Only radially symmetric modes are observed in the spectra.

dominant mode of vibration in the piezos is one of flexure. A square hole in a circularly symmetric piezo is therefore likely to introduce differences in the way in which the piezo can flex, and the method of excitation is unlikely to be uniform around the periphery of the square hole as is assumed in the simulations. This is expected to lead to a corresponding asymmetry in the way in which the membranes are driven and the emergence of modes that are not present in the simulations. In contrast, a circular hole in a circular piezo preserves the radial symmetry and therefore the uniform peripheral driving condition assumed in the simulation is expected to be a more realistic representation of experiments.

Figure 5 shows the measured vibrational response of a 180 nm thick polystyrene (PS) film suspended over a 10 mm diameter circular hole. This film was prepared by spin coating a 1.5wt% solution of 1 MDa PS (Polymer Source, Canada) from a solution in toluene on to a glass microscope slide. A water transfer technique similar to that described by Dalnoki-Veress *et al.* was then used to suspend the film across the hole in a piezo [16]. The film was annealed over a hot plate at a temperature of 110 °C causing the membrane to be pulled taut under the influence of surface tension. The sample thickness was determined using ellipsometry on unused portions of the same PS film that had been transferred on to single crystal silicon wafers. The fundamental frequency for this membrane gives value for the tension of $58.7 \pm 0.4 \text{ mNm}^{-1}$ according to Eq. (2) (assuming $\rho = 1050 \text{ kgm}^{-3}$). This magnitude of the tension is to be expected for a film that is tensioned in this way and is consistent with the surface tension of polystyrene of a similar molecular weight obtained from both measurements and calculations [22].

One potential concern about the membrane vibration technique relates to the assumptions that are made in the

application of Eq. (2). This equation assumes that the membranes (PDMS and PS) remain clamped (rather than being simply supported) around their periphery during vibration. In all the experiments on PDMS, great care was taken to ensure that the films were attached to the piezos by applying superglue all the way to the edges of the hole. Measurements were also performed at a range of different driving amplitudes and no significant changes in the vibrational spectra of PDMS were observed. In the case of the PS films, Van der Waals forces are used to attach the films to the piezo during the water transfer technique [16]. As water is removed from beneath the films, they are observed to form intimate contact with the piezo at all points on the substrate all the way up to the edges of the punched holes. Similar amplitude dependent studies showed no significant changes in the vibrational spectra of the ultrathin films and samples inspected before and after vibration had very similar appearances. All of these observations suggest that the films remain rigidly clamped during vibration and that the application of Eq. (2), and assumptions that the films behave as if they are perfectly clamped, represents a valid assumption for these samples. A breakdown in this assumption could possibly be used to explain the reduced value of E obtained for the 20:1 PDMS relative to conventional rheometry measurements. Loss of adhesion and detachment of the films from the piezo would have the effect of increasing the effective radius of the membrane that was vibrating. This would in turn lead to a reduction in the frequencies of vibration of these films which could be interpreted as a reduction in the value of E . No obvious signs of detachment were observed in these samples around the edge of the holes in the piezos after the experiments. However, this cannot be ruled out completely and this potential anomaly highlights the need to ensure that films remain rigidly attached during vibration if the assumptions underpinning Eq. (2) are required to hold.

IV. CONCLUSION

A thin film vibration technique has been developed which uses inexpensive piezoelectric buzzers to drive free standing membranes of polymers. A simple microphone circuit was used to detect the vibrations of the membranes and the frequencies of the vibrational modes were used to determine the Young's modulus of a commercial PDMS elastomer (Sylgard 184) and the tension in ultrathin free-standing PS membranes. Values were found to be in good agreement with bulk measured values of the Young's modulus of PDMS and literature values of the surface tension of PS, respectively. Finite difference simulations were also shown to reproduce the vibrational spectra of the films and to predict the correct mode shapes.

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