Viscoelastic and poroelastic relaxations of soft solid surfaces

Qin Xu, Lawrence A. Wilen, Katharine E. Jensen, Robert W. Style, and Eric R. Dufresne

1 Laboratory of Soft and Living Materials, ETH Zürich, 8093 Zürich, Switzerland
2 Department of Physics, The Hong Kong University of Science and Technology, Hong Kong, China
3 School of Engineering and Applied Science, Yale University, Connecticut, USA 06511
4 Department of Physics, Williams College, Williamstown, Massachusetts, USA 01267

Understanding surface mechanics of soft solids, such as soft polymeric gels, is crucial in many engineering processes, such as dynamic wetting and adhesive failure. In these situations, a combination of capillary and elastic forces drives the motion, which is balanced by dissipative mechanisms to determine the rate. While shear rheology (i.e. viscoelasticity) has long been assumed to dominate the dissipation, recent works have suggested that compressibility effects (i.e. poroelasticity) could play roles in swollen networks. We use fast interferometric imaging to quantify the relaxation of surface deformations due to a displaced contact line. By systematically measuring the profiles at different time and length scales, we experimentally observe a crossover from viscoelastic to poroelastic surface relaxations.

The mechanics of soft solids has recently drawn great attention for their potential use in various applications, such as design of bio-compatible materials [1-4], cell patterning [5, 6], machining of soft robotics [7], and fabrication of microfluidic devices [8]. These applications rely upon the contact of soft solids with other materials where their wetting and adhesive properties play essential roles.

Soft solids can deform strongly at contact lines, where they meet the interfaces of two other phases [9]. For example, a droplet’s liquid-vapor interface creates a ridge on a soft solid [10]. As a droplet slides on a soft solid, the displacement of the ridge is found to significantly slow down its movement. First observed in [11], this phenomenon was dubbed ‘viscoelastic braking’ because the substrate’s viscoelasticity was presumed to be the underlying dissipation [12-10]. While shear rheology dominates the response of most soft materials, this can break down for polymeric gels. A gel is an elastic network swollen by a fluid. Even when the elastic network is easily compressed, the solvent avoids compression by flowing through the network. This causes local changes to the relative concentration of solvent and the network. The coupling of fluid flow to the deformation of an elastic network is called poroelasticity. The theory of poroelasticity was originally developed for geological applications [17, 18], but has recently been applied to describe the deformation of hydrogels [19-21].

Recent experiments suggest that the flow of solvent through a gel’s elastic network could impact wetting and adhesion. Zhao et al found a slow, approximately logarithmic, relaxation of a wetting ridge upon removal of a droplet, and introduced a poroelastic model for the decay [22]. Berman et al measured the relaxation of an adhesive contact and made a scaling argument for the importance of solvent flow in determining the dynamics of relaxation [23]. These arguments are supported by separate experiments which have quantified how contact lines can extract solvent from the bulk [24], coating the droplet and reducing its surface tension [25].

Despite evidence supporting the relevance of both viscoelastic and poroelastic effects to the surface relaxations of soft gels, previous works have only focused on one relaxation mechanism at the exclusion of another and there is no clear framework for evaluating which of these mechanisms will dominate in a particular situation. The ambiguity is caused by the difficulty in precisely measuring surface dynamics over a broad range of time and length scales.

In this Letter, we apply direct interferometric imaging to measure the relaxation of a wetting ridge after a sudden displacement of the contact line. We observe contributions from both viscoelastic and poroelastic dissipation in the same dewetting process. For relatively large droplets and long timescales, dynamics are dominated by the substrates’ poroelastic response. On the other hand, viscoelasticity dominates for small droplets or short timescales.

Our experimental approach is schematically illustrated in Fig. 1(a). To image the surface deformation of the substrate, we designed a Linnik interference imaging system [26]. This technique quantifies interface topography with a vertical resolution about 10 nm and a temporal resolution limited by the speed of the camera, here about 20 ms. These specifications are superior to confocal microscopy and other methods that have been used to image wetting ridges, but come with some costs. Most importantly, interference microscopy cannot image height gradients bigger than about 35% [27]. We prepare silicone gel (Dow Corning CY52-276) substrates by spin-coating the curing silicone mixture on a microscope slide at 800 rpm for a minute. After the gel is fully cured at 40°C, it forms a 65 µm thick smooth substrate with a Young’s modulus of 3.8 kPa.

To perform dewetting experiments, we deposit liquid on the surface of soft gels by a capillary tube. At the contact line, the droplet’s surface tension pulls on the substrate, forming a microscopic wetting ridge [11, 28].

---

* qin.xu@ust.hk
† eric.dufresne@mat.ethz.ch
In equilibrium, the height of the wetting ridge, \( h_0 \), scales as \( \gamma_\text{lv} \sin \theta / E \). Here, \( \gamma_\text{lv} \) is the liquid-vapor surface tension and \( \theta \) is the macroscopic contact angle \([29]\). For water on a \( \mathcal{O}(\text{kPa}) \) substrate, the height of the wetting ridge is a few microns and the contact angle is around 91° \([30]\). After a certain resting time \( t_{\text{res}} \), we suddenly pull away the droplet to remove the liquid-vapor interface and image the relaxation of the wetting ridge.

Unprocessed interferograms, shown in Figs. 1(b-e), show the relaxation of the interface upon removal of a 0.45 mm radius water droplet after a residence time of \( t_{\text{res}} = 10^3 \) s. The dark region on the right of panel (b) corresponds to reflection from the solid-liquid interface, which has a smaller index-mismatch than the solid-vapor interface on the left. There, clearly resolved fringes indicate the surface topography of the solid-vapor interface. Far from the wetting ridge, they are parallel and evenly spaced due to the gentle tilt of the otherwise flat interface. When the droplet is removed, both sides of the wetting ridge have equal contrast and the decay is directly observed, as shown in panels (c-e). Digital processing of these fringes enables precise quantification of the ridge profile and its decay, shown by the colored data points in Fig. 1(f). Note that the interference profiles start at \( \sim 0.2 \) s after removal of the droplet. At earlier times, the center of the full profile is too steep (\( > 35\% \)) to show interference fringes. For comparison, we superimpose the steady wetting profile of a similar-sized droplet on the same substrate quantified by confocal microscopy, shown by the black data points in Fig. 1(f). This suggests that the ridge quickly retracts from 7.8 \( \mu \text{m} \) to 0.9 \( \mu \text{m} \) in the early stage (\( \sim 10^{-1} \) s), followed by a slow relaxation process in a period of \( \sim 10^1 \) s.

While viscoelasticity may account for the short-time dynamics, it cannot capture the late-stage relaxations, where the complete ridge profile is visible in the interferogram. First, the relaxation is too slow. The viscoelastic spectrum of the gel is shown in Supplement Fig. S5. It follows \( G^*(\omega) = G_0 (1 + i \omega \tau_c)^n \) with a power-law index \( n = 0.54 \) and an intrinsic relaxation time \( \tau_c \approx 0.11 \) s. The observed relaxation of the wetting ridge, lasting about \( 10 \) s, is approximately two orders of magnitude slower than \( \tau_c \) \([13]\). Second, the relaxation of the wetting ridge depends on the residence time of the droplet on the substrate, \( t_{\text{res}} \). For a viscoelastic substrate, we expect relaxation dynamics to be insensitive to the residence time, provided that \( t_{\text{res}} \gg \tau_c \). However, the ridge relaxations of 0.5 mm radius droplets for different \( t_{\text{res}} \) from 0.5 s to 40 mins, show different results, as plotted in Fig. 2(a). These show a significant slowing down of the relaxation with increased residence time. For \( t_{\text{res}} \gtrsim 10 \) mins, the ridge decay had a consistent time course, and required tens of seconds for a full decay. A similar dependence on waiting time was recently observed on an unspecified silicone substrate with a similar elastic modulus \([22]\). Third, the surface relaxation is found to depend on the size of the droplet. The blue symbols (crosses, circles, stars, and squares) in Fig. 2(b) represent the decay of ridge height for a range of water droplet radii from \( R = 0.52 \) to 1.24 mm. The relaxation time increases with the droplet size. Since viscoelastic relaxations are local, and their characteristic time scales are material properties, independent of system size, our observed scale-dependent relaxations in Fig. 2(b) cannot be attributed to viscoelasticity.

Poroelastic relaxations, by contrast, are distributed and scale-dependent \([19]\). Stresses in a porous elastic solid drive flow of fluid through its pores. For deformations observed at length scales much larger than the pores, compositional differences in a porous medium evolve according to the familiar diffusion equation with an effective diffusion coefficient,

\[
D^* = \frac{G_0 k (1 - 2\nu)}{\mu (1 - \nu)},
\]

Here, the elastic network is characterized by its shear modulus, \( G_0 \), Poisson ratio, \( \nu \), and permeability, \( k \). The
fluid is characterised by its shear viscosity, $\mu$. From inspection of Eq. 1 it is clear that poroelastic diffusion can only be significant for compressible networks ($\nu < 1/2$). Since poroelastic relaxation is diffusive, its characteristic time should scale as $\tau_p \sim L_D^2/D^\ast$. Here, $L_D$ is a characteristic length scale set by the macroscopic geometry of the deformation.

Suo and collaborators [31] have recently proposed standard mechanical tests to measure poroelastic properties of soft gels by compressing the elastic network suddenly and measuring the relaxation of normal force. We applied this method to independently assess the poroelastic properties of our soft gels, indenting with a steel sphere and observed scaling of force relaxation data of the gels from (a) collapsed by normalizing time with $R_p h_p$. Inset: schematic of the indentation experiments. (C) Surface profile data from Fig. 1(b) collapsed by normalizing the height by $h_0$ and time by $R h_0$.

FIG. 3. Quantifying poroelastic response. (a) Relaxation of normal force after indentation. Measured normalized force, $\Delta F$, versus time, $t$, for different indentation depths, $h_p$, on soft gels (solid dots) and solvent-extracted (‘dry’) networks (hollow dots). (b) Force relaxation data of the gels from (a) collapsed by normalizing time with $R_p h_p$. Inset: schematic of the indentation experiments. (C) Surface profile data from Fig. 1(b) collapsed by normalizing the height by $h_0$ and time by $R h_0$.

In an indentation experiment, the poroelastic relaxation time is set by the indenter radius, $R_p$, and indentation depth, $h_p$. What length scales determine the relaxation time in our wetting experiments, where there is no significant indentation, only the formation of a wetting ridge? In the absence of a theoretical prediction, we take an empirical approach. It is clear from Fig. 2(b) that the droplet radius is a factor. Suspecting that the ridge height, $h_0$, may also play a role, we measured the relaxation of wetting ridges formed by fluorinated oil droplets, shown as red data points in Fig. 2(b). Fluorinated oil droplets create shorter wetting ridges, which decay faster. Using confocal microscopy, we measured ridge heights of 7.8 $\mu$m for water (Fig. 1(f)) and 2.1 $\mu$m for fluorinated oil (Fig. S4 in [27]). We found that a diffusion length $L_D \sim \sqrt{R h_0}$ nicely collapses the height relaxation data for all droplet sizes and compositions in Fig. 3(c).

The decay of the master curve in Fig. 3(c) suggests a poroelastic diffusion coefficient of order $D^\ast \approx 10^{-8} \text{ m}^2/\text{s}$. This value is consistent with the measured poroelastic diffusion coefficient by stress-relaxation. Precise quantification of the ridge height for dry networks was not possible because solvent extraction leads to strong wrinkling effects on the surface. Nevertheless, qualitative observations of interferograms, shown in the Supplement Fig. S7 [27], suggest a timescale of $\sim 10^{-1}\text{ s}$, comparable to the viscoelastic timescale $\tau_c$, once the free solvent was fully extracted.

We have found that poroelastic timescale governing the full relaxation of a wetting ridge, $\tau_p$, scales as $R h_0/D^\ast$. In these experiments with millimeter-scale droplets, poroelastic relaxation is much slower than viscoelastic relaxation, and therefore is rate-limiting. We expect a cross-over to a regime where viscoelastic response is rate-limiting for small droplets, $R \lesssim D^\ast \tau_c/h_0$. For water droplets, our data suggest that this cross-over should occur for radii around 50 $\mu$m. To work with small droplets, however, we need to make a few modifications of our technique. First, we use glycerol, since it has a lower vapor pressure, but similar surface tension to water. Second, we disperse small droplets across the gel surfaces with an atomizer (Misto). Finally, we remove the liquid-air interface by flooding the surface with glycerol. Figures 3(a-c) exhibits a series of interference images immediately after a $R = 21 \mu$m droplet has been removed by flooding. Note that the topography of such a submerged interface is not accessible by conventional first-surface interferometry, but requires the Linnik method. Since the droplet is too small to obtain the precise wetting profile from the image, we simply measure the maximum deflection of the interference fringe near the droplet, which we will call $L$. Since this value depends not just on the surface profile, but the droplet’s position relative to the fringe, it cannot provide us with absolute information about the height of the ridge. However, its time evolution still contains useful information about the dynamics of relaxation. Thus, we consider $L(t)/L(0)$, shown in Fig. 4(d). To separate viscoelastic and poroelastic effects, we varied the droplet radii $R$ from 15 to 93 $\mu$m. For droplets with radii less than 50 $\mu$m, the relaxation is size independent, with a characteristic time scale of about 0.1 s, comparable to the viscoelastic relaxation time. Thus, we...
conclude that, with our temporal resolution, viscoelastic dissipation dominates as $\tau_p < \tau_c$.

When $\tau_p > \tau_c$, both poroelastic and viscoelastic processes can possibly govern the relaxation, depending on our experimental time scale. Comparison of the static wetting profile with the interferometric profiles in Fig. 4(f) suggests a fast relaxation of the wetting ridge in $O(0.1 \text{ s})$ after removal of a droplet. However, because the profile of the wetting ridge was too steep to be fully resolved in these early times, our subsequent analysis focused only on longer time behaviours, $t > 0.1 \text{ s}$, which were dominated by poroelasticity.

Now, we reconsider the surface relaxation for large droplets in short time scales ($t < 0.1 \text{ s}$). To circumvent the limitations of imaging steep wetting ridges, we shift our attention to the relaxation of the shallow ‘dimple’ just to either side of the wetting ridge, as indicated in Fig. 4(c). This feature arises due to the near-incompressibility of the gel in combination with the finite thickness of the substrates [32]. While the wetting ridge can only be resolved after $0.2 \text{ s}$, we can resolve the dimple profile throughout the whole relaxation process. Using a 2D phase unwrapping algorithm [33], we measure the decay of the dimple at different locations, as labeled on the interferogram in Fig. 4(e). The relaxation of the dimple at each of these locations is indicated by colored circles in Fig. 4(f). It shows a clear two-step process. For $t > \tau_c \approx 10^{-1} \text{ s}$, the decay of the dimple mirrors the poroelastic relaxations of the wetting ridge (black cross dots). For $t < \tau_c \approx 10^{-1} \text{ s}$, the depth of the dimple decays roughly as $t^{-1/2}$, as expected from the viscoelastic rheology of the gel [13].

Our observation shows signatures of both viscoelastic and poroelastic relaxations on soft gel surfaces. The dominant mechanism is determined by the experimental timescale, the viscoelastic relaxation time, $\tau_v$, and the poroelastic relaxation time, $L_D^2/D^*$. In our dewetting experiments, the full relaxation of the wetting ridge required solvent transport over a length scale $(R h_0)^{1/2}$. Further theoretical analysis is needed to understand the origin of this scaling. Intriguingly, the slow and steady sliding of wetting ridges on the same material has been shown to be limited by the viscoelastic response of the substrate [13]. We see no contradiction with the current results, as a sliding wetting ridge involves no large-scale displacement of material. In that case, we expect $L_D \lesssim h_0$, and correspondingly very short poroelastic relaxation times ($\tau_p \ll \tau_c$).

A closer look at the microscopic origins of the poroelastic diffusion coefficient is further warranted. A simple model combining Darcy flow and rubber elasticity suggests $D^* \sim G_0^1/(k_B T)^{2/3} \mu^{-1}$. While this works very well for hydrogels [34], it underestimates the diffusion coefficient of our soft silicone gels by 60 times. Many factors could contribute to this discrepancy. However, we suspect non-affine deformation of the pore-space or a breakdown of Darcy’s law due to a lack of separation of the structural length scales of the solvent and network. The need for further analysis of the poroelastic response of polymer networks with polymeric solvents is further highlighted by the drastically different responses from nearly identical silicone systems. We completed the fully battery of tests described in the main body of this paper on a second soft silicone gel (Gelest HMS-301) with nearly identical shear rheology and a similar fraction of uncrosslinked chains. Despite these similarities, we saw no evidence of poroelastic response in dewetting experiments (Figs. S5 and S6 in [27]). All of the responses were consistent with a purely viscoelastic response, and a much higher poroelastic diffusion coefficient [35]. Thus, shear rheology alone is a poor predictor of the dynamics of relaxation on soft gels, and further efforts are required to determine the microscopic origins of the poroelastic response of networks with free chains.

We acknowledge Dr. Julien Dervaux, Prof. Anand Jagota and Prof. Michael Loewenberg for useful discussions.
5

[1] U. S. Schwarz and S. A. Safran, Rev. Mod. Phys. 85, 1327 (2013).
[2] D. Gonzalez-Rodriguez, K. Guevorkian, S. Douezan, and F. Brochard-Wyart, Science 338, 910 (2012).
[3] S. Lin, H. Yuk, T. Zhang, G. A. Parada, H. Koo, C. Yu, and X. Zhao, Advanced Materials 28, 4497 (2015).
[4] J. Yang, R. Bai, B. Chen, and Z. Suo, Advanced Functional Materials 0, 1901693 (2019).
[5] G. M. Whitesides, E. Ostuni, S. Takayama, X. Jiang, and D. E. Ingber, Annual Review of Biomedical Engineering 3, 335 (2001).
[6] T. Matsumoto, J.-i. Sasaki, E. Alsberg, H. Egusa, H. Yatani, and T. Sohmura, PloS one 2, e1211 (2007).
[7] R. V. Martinez, A. C. Glavan, C. Keplinger, A. I. Oyetibo, and G. M. Whitesides, Advanced Functional Materials 24, 3003.
[8] K. Khare, J. Zhou, and S. Yang, Langmuir 25, 12794 (2009).
[9] R. W. Style, A. Jagota, C.-Y. Hui, and E. R. Dufresne, Annual Review of Condensed Matter Physics 8, 99 (2017).
[10] B. Andreotti and J. H. Snoeijer, Annual Review of Fluid Mechanics 52, 285 (2020).
[11] A. Carré, J.-C. Gastel, and M. E. R. Shanahan, Nature 379, 432 (1996).
[12] D. Long, A. Ajdari, and L. Leibler, Langmuir 12, 5221 (1996).
[13] S. Karpitschka, S. Das, M. van Gorcum, H. Perrin, B. Andreotti, and J. H. Snoeijer, Nature Communications 6, 7891 (2015).
[14] M. Zhao, J. Dervaux, T. Narita, F. Lequeux, L. Limat, and M. Roché, Proceedings of the National Academy of Sciences 115, 1748 (2018).
[15] M. van Gorcum, B. Andreotti, J. H. Snoeijer, and S. Karpitschka, Phys. Rev. Lett. 121, 208003 (2018).
[16] M. van Gorcum, S. Karpitschka, B. Andreotti, and J. H. Snoeijer, Soft Matter , (2020).
[17] M. A. Biot, Journal of Applied Physics 12, 155 (1941).
[18] E. DETOURNAY and A. H.-D. CHENG, in Analysis and Design Methods, edited by C. FAIRHURST (Pergamon, Oxford, 1993) pp. 113 – 171.
[19] Y. Hu, X. Zhao, J. J. Vlassak, and Z. Suo, Applied Physics Letters 96, 121904 (2010).
[20] S. Cai, Y. Hu, X. Zhao, and Z. Suo, Journal of Applied Physics 108, 113514 (2010).
[21] Y. Hu and Z. Suo, Acta Mechanica Solida Sinica 25, 441 (2012).
[22] M. Zhao, F. Lequeux, T. Narita, M. Roch, L. Limat, and J. Dervaux, Soft Matter 14, 61 (2018).
[23] J. D. Berman, M. Randeria, R. W. Style, Q. Xu, J. R. Nichols, A. J. Duncan, M. Loewenberg, E. R. Dufresne, and K. E. Jensen, Soft Matter 15, 1327 (2019).
[24] K. E. Jensen, R. Sarfati, R. W. Style, R. Boltynskiy, A. Chakrabarti, M. K. Chaudhury, and E. R. Dufresne, Proceedings of the National Academy of Sciences 112, 14400 (2015).
[25] A. Hourlier-Fargette, J. Dervaux, A. Antkowiak, and S. Neukirch, Langmuir 34, 12244 (2018).
[26] A. Dubois, L. Vabre, A.-C. Boccara, and E. Beaurepaire, Appl. Opt. 41, 805 (2002).
[27] See Supplemental Information.
[28] R. Pericet-Cámara, A. Best, H.-J. Butt, and E. Bonacurso, Langmuir 24, 10565 (2008).
[29] R. W. Style and E. R. Dufresne, Soft Matter 8, 7177 (2012).
[30] Q. Xu, K. E. Jensen, R. Boltynskiy, R. Sarfati, R. W. Style, and E. R. Dufresne, Nature Communications 8, 555 (2017).
[31] Y. Hu, E. P. Chan, J. J. Vlassak, and Z. Suo, Journal of Applied Physics 110, 086103 (2011).
[32] R. W. Style, R. Boltynskiy, Y. Che, J. S. Wettlaufer, L. A. Wilen, and E. R. Dufresne, Phys. Rev. Lett. 110, 066103 (2013).
[33] M. Takeda, H. Ina, and S. Kobayashi, J. Opt. Soc. Am. 72, 156 (1982).
[34] Y. Hu, X. Chen, G. M. Whitesides, J. J. Vlassak, and Z. Suo, Journal of Materials Research 26, 785795 (2011).
[35] J. D. Berman, M. Randeria, R. W. Style, Q. Xu, J. R. Nichols, A. J. Duncan, M. Loewenberg, E. R. Dufresne, and K. E. Jensen, Soft matter 15, 1327 (2019).