Poroelastic relaxation indentation of thin layers of gels

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We develop a method of poroelastic relaxation indentation (PRI) to characterize thin layers of gels. The solution to the time-dependent boundary-value problem is obtained in a remarkably simple form, so that the force-relaxation curve obtained by indenting a gel readily determines all the poroelastic constants of the gel—the shear modulus, Poisson's ratio, and the effective diffusivity. The method is demonstrated with a layer of polydimethylsiloxane immersed in heptane. © *2011 American Institute of Physics*. [doi:10.1063/1.3647758]

Gels made of crosslinked polymer network and mobile molecules are used in diverse applications, including drug delivery,[1–3] tissue engineering,[4,5] microfluidics,[6,7] and fuel cells.[8] The behavior of the gels changes readily with solvent-polymer chemistry, temperature, concentration of solutes, etc. Gels are poroelastic, involving coupled migration of the solvent and stretching of the network. Experimental characterization of their poroelasticity is challenging.

Recent studies have demonstrated that the poroelasticity of gels can be characterized by indentation.[9–13] Indentation is easy to apply and is capable of probing local properties. To characterize the time-dependent behavior of a material, methods of indentation include pressing the indenter at a constant velocity, or at a constant force, or with oscillating depths, or to a fixed depth. Here we focus on a particular method called the poroelastic relaxation indentation (PRI).[13–15] After the indenter is pressed into a gel to a fixed depth, the force on the indenter relaxes as the solvent in the gel migrates. The solution to the poroelastic boundary-value problem takes a remarkably simple form, so that the force-relaxation curve is readily used to extract the shear modulus, Poisson's ratio and the effective diffusivity of the gel.[13] The measured poroelastic constants of a gel can be correlated with its molecular properties.[16] The results obtained from the PRI agree well with those obtained from a compression test.[17] The PRI has been applied to alginate hydrogels,[13,17] polydimethylsiloxane (PDMS) swollen with organic solvents,[16] and a *p*H-sensitive hydrogel.[18] The method has been demonstrated with conical and spherical indenters.[13,16] The depth of indentation has ranged from micrometers to millimeters, and the time of indentation from seconds to hours.[19]

The PRI developed so far assumes that the radius of contact is much smaller than the size of gels. Many applications, however, use gels in the form of thin layers. Examples include coatings for biocompatible surfaces, membranes for fuel cells, and small samples of biological tissues. In this paper, we develop the PRI to characterize gels of thickness comparable to, or smaller than, the contact radius. Once again we obtain the poroelastic solution in a simple form.

We then demonstrate the method of indentation with a thin layer of PDMS immersed in heptane.

We adopt a theory of poroelasticity suitable for polymer gels.[11,13,14,20] Specifically, both the network and the solvent are taken to be incompressible, so that the change in the volume of the gel is entirely due to the change in the concentration of the solvent. The theory characterizes a gel by three poroelastic constants: the shear modulus G, Poisson's ratio ν, and the effective diffusivity D.

Figure 1 illustrates the method of PRI. A gel of thickness d is placed on a substrate. A spherical indenter, radius R, is pressed into the gel to a depth h, forming a contact radius a. Both the substrate and the indenter are rigid, impermeable, and frictionless. Subsequently, the indentation depth is kept constant and the force is recorded as a function of time, $F(t)$. The object is to use the force-relaxation curve $F(t)$ to obtain the poroelastic constants of the gel.

We first consider the indentation of an elastic material placed on a rigid substrate.[21–27] From theoretical analysis given by Yu *et al.*,[27] we observe that when both the substrate and the indenter are rigid and frictionless, the contact radius and the force take the following forms:

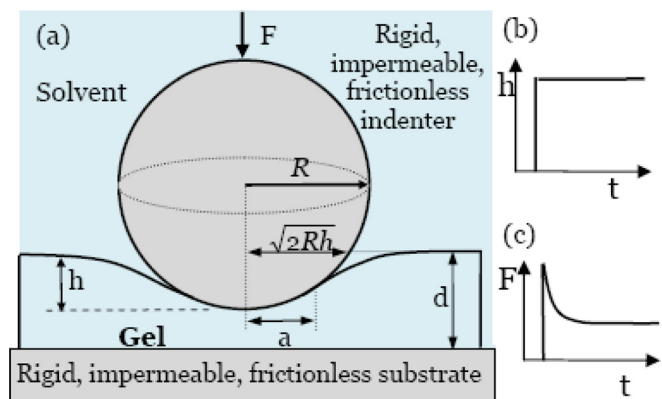$$a = \sqrt{Rh} \cdot l\left(\sqrt{Rh}/d\right), \tag{1}$$

FIG. 1. (Color online) (a) Schematic of the experimental setup. (b) The depth of indentation is kept constant. (c) The force on the indentor is recorded as a function of time.

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$$F = \frac{8Gh\sqrt{Rh}}{3(1-\nu)} \cdot f\left(\sqrt{Rh}/d\right). \tag{2}$$

In other words, the dimensionless functions $l(x)$ and $f(x)$ are independent of Poisson's ratio. When the contact radius is much smaller than the gel thickness, $\sqrt{Rh}/d \to 0$, the Hertzian contact is approached, so that $a \to \sqrt{Rh}$ and $F \to 8Gh\sqrt{Rh}/3(1-\nu)$. When the contact radius is much larger than the thickness of the gel, $\sqrt{Rh}/d \to \infty$, the contact radius approaches the radius of a spherical cap of height h, so that $a \to \sqrt{2Rh}$; see Fig. 1(a). In this case, we solve the elastic boundary-value problem analytically, and obtain $F \to 2\pi Gh^2R/3d(1-\nu)$. For intermediate values of $\sqrt{Rh}/d$, we solve a Fredholm integral equation numerically,[27,28] and plot the two functions $l(x)$ and $f(x)$ in Fig. 2. Also included in the figure are the fitting formulas of the functions.

We next consider the indentation of a layer of a poroelastic gel on a rigid substrate. Instantaneously after the indenter is pressed into the gel, the solvent in the gel does not have time to migrate, and the gel behaves like an incompressible elastic solid. Setting $\nu = 1/2$ in Eq. (2), we obtain the short-time limit:

$$F(0) = \frac{16Gh\sqrt{Rh}}{3} \cdot f\left(\sqrt{Rh}/d\right). \tag{3}$$

After the indenter is held at the fixed depth for a long time, the solvent in the gel redistribute into a state of equilibrium, which is the same as that for a compressible elastic material.[11,13,14,20] Consequently, the long-time limit takes the same form as Eq. (2), namely,

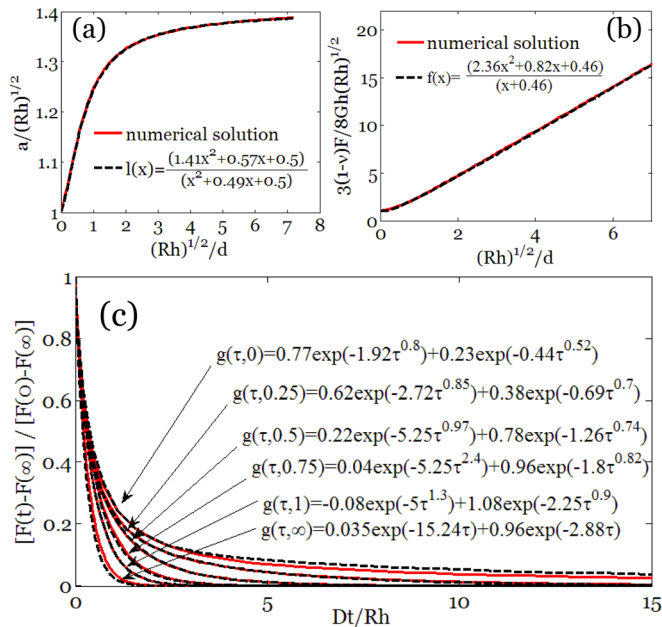$$F(\infty) = \frac{8Gh\sqrt{Rh}}{3(1-\nu)} \cdot f\left(\sqrt{Rh}/d\right). \tag{4}$$

FIG. 2. (Color online) (a) The normalized radius of contact is plotted as a function of $\sqrt{Rh}/d$. (b) The normalized force on the indenter is plotted as a function of $\sqrt{Rh}/d$. (c) The normalized force is plotted as a function of the normalized time for several values of $\sqrt{Rh}/d$. The red curves are numerical results. The black dashed curves are curve fits to the numerical results.
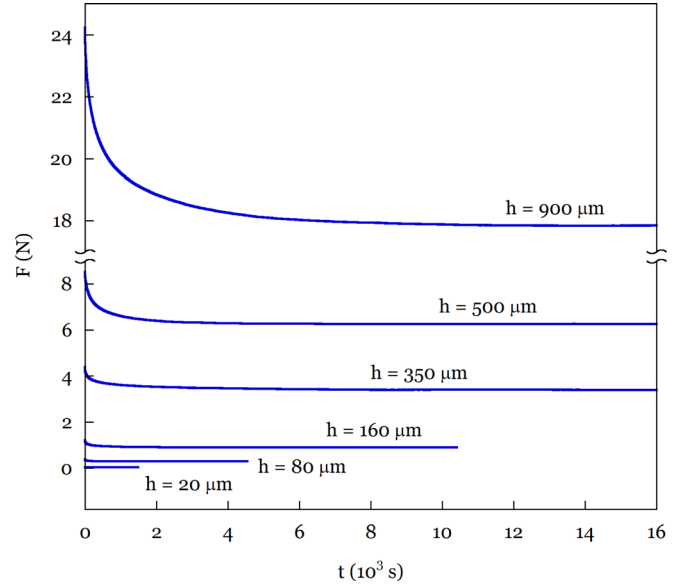

FIG. 3. (Color online) The experimentally recorded force as a function of time $F(t)$ for six depths of indentation.

We solve the poroelastic problem by using the finite-element software ABAQUS. The numerical results show that the force-relaxation curve $F(t)$ can be written in the form:

$$\frac{F(t) - F(\infty)}{F(0) - F(\infty)} = g\left(\frac{Dt}{Rh}, \frac{\sqrt{Rh}}{d}\right). \tag{5}$$

In other words, the dimensionless function $g(\tau, x)$ is independent of Poisson's ratio. Numerical results of $g(\tau, x)$ are plotted in Fig. 2(c). All other variables being fixed, the thinner the gel, the faster it relaxes. When the contact radius is much smaller than the gel thickness, $\sqrt{Rh}/d \to 0$, substrate effect is negligible. We fit the numerical results for this case to a formula, listed in Fig. 2(c), which provides a slightly better fit than the one given in our previous paper.[13] Individual expressions for $\sqrt{Rh}/d = 0.25$, 0.5, 0.75, and 1 are also included. When the contact radius is much larger than the gel thickness, $\sqrt{Rh}/d \to \infty$, the solvent flux is confined in the radial direction in the gel. In this case Here, we solve the poroelastic problem analytically by using the method of separation of variables,[17] giving
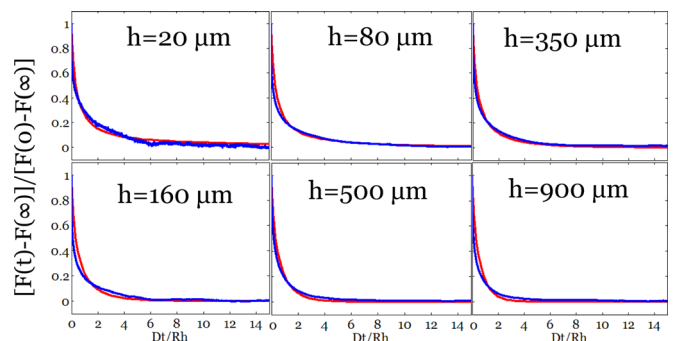

FIG. 4. (Color online) The force-relaxation curves recorded in the six runs of the experiment are compared with the function $g(Dt/Rh, \sqrt{Rh}/d)$ obtained from the theory of poroelasticity.

TABLE I. Poroelastic constants obtained from six runs of the experiment.

H (μm)	20	80	160	350	500	900
G (kPa)	684	750	759	732	766	767
ν	0.40	0.33	0.33	0.35	0.32	0.32
D (10^{-9} m^2/s)	2.9	2.9	3.3	3.2	3.1	3.0

$$g(\tau,\infty) = \sum_{n=1}^{\infty} \frac{16}{\lambda_n^3} \frac{J_2(\lambda_n)}{J_1(\lambda_n)} \exp\left(-\frac{\lambda_n^2}{2}\tau\right), \qquad (6)$$

where λ_n are the roots of $J_0(\lambda) = 0$, and $J_i(x)$ are the Bessel functions of the first kind. The infinite series (6) is accurately represented by the first two terms listed in Fig. 2(c). Note that the numerical results closely approach the analytical result, $g(\tau,\infty)$, when $\sqrt{Rh}/d \geq 1.5$. For instance, the maximum deviation between the numerical curve at $\sqrt{Rh}/d = 1.5$ and $g(\tau,\infty)$ is only 3% of the full range.

To demonstrate this method of indentation PRI, we indent a layer of PDMS immersed in heptane, with thickness d = 3.96 mm in the fully swollen state. Much of the experimental detail follows our previous paper.[16] Here, A stainless-steel spherical indenter, radius $R = 10$ mm, is pressed into the PDMS gel to six depths $h = 20$, 80, 160, 350, 500, and 900 μm, corresponding to $\sqrt{Rh}/d = 0.11, 0.23, 0.32, 0.47, 0.56, 0.76$. The recorded force-relaxation curves are given in Fig. 3. As expected both the magnitudes of the force and the relaxation time varies with the indentation depth.

The shear modulus of the gel is extracted by using Eq. (3) from $F(0)$ recorded in each experiment. Equations (3) and (5) give $F(0)/F(\infty) = 2(1 - \nu)$. This relation is used to extract Poisson's ratio of the gel by using the value $F(0)/F(\infty)$ recorded in each run of the experiment. Figure 4 plots each force-relaxation curve again, with the force normalized as $[F(t) - F(\infty)]/[F(0) - F(\infty)]$, and the time normalized as Dt/Rh. A value of the effective diffusivity D is determined such that the curve in each experiment fits $g(\tau,x)$.

Table I lists the shear modulus, Poisson's ratio, and the effective diffusivity determined by the above procedure. The average values are $G = 740 \pm 30$ kPa, $\nu = 0.34 \pm 0.03$ and $D = (3.1 \pm 0.2) \times 10^{-9}$ m^2/s, which are are consistent with values reported previously.[16] This agreement confirms that the method of indentation PRI works well for both thick and thin layers of gels.

In summary, we have developed a method of indentation to determine the poroelastic constants of thin gel layers. The method is demonstrated with PDMS saturated with heptane. We will report in a separate paper the application of the method PRI to characterize the poroelastic relaxation of hydrogel layers of different thicknesses.[29] The ease of use of PRI should enable quantitative characterization of thin layers of gels and tissues.

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