Bending of gel beams: method for characterizing elastic properties and permeability

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When a saturated gel is deformed, its mechanical response is profoundly influenced by the flow of liquid in its pores. For example, if a gel bar is suddenly deformed in 3-point bending, the liquid cannot immediately flow out of the pores, so the gel initially responds incompressibly; consequently, its deflection provides a measure of its shear modulus, \( G_p \), rather than Young's modulus, \( E_p \). In this paper, the kinetics of deformation of such a rod are analyzed, showing that it is possible to obtain the permeability, \( D \), of the gel from the time-dependence of the load, as well as finding both \( G_p \) and \( E_p \). Analyses are presented for the time dependence of the load at constant deflection for a square and cylindrical beam, and for load at constant deflection rate for a square beam. The method is applied to determine \( G_p \), \( E_p \), and \( D \) for a silica gel made from tetraethoxysilane.

1. Introduction

It necessary to know the viscosity and/or elastic modulus and Poisson’s ratio of a gel in order to analyze the drying stresses [1] or the thermal expansion kinetics [2]. For an ordinary solid, the elastic modulus can be obtained by measuring the load required to produce a certain deflection. To measure the modulus of a gel requires consideration of the movement of liquid in the pores [3,4], because part of the applied load is supported by the liquid, and part by the solid network, when a gel is deformed. To measure the properties of the solid phase, the load must be sustained until flow of the liquid allows the pressure in the liquid to drop to zero, and the load to be transferred entirely to the solid network. If a constant strain is imposed on a gel, the load decreases with time as the liquid flows, and this load relaxation resembles a viscoelastic response, even if the network is purely elastic. There may also be a true viscoelastic response if the network is viscoelastic, and such behavior has been observed [3] in silica gels whose pores are full of the mother liquor (i.e., the liquid from which the gel was produced). This is attributed to chemorheology, which means chemical attack on strained bonds in the network. As we shall see, this behavior is observed when silica gels contain water, but not when they contain pure ethanol or acetone, presumably because the latter liquids are chemically inert with respect to the network.

In this work, we are interested in the apparent viscoelastic response produced by fluid movement within a purely elastic gel network. We will determine the time dependence of the load on a beam subjected to a constant deflection, and show that this experiment can yield both Young’s modulus and Poisson’s ratio for the network. Moreover, the rate of load relaxation can be used to determine the permeability of the network. We also examine the case of a constant deflection rate, and establish the dependence of the apparent modulus on the strain rate.

In section 2, we analyze the deformation of a porous beam whose pores are filled with an incompressible liquid (as in a saturated gel). Solutions are presented for load decay under constant...
deflection for square and cylindrical beams. In section 3, we find the load produced under a constant deflection rate, and establish the difference between the apparent and true elastic modulus. Experimental results for a two-step base-catalyzed silica gel are presented in sections 4 and 5. It is demonstrated that the gel is purely elastic when the pores are full of ethanol or acetone, but is viscoelastic when it contains water. The rate of load relaxation is shown to depend on the size of the bar and the viscosity of the pore fluid in the manner predicted by the theory. Moreover, the permeability determined by the beam-bending method is shown to agree with that found from the thermal expansion method [2].

2. Constant deflection of a beam

2.1. Strain and curvature

The stresses and strains in an elastic beam subjected to 3-point bending are found in standard textbooks [5]. What makes the present problem novel is that the constitutive equations include a term for the pressure in the liquid in the pores [1]:

\[ \varepsilon_x = \frac{1}{E_p} \left[ \sigma_x - \nu_p (\sigma_y + \sigma_z) \right] - \frac{P}{3K_p}, \]  
\[ \varepsilon_y = \frac{1}{E_p} \left[ \sigma_y - \nu_p (\sigma_x + \sigma_z) \right] - \frac{P}{3K_p}, \]  
\[ \varepsilon_z = \frac{1}{E_p} \left[ \sigma_z - \nu_p (\sigma_x + \sigma_y) \right] - \frac{P}{3K_p}, \]

where \( \varepsilon_x, \varepsilon_y, \varepsilon_z \) and \( \sigma_x, \sigma_y, \sigma_z \) are the principal strains and total stresses, \( E_p \) is Young’s modulus, and \( \nu_p \) is Poisson’s ratio for the porous network; that is, these are the properties that one would measure if the liquid were drained from the pores (i.e., if the pressure were reduced to zero). Total stresses represent the sum of forces on the liquid and solid phases on a cross-section divided by the area of the section [1]. The stress in the liquid is \( P \) (defined as positive when tensile, so it is a stress, differing from the pressure only in sign) and \( K_p \) is the bulk modulus of the drained network. The bulk and shear moduli of the network are defined by

\[ K_p = \frac{E_p}{3(1 - 2\nu_p)}, \]  
\[ G_p = \frac{E_p}{2(1 + \nu_p)}. \]

These constitutive equations, originally developed by Biot [6], treat the gel as a two-phase porous material. The application of these equations to gels has been discussed by Johnson and co-worker [7,8]; they are equivalent to those used by Tanaka and co-workers [9,10] to study the mechanics of polyacrylamide gels.

The bending of a beam of depth, \( 2a \), and length, \( L \), is shown schematically in fig. 1. The neutral axis is a plane whose length, \( L \), in the \( z \)-direction is not changed by the deflection; planes above the axis are compressed (\( \varepsilon_z < 0 \)) and those below are stretched. The (negative) deflection, \( X(z) \), has its maximum absolute value, \( |X(L/2)| = \Delta \), at the midpoint of the beam; the radius of curvature, \( \rho(z) \), is positive when the beam is concave up. For simple beam theory to apply, we must have \( \rho \gg L \), so the curvature as drawn is highly exaggerated. The axial strain in
the beam is related to the radius of curvature by ([5], p. 381)
\[ \varepsilon_z = -x/\rho, \] (3)
where \( x \) is the distance from the neutral axis. This is a purely geometrical relationship, independent of the constitutive behavior of the beam. We now proceed to find \( \Delta \) and \( \rho \) for the gel beam.

In the beam, \( \sigma_x = \sigma_y = 0 \), so the volumetric strain, \( \varepsilon \), found from eq. (1), is
\[ \varepsilon = \varepsilon_x + \varepsilon_y + \varepsilon_z = (\sigma_z - 3P)/(3K_p). \] (4)

At the time \( t = 0 \), when the deflection \( \Delta \) is instantaneously applied, the beam is incompressible, because the liquid is not able to flow instantly from the pores. Therefore \( \varepsilon_0 = 0 \) (where the subscript 0 indicates an initial value here and throughout the paper), and eq. (4) indicates that
\[ P(x, y, z, 0) = \sigma_0/3. \] (5)

Substituting eq. (5) into eq. (1c), we find after some rearrangement
\[ \sigma_{z0} = 3G_p \varepsilon_{z0} = -3G_p x/\rho_0, \] (6)
where the second equality follows from eq. (3), and \( \rho_0 \) is the initial radius of curvature. The bending moment of the beam is related to the total stress by ([5], p. 183)
\[ M = -\int_A \sigma_z x \, dA, \] (7)
where the integral is taken over the cross-sectional area of the beam. From eqs. (6) and (7), the initial moment is found to be
\[ M_0 = \frac{3G_p}{\rho_0} \int_A x^2 \, dA = \frac{3G_p I}{\rho_0}, \] (8)
where \( I \) is the moment of inertia of the beam. For a point load on a simply supported beam, the bending moment is ([5], p. 396)
\[ M = Wz/2. \] (9)
Both the bending moment and the load are positive quantities. The radius of curvature is related to the deflection by
\[ \frac{1}{\rho} = \frac{d^2 X}{dz^2}, \] (10) so eqs. (8)–(10) indicate that the initial load and deflection are related by
\[ \frac{W_0 z}{6G_p I} = \frac{d^2 X_0}{dz^2}. \] (11)

There is no deflection at the support, so \( X = 0 \) when \( z = 0 \), and symmetry requires that \( dX/dz = 0 \) when \( z = L/2 \), so the solution of eq. (11) for \( 0 \leq z \leq L/2 \) is
\[ X_0(z) = \frac{W_0(4z^3 - 3L^2z)}{144G_p I}. \] (12)

The initial maximum deflection (here defined as positive) is therefore
\[ \Delta_0 = |X_0(L/2)| = \frac{W_0 L^3}{144G_p I} \] (13)
and, from eqs. (10) and (12), the initial curvature is
\[ \frac{1}{\rho_0} = \frac{24\Delta_0 z}{L^3}. \] (14)

As time goes on, the liquid flows until the pressure goes to zero; then eq. (1) reduces to the usual constitutive relation for an elastic beam, and the standard analysis applies. The final deflection is then known to be ([5], p. 397)
\[ \Delta_\infty = \frac{W_\infty L^3}{48E_p I} \] (15)
and the final curvature is
\[ \frac{1}{\rho_\infty} = \frac{W_\infty z}{2E_p I}. \] (16)

Since the deflection is held constant, \( \Delta_0 = \Delta_\infty \), we find from eqs. (13) and (15) that
\[ \frac{W_\infty}{W_0} = \frac{E_p}{3G_p} = \frac{2(1 + \nu_p)}{3}, \] (17)
so that a comparison of the initial and final loads gives a measure of Poisson’s ratio. Substituting from eq. (17) into eq. (16), we find that the initial and final curvatures are identical (so we henceforth drop the subscript 0 on \( \Delta \) and \( \epsilon_z \)). Consequently, the axial strain is independent of time,
and is given by eqs. (3) and (14):
\[ \varepsilon_z = - \frac{24 \Delta x z}{L^3} \] (18)
and the maximum strain, which occurs at the midpoint \((z = L/2)\) of the beam, is
\[ \varepsilon_z = - \frac{12 \Delta x}{L^2}. \] (19)

2.2. Continuity equation

Equation (17) shows that the load varies by a factor of \(2(1 + \nu_p)/3\) as the pressure in the pore liquid drops toward zero. To calculate the kinetics of the relaxation of the load, we need to know \(P(x, y, z, t)\), which we obtain from the continuity equation [1]:
\[ -\dot{\varepsilon} = \frac{D}{\eta_L} \nabla^2 P, \] (20)
where the volumetric strain is given by eq. (4) and the superscript dot indicates a derivative with respect to time throughout this paper. The viscosity of the liquid in the pores is \(\eta_L\), and the permeability, \(D\), is defined by Darcy's law [1,11]:
\[ J = \frac{D}{\eta_L} \nabla P, \] (21)
which states that the flux of liquid, \(J\), is proportional to the gradient in stress in the liquid. In the following analysis, we will ignore flow of liquid along the axis of the beam, because it is assumed to be so much longer than it is thick that virtually all of the flow will be normal to the axis. The strain is given by eq. (18), so the stress is found from eq. (1c) to be
\[ \sigma_z(x, y, z, t) = -\frac{24 \Delta E_p x z}{L^3} \]
\[ + (1 - 2\nu_p)P(x, y, z, t) \] (22)
and the moment is found from eq. (7) to be
\[ M(t) = \frac{24 \Delta E_p L}{L^3} \]
\[ - (1 - 2\nu_p) \int_A P(x, y, z, t)x \, dA. \] (23)
The initial moment is found from eqs. (8) and (14) to be
\[ M(0) = \frac{72 G_p \Delta I_z}{L^3}. \] (24)
According to eq. (9), the load is related to the moment by
\[ W(t) = 2M(t)/z, \] (25)
so, using eqs. (23)-(25), we find
\[ \frac{W(t)}{W(0)} = \frac{2(1 + \nu_p)}{3} \]
\[ - \frac{(1 - 2\nu_p)L^3}{72 G_p \Delta I_z} \int_A P(x, y, z, t)x \, dA. \] (26)
Now we must find the stress in the liquid, \(P\).

From eqs. (4) and (22), we find that
\[ \varepsilon = -\frac{24 \Delta (1 - 2\nu_p) x z}{L^3} \]
\[ - \frac{(1 - 2\nu_p)P(x, y, z, t)}{G_p}, \] (27)
Since the deflection \(\Delta = \text{constant}\),
\[ \dot{\varepsilon} = -\frac{(1 - 2\nu_p)\dot{\dot{P}}}{G_p} \] (28)
and eq. (20) becomes
\[ \frac{D}{\eta_L} \nabla^2 P = \frac{(1 - 2\nu_p)\dot{\dot{P}}}{G_p}. \] (29)
We will now solve this equation for square and cylindrical beams.

2.3. Square beam

For a beam with a square cross-section having edge length \(2a\), eq. (29) becomes
\[ \frac{\partial P}{\partial \theta} = \frac{\delta^2 P}{\delta v^2} + \frac{\delta^2 P}{\delta w^2}, \] (30)
where we have introduced the dimensionless variables \(v = x/a\), \(w = y/a\), and \(\theta = t/T_o\), where the
relaxation time is defined as
\[ \tau_b = \eta_L a^2 (1 - 2\nu_p) / D G_p. \] (31)
The moment of inertia of the square beam is
\[ I = 4a^4 / 3 \] [12]. The initial condition is, from eqs. (5), (6), and (14),
\[ P(v, w, z, 0) = p_0 v, \] (32)
where
\[ p_0 = -24G_p a\Delta z / L^3. \] (33)
At the surface of the rod, the liquid escapes freely, so the pressure is always zero there; therefore the boundary conditions are
\[ P(\pm 1, w, z, \theta) = P(v, \pm 1, z, \theta) = 0. \] (34)
Fortunately, eq. (30) has the form of the heat flow equation, so solutions can be found from standard reference books [13]. For the present conditions, it is known ([13], p. 33) that the solution has the form
\[ P(v, w, z, \theta) = P_1(v, z, \theta) P_2(w, \theta), \] (35)
where
\[ \frac{\partial P_1}{\partial \theta} = \frac{\partial^2 P_1}{\partial v^2}. \] (36)
subject to the conditions
\[ P_1(v, z, 0) = p_0 v \] (37a)
\[ P_1(\pm 1, z, \theta) = 0, \] (37b)
and
\[ \frac{\partial P_2}{\partial \theta} = \frac{\partial^2 P_2}{\partial w^2}. \] (38)
subject to the conditions
\[ P_2(w, 0) = 1 \] (39a)
\[ P_2(\pm 1, \theta) = 0. \] (39b)
The result for \( P_1 \) is ([13], p. 96)
\[ P_1(v, z, \theta) = -p_0 \left( \frac{2}{\pi} \right) \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin(n\pi v) \]
\[ \times \exp(-n^2\pi^2\theta) \] (40)
and for \( P_2 \) is ([13], p. 97)
\[ P_2(w, \theta) = - \left( \frac{4}{\pi} \right) \sum_{m=1}^{\infty} \frac{(-1)^m}{2m-1} \]
\[ \times \cos \left( \frac{(2m-1)\pi w}{2} \right) \]
\[ \times \exp \left[ -\frac{(2m-1)^2\pi^2\theta}{4} \right]. \] (41)
For the square beam, the integral in eq. (26) becomes
\[ \int_A P_x \, dA = a^3 \int_{-1}^{1} \int_{-1}^{1} P(v, w, z, \theta) v \, dv \, dw \]
\[ = a^3 \rho_0 \left( \frac{64}{\pi^3} \right) S_1(\theta) S_2(\theta), \] (42b)
where
\[ S_1(\theta) = \sum_{n=-\infty}^{\infty} n^{-2} \exp(-n^2\pi^2\theta) \] (43)
and
\[ S_2(\theta) = \sum_{m=1}^{\infty} \frac{1}{(2m-1)^2} \exp \left[ -\frac{(2m-1)^2\pi^2\theta}{4} \right]. \] (44)
The initial values of these sums are [14] \( S_1(0) = \pi^2/6 \) and \( S_2(0) = \pi^2/8 \).
From eqs. (26) and (42b), we find that the kinetics of load decay for the square beam are described by
\[ \frac{W(\theta)}{W(0)} = \frac{2(1+\nu_p)}{3} + \frac{16(1-2\nu_p)}{\pi^4} S_1(\theta) S_2(\theta). \] (45)
This function is presented in fig. 2, along with the following approximation (obtained by solving eq. (30) using the Laplace transform, as in appendix A of ref. [15]):
\[ \frac{W(\theta)}{W(0)} \approx 1 - (1-2\nu_p) \]
\[ \times \left[ \frac{8}{3\sqrt{\pi}} \theta^{1/2} - \left( 1 + \frac{4}{\pi} \right) \theta + \frac{2}{\sqrt{\pi}} \theta^{3/2} \right], \]
\[ \theta \leq 0.3. \] (46)
The approximation is seriously in error for \( \theta > 0.8 \), but is excellent for \( \theta \leq 0.3 \), where most of the relaxation takes place.

### 2.4. Cylindrical beam

For a beam with a circular cross-section with radius \( a \), eq. (29) becomes

\[
\dot{P}(u, \phi, z, 0) = -2 \dot{\phi} \sin \phi \frac{\partial P}{\partial \phi} - \frac{1}{u} \frac{\partial P}{\partial u} + \frac{1}{u^2} \frac{\partial^2 P}{\partial \phi^2},
\]

where \( u = r/a \), \( r \) is the radial coordinate, and \( \phi \) is the polar angle; the load is applied at \( u = 1 \), \( \phi = \pi/2 \), \( z = L/2 \). In this case, the moment of inertia of the beam is \( I = \pi a^4/4 \) [12]. The initial and boundary conditions are

\[
P(u, \phi, z, 0) = p_0 u \sin \phi
\]

\[
P(1, \phi, z, \theta) = 0,
\]

where \( p_0 \) is the constant defined in eq. (33). The solution is given by ([13], p. 210)

\[
P(u, \phi, z, \theta) = -2p_0 \sin \phi \sum_{n=1}^{\infty} \frac{J_1(\beta_n u)}{\beta_n J_0(\beta_n)} \times \exp(-\beta_n^2 \theta),
\]

where \( J_0 \) and \( J_1 \) are Bessel's functions of the first kind of order 0 and 1, respectively, and the constants \( \beta_n \) are the roots of

\[
J_1(\beta_n) = 0.
\]

The integral in eq. (26) becomes

\[
\int_A P \, dA = a^3 \int_0^1 \int_0^{2\pi} P(u, \phi, z, \theta) u^2 \times \sin \phi \, d\phi \, du
\]

\[
= 2\pi a^3 p_0 S_0(\theta),
\]

where

\[
S_0(\theta) = \sum_{n=1}^{\infty} \beta_n^{-2} e^{-\beta_n^2 \theta}.
\]

Numerical evaluation indicates that \( S_0(0) \approx 1/8 \), and this seems to be an exact result.

From eqs. (26) and (51b), we find that the kinetics of load decay for the cylindrical beam are described by

\[
\frac{W(\theta)}{W(0)} = \frac{2(1 + \nu_\nu)}{3} + \frac{8(1 - 2\nu_\nu)}{3} S_0(\theta).
\]

This function is presented in fig. 3, where it is seen to be remarkably similar to the result ob-
Fig. 4. Relaxation function for cylindrical beam, with data for times < \( \theta_i \) discarded, and the curve normalized by \( W(\theta) \).

Note that the initial relaxation of the load is extremely rapid, so an accurate measurement of that part of the curve would be difficult. This point is illustrated in fig. 4, where data from fig. 3 for times shorter than \( \theta_i \) have been discarded and the data are normalized by \( W(\theta_i) \). This simulates the data that would be obtained if the measurements began shortly after the deflection of the beam was achieved, and the data were normalized by the first measured value. The shapes of the curves give no clue that data have been lost, but the plateau value shifts considerably, even for the small values of \( \theta_i \) used, so an attempt to apply eq. (17) would result in an erroneous value for \( v_\rho \). Fortunately, as shown in fig. 5, when the erroneous curves are plotted against the square root of time, they appear concave down at short times. This type of plot could be used in practice to assure that no data have been lost: if the curves are concave up when plotted against \( \sqrt{\theta} \), then the data at short times have been captured.

3. Moving crosshead

The preceding analyses assume that the crosshead descends instantaneously to produce a certain deflection, and that no liquid flows from the bar during the descent. In real instruments there will obviously be a finite rate of descent, so we now examine the effect of deflection rate, \( \Delta \), on the measured load. The continuity equation is different in this case, because \( \Delta \) is not constant. From eq. (27),

\[
\dot{\varepsilon} = -\frac{24(1 - 2\nu_p)xz\Delta}{L^3} - \frac{(1 - 2\nu_p)P}{G_p},
\]

so eq. (20) becomes

\[
\nabla^2 P - cv = \partial P/\partial \theta,
\]

where

\[
c = 24G_paz/\Delta/\tau_b/L^3.
\]

For a square beam, the boundary conditions are given by eq. (34), and the initial condition is \( P(v, w, z, 0) = 0 \). The solution is obtained by taking the Laplace transform of eq. (56) with respect
to $\theta$, then expanding the transformed variable in a double Fourier sine series. The result is

$$P(v, w, z, \theta) = -4c \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{(-1)^m (-1)^n \sin(v A_m) \cos(w B_n)}{\sqrt{A_m B_n (A_m + B_n)}} \times \{1 - \exp[-(A_m + B_n) \theta]\}, \quad (58)$$

where

$$A_m = (m \pi)^2, \quad (59a)$$

$$B_n = [(2n - 1) \pi/2]^2. \quad (59b)$$

From eq. (58) it can be seen that

$$\frac{\partial P}{\partial \theta} \bigg|_{\theta=0} = \left(\frac{2c}{\pi}\right) \sum_{m=1}^{\infty} \frac{(-1)^m}{m} \sin(m \pi v) = -c v \quad (60)$$

(where the second equality follows from the demonstrable fact that the sum is the sine series expansion for $v$). Thus, at short times, the stress in the liquid is

$$P(v, w, z, \theta) \approx -c v \theta \quad (61)$$

which is the same as eq. (32), since $\Delta = \Delta t = \Delta \tau_0 \theta$. Equation (42a) becomes, with eq. (58),

$$\int_{-1}^{1} \int_{-1}^{1} P_{v} \, dv \, dw = -\frac{4}{3}c S_3(\theta),$$

where

$$S_3(\theta) = 12 \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1 - \exp[-(A_m + B_n) \theta]}{A_m B_n (A_m + B_n)}. \quad (63)$$

At long times,

$$\lim_{\theta \to \infty} S_3(\theta) = 12 \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{A_m B_n (A_m + B_n)} \quad (64a)$$

$$= \frac{1}{15} - 6 \sum_{m=1}^{\infty} \frac{\tanh(m \pi)}{(m \pi)^5} \approx 0.015469718. \quad (64b)$$

The load required to create the deflection is found from eqs. (23), (25), and (62):

$$W(\theta) = \frac{48 A E_p I}{L^3} \left[1 + \frac{(1 - 2v_p)}{2(1 + v_p)} \frac{S_3(\theta)}{\theta}\right]. \quad (65)$$

As shown in fig. 6, to a very high degree of approximation,

$$S_3(\theta)/\theta \approx 1 - 301/2 + 3.360 - 1.3203/2, \quad 0 < 1, \quad (66)$$

so when $\theta$ is small $S_3(\theta)/\theta \to 1$ and eq. (65) becomes equivalent to eq. (13). That is, as indicated by eq. (61), the initial response as the crosshead descends is the same as for an instantaneous deflection (because the liquid does not begin to flow from the bar until a pressure gradient develops, and in the meantime the beam is incompressible). If the bar is assumed to behave in a normal elastic manner (i.e., if one neglects the effect of fluid flow), then an apparent modulus, $E_p^A$, is obtained by naive application of eq. (15). This is related to the true modulus, found from eq. (65), by

$$E_p^A = E_p \left[1 + \frac{(1 - 2v_p)}{2(1 + v_p)} \frac{S_3(\theta)}{\theta}\right] \quad (66)$$

$$\approx \begin{cases} 3G_p, & \theta \to 0, \\ E_p, & \theta \to \infty. \end{cases} \quad (67)$$

Fig. 6. The quantity $S_3(\theta)$, from eq. (63), divided by the reduced time, $\theta$; the dashed curve (barely visible) is the approximation given by eq. (66).
When \( \nu_p = 0.2 \), the error in \( E_p^A \) is <5% when \( \theta > 0.2 \).

For the experiment to approximate the instantaneous deflection that was supposed in the preceding sections, the load must be close to the value given by eq. (13). The error produced by a finite speed of descent is found from eqs. (13) and (65):

\[
\frac{W_0 - W(\theta)}{W_0} = \frac{(1 - 2\nu_p)}{3} \left[ 1 - S_j(\theta) \right].
\]

As shown in fig. 7 (where it is assumed that \( \nu_p = 0.2 \)), an error of 5% in \( W \) accumulates if the time required to produce the deflection is \( \theta = 0.0085 \); to have <1% error, the deflection must be produced before \( \theta = 0.0003 \). A 5% error in \( W \) leads to ~30% error in the apparent value of \( \nu_p \) [from eq. (17)] because of the large shift in the plateau value (shown in fig. 4).

4. Experimental procedure

4.1. Gel preparation

The silica gel studied in this work was of a type known as B2 [16]; the methods for sample preparation and measurement of the modulus are similar to those described in ref. [4]. The samples were made by a two-step hydrolysis process, where the initial hydrolysis of tetraethoxysilane (TEOS) is achieved using acid catalysis and a substoichiometric amount of water; then the final hydrolysis is performed using additional water with a basic catalyst. The initial hydrolysis is performed during refluxing for 1.5 h in a solution (pH = 0.3) with molar ratio \( \text{TEOS} / \text{H}_2\text{O} / \text{C}_2\text{H}_5\text{OH} / \text{HCl} = 1/1/3.8/7.3 \times 10^{-4} \); the solids content of this solution is estimated to be \( \nu_s = 0.065 \) (assuming a density of 2.0 g/cm\(^3\) for the solid phase). Ten aliquots of that solution are mixed with one aliquot of 0.05M \( \text{NH}_4\text{OH} \) to produce a final ratio of \( \text{H}_2\text{O} / \text{TEOS} = 3.7 \) and pH \( \approx 7.9 \); the solids content of this sol is \( \nu_s \approx 0.059 \). The sol was molded in polystyrene pipette tubes (to which the gel does not adhere), allowed to gel into rods (which requires ~2 h), aged in the mold, then allowed to slide from the mold into ethanol or acetone.

To compare the viscoelastic response of gels in water and ethanol, 12 rods ~7 mm in diameter were cast and aged in the mold for 24 h at room temperature. This type of gel contains many uncondensed OH and OR groups in the network, and some partially condensed polysilicate oil in the pores. Consequently, if the gel is placed directly into water, it shrinks and cracks, and turns opaque (because of phase separation of the oil [4]). To avoid these problems in those cases where we wanted pure water in the pores, the gels were washed first in a 50/50 (by volume) solution of water and ethanol for 22 h, then in pure water. The resulting gels had a slight haze, but were transparent and intact. The diameters of the rods decreased to ~6.75 mm after washing in the 50/50 mixture; in pure water, the diameter decreased to 6.25 mm in 24 h, 6.07 mm in 72 h, 5.92 mm in 96 h, then remained at that diameter up to 192 h. Samples left in pure ethanol showed no change in diameter with time. The load/deflection curves were obtained by immersing the wet gel and the 3-point bending fixture in a bath of the same liquid that was in the pores of the gel.

To study the effect of rod diameter on the kinetics of load relaxation, rods were cast from a single batch of sol with diameters from ~5.5 to 12 mm. The gels were aged in the molds at
36 ± 0.5°C for 48 h, then transferred to a bath containing 4.5 l of circulating ethanol (~ 11 times the total volume of gel). The rods were held in this bath at 35°C for 4 days, then held in the same bath at room temperature until the measurements were made (starting ~ 7 weeks later). Comparing the diameters of the rods to the inner diameters of the molds, the gels were found to have contracted by ~ 15% in volume, so the solids content of the gels tested was \( v_s \approx 0.069 \). Three rods of 11.8 mm diameter (total 57 ml of gel) were washed in 1.0 l of acetone for 12 days; the load relaxation was then measured with the sample immersed in acetone. Three rods of 5.5 mm diameter (total 7.8 ml gel) were washed in 0.8 l of anhydrous isobutanol for 3 days; the load relaxation was then measured with the sample immersed in isobutanol. In all cases, after mechanical testing, the diameters were measured at several points around the perimeter and along the length with an accurate hand gauge, \(^*\) and found to vary by \( \leq 1\% \) for a given sample.

### 4.2. Beam bending

The load/deflection data were obtained using an Instron 1122 mechanical testing machine with a 2000 g load cell. \(^**\) The cell was calibrated at the beginning and end of each day's work using brass weights; no drift in calibration was ever observed. The instrument was found to give a precisely linear measurement of load even for a full-scale range of 20 g. As in ref. [3], the 3-point bending fixture was immersed in the same liquid that was in the pores of the gel; the fixtures were made from aluminum plates 3.2 mm thick, bent into a square U-shape, and provided with rounded notches wider than the sample diameter to hold the gel. A series of fixtures with spans ranging from 3.6 to 13.1 cm was made, to test the effect on the measured modulus of the ratio of sample diameter to span. The pushrod making contact with the gel was a stainless steel rod 1.5 mm in diameter, whose axis was carefully aligned perpendicular to the axis of the gel rod. As the pushrod entered the liquid, the measured load increased as a result of buoyant force; by measuring the load with no sample present, it was established that the buoyant effect was 0.1 g/mm displacement (for ethanol or acetone), and the load, \( W \), was corrected correspondingly. All runs were performed with the bath at a temperature of 20.5 ± 0.5°C.

Two types of experiments were performed: constant downdrive (at the slowest available speed, 0.05 mm/min) to test eq. (65), and relaxation at constant deflection to test eq. (53). The machine is not designed to produce a sudden deflection, so to achieve this it was necessary to set it for a fast downdrive speed (100–500 mm/min) and quickly turn it on and off; with care, one could in this way achieve a deflection of 1–2 mm in a time of ~ 1s. As we shall see, the finite time of application of the deflection compromises the initial data for load relaxation. Data were collected at a rate of ~ 8 points/s from the Instron IEEE-488 interface using custom C code and Iotech drivers \(^\S\) on a Macintosh SE® computer. Load data are transmitted directly from the load cell, but the machine has no strain gauge, so it obtains deflections by multiplying the nominal downdrive speed by the time of operation. This leads to some inaccuracy in the deflection measured in the relaxation experiments, because of the time required for the crosshead to accelerate and decelerate. However, the errors are not large, as indicated by the agreement between moduli determined from the two types of experiment (namely, relaxation and slow down-drive).

In the load relaxation experiments, the load was found to rise over a period of ~ 1–2 s (depending on the final deflection and the downdrive speed), then to decay at constant deflection. The point of zero time was chosen to correspond to the maximum in the load. Clearly some relaxation occurs as the load is rising, so the loading

\(^*\) Starrett No. 1015MB-881 hand gauge.
\(^**\) Instron, load cell no. 2511-201.
\(^\S\) Mac SCSI 488 bus controller, IOTECH Inc., 25971 Cannon Rd., Cleveland, OH 44146, USA.
time is related to the parameter \( \theta_t \) discussed in connection with fig. 4.

The data were fit to eq. (53) using a non-linear least-squares procedure. The data were smoothed by averaging 10 successive points, resulting in sets of 500–2000 data pairs; the time interval used in the calculation was \( \sim 1 \) s. In principle, correction could be made for the finite rate of deflection, but we did not have good data for \( \Delta(t) \) during loading, so no correction was attempted.

4.3. Thermal expansion

For comparison with the beam-bending results, the permeability was also obtained using the thermal expansion method described in ref. [2]; the apparatus and technique are described in detail in that paper. Briefly, a rod of gel \( \sim 10 \) cm long immersed in ethanol is subjected to a thermal cycle involving slow heating and cooling, and the axial expansion is measured with an optical probe. The expansion of the gel is influenced by the expansion of the liquid in the pores: if all of the liquid remains in the gel, the expansion of the gel equals that of the liquid; if all of the liquid flows out, the expansion of the gel is simply that of the solid phase (which is unmeasurably small in this experiment). Therefore, the expansion of the gel is strongly related to the permeability of the network (i.e., the ease with which the expanding liquid can escape from the network), and the kinetics of the volume change during the thermal cycle can be analyzed to obtain the permeability. Neglecting the thermal expansion of the solid phase itself, the axial strain, \( \varepsilon_z \), of the gel rod has been shown to be [2]

\[
\varepsilon_z = \varepsilon_s + \sum_{n=1}^{\infty} \left( \frac{4}{\beta B_n^2} \right) \int_0^\beta \exp \left[ -B_n^2 (\xi - \xi') \right] \frac{\partial}{\partial \xi} \left[ \varepsilon_T - \varepsilon_s - (1 - \beta) (\varepsilon_z - \varepsilon_s) \right] d\xi'.
\]

(69)

Here \( \varepsilon_s \) is the strain produced by syneresis and

\[
\beta = \frac{1 + \nu_p}{3(1 - \nu_p)}.
\]

(70)

\( B_n \) is the \( n \)th root of \( J_0 \), the Bessel function of the first kind of order zero:

\[
J_0(B_n) = 0.
\]

(71)

The reduced time, \( \xi \), is defined by

\[
\xi = \int_0^\tau \frac{dt'}{\tau(t')},
\]

(72)

where the relaxation time, \( \tau \), is

\[
\tau = \frac{\beta \eta_L a^2}{DK_p}.
\]

(73)

The thermal strain is

\[
\varepsilon_T = (1 - \nu_b) \alpha_L [T(t) - T(0)],
\]

(74)

where \( \nu_b \) is the relative density of the network (i.e., the volume fraction of solid phase) and \( \alpha_L \) is the linear thermal expansion coefficient of the liquid. The relaxation time defined for this experiment, \( \tau_b \), is related to that for load relaxation in the cylindrical beam by

\[
\tau_b = 2(1 - \nu_p) \tau.
\]

(75)

In the analysis leading to eq. (69), the network of the gel is assumed to be elastic, so both \( \tau \) and \( \tau_b \) are characteristic times for relaxation produced by flow of liquid, not by viscoelastic behavior of the solid phase.

Rods of gel were taken (following washing in ethanol) from the same batch that was used for the beam-bending study. They were subjected to a thermal cycle involving heating at \( \sim 0.5^\circ C/\text{min} \) from \( \sim 29 \) to \( 33^\circ C \), holding near that temperature for \( \sim 30 \) min, cooling at a similar rate to \( \sim 29^\circ C \) and holding for \( \sim 15 \) min. Typically, several runs were made for each sample. To test the expansion of the apparatus itself, a rod of silica glass 10 cm long was used in place of the gel sample, and subjected to the same thermal cycle. Data were digitized with a 16-bit A/D converter \( \dagger \) and collected using WorkBench® software and a Macintosh SE® computer. The measured expansion was fitted to eq. (69) using a

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\( \dagger \) The FORTRAN code is available from the author.

\( \ddagger \) Fotonic Sensor MTI 1000 with probe module MTI 3812, MTI Instruments Div., Latham, NY, USA.
slightly modified version * of the scheme described in the appendix of ref. [2].

5. Results

5.1. Test of elasticity

The first fact to establish was that the gels behaved elastically under load. The experiment was to run the crosshead down until an easily measurable load was produced (typically 20–50 g), then to stop the crosshead and measure the load, \( W \), as a function of time. In all such tests, the baseline drift was checked at the end of the experiment by raising the crosshead to the starting point and observing the residual 'load'; it was found to be negligible in all the cases reported below. The final load, \( W' \), was found to decrease as downdrive rate was increased for rates \( \leq 50 \) mm/min (because of excessive relaxation during application of the load), so rates of 200–500 mm/min were used for these experiments. The elastic character of the gel is demonstrated in fig. 8, where \( W(t) \) is shown from the time that the downdrive stopped. The load on the gel containing ethanol is shown to relax by \( \sim 20\% \) in a few minutes, then to remain at that level for 4 h; according to eq. (53), the change in load implies \( \nu_P \approx 0.2 \). The same value of Poisson's ratio has been measured on very low-density aerogels of silica [17], and on re-impregnated silica gels [18]. Elastic behavior is also observed in acetone. **

By contrast, gels containing water exhibit a continual viscoelastic relaxation of load, behavior **

\[ W(t) \]

\[ t \ (\text{min}) \]

\[ W(t) \]

\[ t \ (\text{min}) \]

\[ \frac{W(t)}{W(0)} \]

\[ t \ (\text{min}) \]

\[ \frac{W(t)}{W(0)} \]

\[ t \ (\text{min}) \]

\[ \frac{W(t)}{W(0)} \]

\[ t \ (\text{min}) \]

Fig. 8. Normalized load as a function of time on silica gel rods whose pores contain ethanol or water. Several different aging treatments in water are compared. (Same data in both plots; short times emphasized in (a).)

Fig. 9. Comparison of two samples of ethanol-containing silica gel (different samples cast from the same sol).

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** Model 576-2 A/D converter with 500 AIM7 thermocouple card, Keithley Instrument Co., Fairfax, VA with Mac SCSI 488 bus controller, IOTECH Inc., 25971 Cannon Rd., Cleveland, OH 44146, USA.

* To allow for syneresis, eq. (69) of that paper should be modified by replacing \( \epsilon_s \) and \( \epsilon_T \) with \( \epsilon_s - \epsilon_s \) and \( \epsilon_T - \epsilon_s \), respectively. The FORTRAN code for the procedure is available from the author.

** Our recent results on an acid-catalyzed gel (type A-2 [16]) seem to indicate that some viscoelastic relaxation occurs even in alcohol, so the elastic behavior of B-2 in non-aqueous solvents may not be general for silica gels. This point is presently under investigation.
that is attributed to chemical attack of the water on the strained siloxane bonds in the network. The rate and degree of relaxation depend on the aging treatment.

The reproducibility of the data is excellent, as indicated by the two curves for ethanol-containing gels shown in fig. 9. The difference in relaxation time between the ethanol-containing sample in fig. 8 and the samples in fig. 9 results from differences in aging in the mother liquor (48 h at 35°C for the former and 24 h at ~20°C for the latter).

5.2. Constant deflection rate

Figure 10 shows the load/deflection curve for a gel rod 11.8 mm in diameter deflected in ethanol at a rate of 0.05 mm/min on a span of 5.4 cm. By using such a slow it is possible to continue the experiment until \( \theta > 0.2 \) without producing an excessive strain in the beam; as explained in section 3, this is required in order to obtain an accurate measure of \( E_p \). The curve deviates from linearity only at the beginning, as expected from eq. (65). The calculated curve (barely visible) is not a fit to the data; the parameters were obtained from the load relaxation experiment shown in fig. 12. Thus, eq. (65) is obeyed, and the results of the two types of experiment (namely, constant \( \Delta \) and constant \( \Delta \)) are consistent. The modulus of the gel is shown in table 1.

The present analysis is based on simple beam theory, which applies only if the span is large compared to the diameter of the rod. To confirm that the span was wide enough for our samples, rods with diameters of \( d = 7.186 \pm 0.008 \) and 11.858 ± 0.016 m were tested on several spans, \( L \). The results shown in fig. 11 indicate that the modulus changes less than 10% as \( L/d \) increase from 7.5 to 13.5. The only such data in the literature for a comparable material were obtained on plates of silica aerogel, where a constant modulus was found for span-to-thickness ratios \( \geq 10 \) [19]. All of the data presented below are for ratios in the range \( 7.5 \leq L/d \leq 13.5 \), so the modulus is believed to be correct to within ~10%.

<table>
<thead>
<tr>
<th>( d ) (cm)</th>
<th>( L ) (cm)</th>
<th>( L/d )</th>
<th>( dW/d\Delta ) (g/mm)</th>
<th>( E_p ) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.18</td>
<td>13.2</td>
<td>11.15</td>
<td>6.09</td>
<td>3.01</td>
</tr>
<tr>
<td>1.19</td>
<td>13.1</td>
<td>11.05</td>
<td>6.38, 6.53</td>
<td>3.02, 3.09</td>
</tr>
<tr>
<td>1.19</td>
<td>9.7</td>
<td>8.18</td>
<td>15.9</td>
<td>3.06</td>
</tr>
<tr>
<td>0.722</td>
<td>9.7</td>
<td>13.49</td>
<td>2.40</td>
<td>3.40</td>
</tr>
<tr>
<td>0.722</td>
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<td>7.51</td>
<td>13.45, 12.58</td>
<td>3.30, 3.09</td>
</tr>
<tr>
<td>0.722</td>
<td>3.6</td>
<td>5.01</td>
<td>38.59, 37.01</td>
<td>2.80, 2.69</td>
</tr>
</tbody>
</table>

Fig. 10. Load, \( W \) (g), versus deflection, \( \Delta \) (mm), for 11.8 mm rod in ethanol. Dashed curve calculated using eq. (65) with parameters obtained from load relaxation experiment on the same sample (see fig. 12)

Fig. 11. Dependence of Young's modulus (obtained using downdrive rate of 0.05 mm/min) on ratio of span, \( L \), to diameter of rod, \( d \).
5.3. Load relaxation

The results of a load-decay experiment on an 11.8 mm rod of gel in ethanol are shown in fig. 12, together with the fit of the data to eq. (53); the quality of this fit is typical of our results. The fit indicates that \( \nu_p = 0.22 \) for this gel. Figure 13 compares the load decay kinetics for rods with different diameters. A thinner rod relaxes more quickly, because its smaller diameter makes it easier for liquid to flow out. When the same curves are plotted against the reduced time \( \theta \), which takes account of the dependence of \( \tau_b \) on the square of the diameter, fig. 14 shows that the curves converge. This indicates that the dependence of relaxation kinetics on sample size is well described by the theory. The plateau value is higher for the thinner rods, because of relaxation occurring during application of the load.

The error produced by the finite deflection rate is revealed by replotting the data from fig. 14 versus \( \sqrt{\theta} \). As shown in fig. 15, the curves defined by the datapoints are all concave down; however, all of the measured curves fall on or below the curve for \( \theta_i = 0.001 \) from fig. 5. This is consistent with the loading time of \( \sim 1-2 \) s and the relaxation times of 640, 915, and 2500 s for these samples. When the points from the curve for \( \theta_i = 0.001 \) from fig. 5 are used as input in the fitting routine, a fit comparable to those in fig. 14 is obtained, but \( \tau_b \) and \( \nu_p \) are both found to be \( \sim 15\% \) higher than their true values (i.e., the input values used in calculating the curves in fig. 5). Therefore, the parameters obtained from the present experiments are expected to lie above the true values, but to be correct to within 15\%. The moduli determined from this series of experiments, which are summarized in table 2, are less
Table 2
Load relaxation at constant deflection

<table>
<thead>
<tr>
<th>$d$</th>
<th>$L$</th>
<th>$\Delta$</th>
<th>$\Delta$</th>
<th>$W(0)$</th>
<th>$\varepsilon_r$</th>
<th>$\tau$</th>
<th>$\nu_p$</th>
<th>$G_p$</th>
<th>$E_p$</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>(cm)</td>
<td>(cm)</td>
<td>(mm/min)</td>
<td>(cm)</td>
<td>(g)</td>
<td>(%)</td>
<td>(s)</td>
<td>(MPa)</td>
<td>(MPa)</td>
<td>(MPa)</td>
<td></td>
</tr>
<tr>
<td>1.18</td>
<td>13.2</td>
<td>500</td>
<td>0.46</td>
<td>32.5</td>
<td>1.9</td>
<td>2500</td>
<td>0.218</td>
<td>1.17</td>
<td>2.85</td>
<td>ethanol</td>
</tr>
<tr>
<td>1.17</td>
<td>9.7</td>
<td>500</td>
<td>0.22</td>
<td>38.2</td>
<td>1.6</td>
<td>760</td>
<td>0.244</td>
<td>1.17</td>
<td>2.91</td>
<td>acetone</td>
</tr>
<tr>
<td>0.722</td>
<td>5.4</td>
<td>200</td>
<td>0.11</td>
<td>12.0</td>
<td>1.6</td>
<td>905</td>
<td>0.223</td>
<td>0.90</td>
<td>2.20</td>
<td>ethanol</td>
</tr>
<tr>
<td>0.546</td>
<td>5.4</td>
<td>500</td>
<td>0.21</td>
<td>10.4</td>
<td>2.4</td>
<td>640</td>
<td>0.236</td>
<td>1.21</td>
<td>2.99</td>
<td>ethanol</td>
</tr>
<tr>
<td>0.547</td>
<td>5.4</td>
<td>200</td>
<td>0.21</td>
<td>10.8</td>
<td>2.4</td>
<td>1790</td>
<td>0.216</td>
<td>1.07</td>
<td>2.61</td>
<td>butanol</td>
</tr>
</tbody>
</table>

$^{a)}$ Maximum strain at surface of rod, $|\varepsilon_r(a)|$.
$^{b)}$ Calculated using $E_p = 2(1 + \nu_p)G_p$.

accurate than those obtained using a slow down-drive rate, because of the uncertainty in the deflection ($\Delta$).

Figure 16 compares the relaxation kinetics of rods 11.8 mm in diameter in ethanol and acetone. The acetone-containing sample relaxes faster, because the viscosity of acetone at room temperature is $\sim \frac{1}{4}$ of that of ethanol [20]. When plotted against the reduced time (fig. 16(b)), the initial portions of the relaxation curves come together as expected, but the plateau values are different. This is a result of excessive relaxation during

![Graph](image-url)

Fig. 15. Data from fig. 14 plotted against $\sqrt{\theta}$, and theoretical curves from fig. 5 corresponding to shifts of $\theta_0 = 0$ (Theory) and $\theta_0 = 0.001$ (Theory, shifted).

![Graph](image-url)

Fig. 16. Relaxation of load on 11.8 mm rod of gel at constant deflection in ethanol (same data as in fig. 12) and in acetone, plotted against (a) elapsed time and (b) reduced time (corresponding to $\tau_p = 2500$ s in ethanol and 760 s in acetone).
loading of the acetone-containing gel; the effect is similar to that for the 5.5 mm rod in ethanol (see fig. 14), because the relaxation times of those two samples are similar. Again, the error in the relaxation time obtained from the fit is expected to be ≤ 15%.

The success of the theory is illustrated in fig. 17, where the relaxation time is shown to be proportional to diameter squared for the three rods in ethanol (open circles). The closed circle represents the relaxation time found for the 11.7 mm rod tested in acetone, whose viscosity is 3.7 times lower than that of ethanol [20]; the difference in viscosity moves the datum to a point between those for rods with diameters of 5.5 and 7.2 mm in ethanol. The closed triangle represents the relaxation time found for the 5.5 mm rod tested in isobutanol, whose viscosity is 3.3 times higher than that of ethanol [21]; the difference in viscosity moves the datum to a point between those for rods with diameters of 7.2 and 11.8 mm in ethanol. The fact that the points fall on the same line shows that the dependence of the relaxation time on liquid viscosity is as predicted by eq. (31).

5.4. Thermal expansion

Figure 18 shows the thermal cycle and the corresponding dilatation of a rod of gel 7.2 mm in diameter and ~10 cm long in ethanol. In fig. 18(a), the syneresis strain is neglected, so the fitted curve has one free parameter, the relaxation time, \( \tau \); in addition the calculation uses the relative density of the network, \( \nu_s = 0.069 \), and the physical properties of ethanol, \( \alpha_L = 3.7 \times 10^{-4}/^\circ C \) and \( \eta_L (\text{Pa s}) = 5.2 \times 10^{-6} \exp[1592/T(\text{K})] \) [20]. When the same thermal cycle is run

![Graph showing relaxation time versus viscosity](image)

Fig. 17. Relaxation time for load decay versus \( \eta_L d^2 \), where \( d \) is the diameter of the rod and \( \eta_L \) is the viscosity (1.2 mPa s for ethanol, 0.32 mPa s for acetone, 3.9 mPa s for isobutanol at \( T = 20^\circ C \)). Open circles for samples tested in ethanol, closed circle for sample in acetone, closed triangle for sample in isobutanol; vertical bar for several samples measured using thermal expansion method.

![Graph showing measured and calculated axial strain](image)

Fig. 18. Measured and calculated axial strain, \( \Delta h/h \), for gel rod with diameter of 7.2 mm and length of 9.5 cm subjected to thermal cycle shown by solid curve. (a) Calculation is one-parameter fit to eq. (69) yielding relaxation time \( \tau = 465 \) s; (b) calculation is two-parameter fit yielding \( \tau = 440 \) s and syneresis strain rate \( \dot{\epsilon}_s = -5.5 \times 10^{-9}/s \).
Table 3
Thermal expansion results

<table>
<thead>
<tr>
<th>Run</th>
<th>$\dot{\varepsilon}_s \times 10^9$</th>
<th>$\tau$</th>
<th>$\tau_{b}$</th>
<th>$D H_p \times 10^{11}$</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(s$^{-1}$)</td>
<td>(s)</td>
<td>(s)</td>
<td>(N)</td>
<td>(nm$^2$)</td>
</tr>
<tr>
<td>Sample 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>465</td>
<td>725</td>
<td>3.26</td>
<td>9.5</td>
</tr>
<tr>
<td>3</td>
<td>-5.5</td>
<td>440</td>
<td>690</td>
<td>3.47</td>
<td>10.1</td>
</tr>
<tr>
<td>Sample 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-11.0</td>
<td>740</td>
<td>1150</td>
<td>2.05</td>
<td>6.0</td>
</tr>
<tr>
<td>3</td>
<td>-8.5</td>
<td>670</td>
<td>1050</td>
<td>2.25</td>
<td>6.6</td>
</tr>
<tr>
<td>6</td>
<td>-6.7</td>
<td>630</td>
<td>980</td>
<td>2.41</td>
<td>7.0</td>
</tr>
</tbody>
</table>

a) Each sample was subjected to several runs over a period of days.
b) Calculated from $\tau_{b} = 2(1 - \nu_p)\tau$, assuming $\nu_p = 0.22$.
c) Assuming $\nu_p = 0.22$, $E_p = 3.0$ MPa, so $H_p = 3.43$ MPa.
d) Assumed to be zero, so only fitting parameter was $\tau$.

with the sample replaced by a silica rod, unreproducible random strains of $\pm 2.5\ \mu m$ are obtained. That is roughly the magnitude of the difference between the measured and calculated strains in fig. 18(a), but those errors are systematic, not random. A much better fit is obtained by allowing for a constant syneresis strain rate of $\dot{\varepsilon}_s = -5.5 \times 10^{-9}/s$; this rate is too slow to be detected by ordinary methods. By way of comparison, the syneresis rate of an acid-catalyzed silica gel in its mother liquor is $\sim 50$ times faster ($2.5 \times 10^{-7}/s$) [22], but becomes undetectable when the gel is washed in ethanol [23]. With or without syneresis, the fit yields $\tau \approx 450$ s for this sample (see table 3). On successive runs over a two day period, another sample from the same batch exhibited relaxation times decreasing from 740 to 630 s, and a syneresis rate decreasing in magnitude from $-11 \times 10^{-9}/s$ to $-6.7 \times 10^{-9}/s$. These changes are a reasonable consequence of the aging produced during the experiment: the modulus increases, causing a decrease in $\tau$, and the syneresis rate decreases. The reason for the large discrepancy in $\tau$ between the two samples is not understood. These values can be used to calculate $\tau_{b}$ from eq. (75); assuming $\nu_p = 0.22$, one obtains the values represented by the vertical bar in fig. 17. Clearly these two methods, based on different principles, give results in good agreement.

From the slope of fig. 17 and the measured properties $G_p = 1.2$ MPa and $\nu_p = 0.22$, the per-

6. Conclusions

The relaxation of load on a beam of wet gel gives a remarkable amount of useful information: the initial load gives the shear modulus, the final load gives Young's modulus, and comparison of those values gives Poisson's ratio for the network. Moreover, the kinetics of relaxation can be analyzed to determine the permeability of the network to fluid flow. In this paper, the rate of relaxation has been analyzed for relaxation of load at constant deflection in square and cylindrical bars, and for constant rates of deflection for square bars. Experimental results on silica gels are in good agreement with the predictions for the dependence of the load relaxation time, $\tau_{b}$, on the diameter of the rod and the viscosity of the pore liquid. Moreover, parameters derived from measurements of load relaxation accurately predict the load/deflection curve for the same gel. An important point is that we have shown that the gel network behaves elastically in the presence of chemically inert solvents, such as ethanol and acetone, but viscoelastically in water.

The relaxation times found from beam bending agree with those obtained from analysis of the thermal expansion kinetics. Indeed, one could argue that there is no point in using the latter method, since analysis of thermal expansion requires knowledge of the mechanical properties (to extract $D$ from $\tau$), so one might as well obtain the permeability together with the mechanical properties from the beam-bending experiment. Moreover, the thermal expansion method requires knowledge of $\kappa L$, the temperature dependence of $\eta L$, either of which could be different from the known values for bulk liquids, and $\nu_s$. On the other hand, the beam-bending technique does not reveal the occurrence of syneresis (unless it is rather fast), so the thermal...
expansion method is valuable in cases in which syneresis is important. The recommended course is to recognize that the methods are complementary, and to use them together.

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References