PAPER

Experimental determination of equations of state for ideal elastomeric gels

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A polymer network can absorb a solvent and swell, forming an elastomeric gel. The model of ideal elastomeric gels is based on two assumptions. First, the volume of a gel is the sum of the volume of the dry network and that of the solvent. Second, the free energy of the gel is the sum of the free energy due to stretching the network and that due to mixing the polymer and the solvent. These assumptions lead to a set of equations of state, which can be tested experimentally without invoking any specific models of statistical mechanics. Here we test the model of ideal elastomeric gels by conducting experiments with polyacrylamide hydrogels, and by extracting from the literature four sets of data on polyacrylamide hydrogels and polyacrylamide–water solutions. For an ideal elastomeric gel, the effect of mixing the polymer and the solvent is represented by the osmotic pressure as a function of the swelling ratio. We show that this function obtained by several distinct experimental methods is consistent. Specifically, the function obtained from a gel under different states of applied stress is the same, the function obtained from a free-swelling gel is the same as that obtained from the constrained-swelling gel, the function is independent of the crosslink density, and the function obtained from the gels is similar to that obtained from the solutions. We further show that the Flory–Huggins model of mixing with a constant Flory–Huggins parameter does not fit the experimental data well, but does capture the trend of the data over four orders of magnitude in the osmotic pressure.

1. Introduction

A polymer network can absorb a solvent and swell, forming an elastomeric gel (Fig. 1). The amount of swelling depends on the molecular interaction between the polymer and the solvent, and changes greatly in response to environmental stimuli such as temperature,[1] pH[2,3] and salinity.[4] Such stimuli-responsive gels are being developed as vehicles for drug delivery,[5] sensors and actuators in micro-devices,[6,7] and packers in oilfields.[8] The gels in
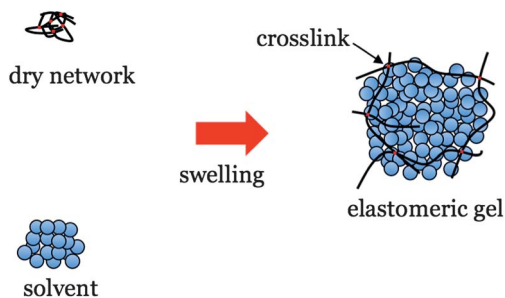

Fig. 1 A polymer network absorbs a solvent and swells, forming an elastomeric gel.

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devices are typically constrained by hard materials. The devices operate by exploiting the chemomechanical interaction of the gels: how the mechanical constraint affects swelling and how stimuli generate mechanical forces.

The chemomechanical interaction of gels has been described by many theories.[9,10] The classic theory of Flory and Rehner[11] combines two models of statistical mechanics: the Gaussian-chain model describes the elasticity of the network and the Flory–Huggins model describes the mixing of the polymer and the solvent.[12,13] While these models of statistical mechanics relate macroscopic behavior of gels to molecular processes of the network and the solvent, the relation is inexact: the models are often modified in various ways to fit experimental data.[14,15]

For applications of gels in devices, it is desirable to develop experimental methods that characterize the chemomechanical behavior of gels without being constrained by models of statistical mechanics. In this connection, a commonly held notion is useful: stresses applied on a gel are balanced by the elasticity of the network and the osmosis of the solution. Cai and Suo[16] showed that this notion can be developed from two basic assumptions made in the Flory–Rehner theory. First, the volume of a gel is assumed to be the sum of the volume of the dry network and that of the solvent absorbed. Second, the free energy of the gel is assumed to be the sum of two parts: the free energy associated with stretching the network and the free energy associated with mixing the polymer and the solvent. The first assumption is known as molecular incompressibility,[17] and the

second the Frenkel–Flory–Rehner (FFR) hypothesis.[18–21] These basic assumptions are independent of specific models of statistical mechanics, and can be directly used to represent experimental data. Specifically, the two assumptions lead to a set of equations of state, which fit several sets of experimental data in the literature remarkably well.[16]

Here we further develop the approach of Cai and Suo by performing additional experiments on polyacrylamide hydrogels. We choose this type of gels because they are widely used, and because we can extract from the literature several sets of data on polyacrylamide hydrogels and polyacrylamide–water solutions. The combined datasets allow us to test the approach over a large range of swelling ratio J (*i.e.*, the volume of the gel over that of the dry network). Within this approach, the effect of mixing the polymer and the solvent is represented by the osmotic pressure as a function of the swelling ratio, $\Pi_{mix}(J)$. A classic method to determine $\Pi_{mix}(J)$ involves semipermeable membranes and is limited by the strength of membranes, so that typical results are obtained from solutions of low concentrations and low osmotic pressure.[22–24] This limitation is removed by determining the function $\Pi_{mix}(J)$ by mechanical measurements performed on gels. We show that these distinct methods yield a similar function $\Pi_{mix}(J)$, that the function is independent of the crosslink density, and that the gels have the same $\Pi_{mix}(J)$ function as the solutions. We further show that the Flory–Huggins model of mixing with a constant interaction parameter does not fit the experimental data well, but does capture the trend of the data over four orders of magnitude in osmotic pressure.

2. Ideal elastomeric gels

The two basic assumptions specify a model, which we call the model of ideal elastomeric gels.[16] To focus on the main ideas, here we consider the deformation in principal directions (Fig. 2). The equations of state for ideal elastomeric gels are derived by following the same method as in previous papers.[16,17] In the reference state, the block is a unit cube of a dry polymer network, containing no solvent and subject to no applied force. In the current state, submerged in a solvent-containing environment and subject to applied forces, the network absorbs C number of solvent molecules and stretches into a rectangular block of dimensions λ_1, λ_2 and λ_3. The ratio of the volume of the gel to

that of the dry network, J, known as the swelling ratio, relates to the dimensions of the rectangular block by $J = \lambda_1\lambda_2\lambda_3$.

Recall the two basic assumptions of ideal elastomeric gels. First, the gel is a soft material; when subject to the applied forces, the gel changes its shape readily, but the volumes of individual polymer chains and individual solvent molecules remain nearly unchanged. As an idealization, the volume of the gel is assumed to equal the sum of the volume of the dry network and that of the solvent:

$$J = 1 + \Omega C \tag{1}$$

where Ω is the volume per solvent molecule. This assumption is known as the assumption of molecular incompressibility.[17] In reality, when a polymer and a solvent mix, the volume of the mixture differs somewhat from the sum of the volumes of the polymer and solvent. The effect of the volume of mixing has been considered in the model of ideal elastomeric gels,[16] but will be neglected in this paper.

Second, the density of crosslinks in the gel is typically very low; each polymer chain consists of a large number of monomers, so that crosslinks negligibly affect the molecular interaction between the polymer and the solvent. As an idealization, the Helmholtz free energy of the gel is assumed to be the sum of the free energy due to the stretching of the network and that due to the mixing of the polymer and the solvent:

$$W = W_{stretch}(\lambda_1,\lambda_2,\lambda_3) + W_{mix}(J). \tag{2}$$

This assumption is known as the Frenkel–Flory–Rehner (FFR) hypothesis.[18–21] The free energy of the gel, W, is defined as the excess in the gel relative to the sum of its constituents—that is, W is the free energy of the gel minus that of the polymer and that of the pure solvent. The free energy due to the stretching of the network, $W_{stretch}(\lambda_1,\lambda_2,\lambda_3)$, is a function of the stretches, and depends on the crosslink density. The free energy due to the mixing of the polymer and the solvent, $W_{mix}(J)$, is a function of the swelling ratio, but is independent of the crosslink density.

When a dry network is submerged in a solvent-containing environment and subject to applied forces, the network takes some time to absorb the solvent and attain a state of thermodynamic equilibrium. The condition of equilibrium is formulated as follows. Define the stresses σ_1, σ_2 and σ_3 as the applied forces divided by the areas of the faces of the rectangular block. Thus, the forces applied on the faces of the rectangular block are $\sigma_1\lambda_2\lambda_3$, $\sigma_2\lambda_3\lambda_1$ and $\sigma_3\lambda_1\lambda_2$. The applied forces can be represented by hanging weights. Associated with a small change in the dimensions of the rectangular block, the potential energy of the hanging weights changes by $-\sigma_1\lambda_2\lambda_3 d\lambda_1 - \sigma_2\lambda_3\lambda_1 d\lambda_2 - \sigma_3\lambda_1\lambda_2 d\lambda_3$. The gel is immersed in a solvent-containing environment such that the gel and the environment can only exchange one species of molecules: the solvent. The chemical potential of the solvent in a saturated mixture of the pure liquid and its vapor is set to be zero. Let μ be the chemical potential of the solvent in the environment—that is, μ is the increase of the Helmholtz free energy when the environment gains one solvent molecule from the pure solvent in the state of liquid–vapor mixture. Associated with the transfer of dC number of solvent molecules from the environment to the gel, the free energy of the environment
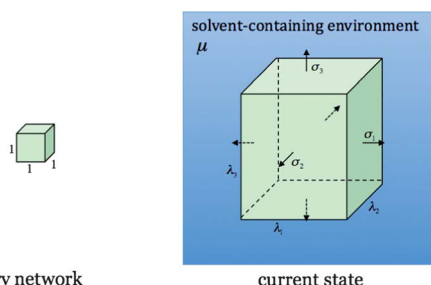

Fig. 2 In the reference state, a unit cube of a dry polymer network contains no solvent and is subject to no applied stress. In the current state, immersed in a solvent-containing environment and subject to applied stresses, the network absorbs the solvent and is stretched into a rectangular block.

changes by $-\mu\mathrm{d}C$. The gel, the hanging weights and the environment together form a composite thermodynamic system. The Helmholtz free energy of the composite is the sum of the Helmholtz free energy of the gel, the potential energy of the weights, and the Helmholtz free energy of the environment. In equilibrium, the change of the Helmholtz free energy of the composite vanishes:

$$\mathrm{d}W - \sigma_1\lambda_2\lambda_3\mathrm{d}\lambda_1 - \sigma_2\lambda_3\lambda_1\mathrm{d}\lambda_2 - \sigma_3\lambda_1\lambda_2\mathrm{d}\lambda_3 - \mu\mathrm{d}C = 0. \quad (3)$$

A combination of eqn (1)–(3) gives

$$\left[\frac{\partial W_{\mathrm{stretch}}}{\partial\lambda_1} - \left(\sigma_1 + \Pi_{\mathrm{mix}}(J) + \frac{\mu}{\Omega}\right)\lambda_2\lambda_3\right]\mathrm{d}\lambda_1$$
$$+ \left[\frac{\partial W_{\mathrm{stretch}}}{\partial\lambda_2} - \left(\sigma_2 + \Pi_{\mathrm{mix}}(J) + \frac{\mu}{\Omega}\right)\lambda_3\lambda_1\right]\mathrm{d}\lambda_2 \quad (4)$$
$$+ \left[\frac{\partial W_{\mathrm{stretch}}}{\partial\lambda_3} - \left(\sigma_3 + \Pi_{\mathrm{mix}}(J) + \frac{\mu}{\Omega}\right)\lambda_1\lambda_2\right]\mathrm{d}\lambda_3 = 0$$

with

$$\Pi_{\mathrm{mix}}(J) = -\frac{\mathrm{d}W_{\mathrm{mix}}(J)}{\mathrm{d}J}. \quad (5)$$

The network, the solvent and the applied forces equilibrate when eqn (4) holds for arbitrary and independent small changes in the three stretches, λ_1, λ_2 and λ_3. Consequently, the expression in the bracket in front of each of the three terms in eqn (4) must vanish individually, giving three independent equations:

$$\sigma_1 = \frac{\partial W_{\mathrm{stretch}}(\lambda_1, \lambda_2, \lambda_3)}{\lambda_2\lambda_3\partial\lambda_1} - \Pi_{\mathrm{mix}}(J) - \frac{\mu}{\Omega}, \quad (6a)$$

$$\sigma_2 = \frac{\partial W_{\mathrm{stretch}}(\lambda_1, \lambda_2, \lambda_3)}{\lambda_3\lambda_1\partial\lambda_2} - \Pi_{\mathrm{mix}}(J) - \frac{\mu}{\Omega}, \quad (6b)$$

$$\sigma_3 = \frac{\partial W_{\mathrm{stretch}}(\lambda_1, \lambda_2, \lambda_3)}{\lambda_1\lambda_2\partial\lambda_3} - \Pi_{\mathrm{mix}}(J) - \frac{\mu}{\Omega}. \quad (6c)$$

The quantity $\Pi_{\mathrm{mix}}(J)$ is the osmotic pressure in the gel in equilibrium with the pure solvent. The quantity μ/Ω is the additional osmotic pressure in the gel due to the chemical potential of the solvent in the environment. The applied stresses are balanced by the elasticity of the network, the osmosis due to the mixing of the polymer and the solvent, and the osmosis due to the chemical potential of the solvent in the environment. Eqn (1) and (6) constitute four equations of state, relating the eight thermodynamic variables: λ_1, λ_2, λ_3, C, σ_1, σ_2, σ_3 and μ. (We do not count the swelling ratio J as a distinct additional variable because by definition $J = \lambda_1\lambda_2\lambda_3$.)

The equations of state involve two functions: $W_{\mathrm{stretch}}(\lambda_1,\lambda_2,\lambda_3)$ and $\Pi_{\mathrm{mix}}(J)$. The latter is derived from $W_{\mathrm{mix}}(J)$ through eqn (5). In the Flory–Rehner theory,[11] the two functions are specified by models of statistical mechanics: the Gaussian-chain model gives the free energy due to the stretching of the network, $W_{\mathrm{stretch}}(\lambda_1,\lambda_2,\lambda_3)$, and the Flory–Huggins model gives the free energy due to the mixing of the polymer and the solvent, $W_{\mathrm{mix}}(J)$. As an alternative approach, one does not calculate the two functions from any specific models of statistical mechanics; rather, one determines the function $W_{\mathrm{stretch}}(\lambda_1,\lambda_2,\lambda_3)$ through experimental measurements of stress–stretch curves, and determines the function $W_{\mathrm{mix}}(J)$ through experimental measurements of osmotic pressure. One can also adopt various combinations of models of statistical mechanics and experimental measurements.

The function $\Pi_{\mathrm{mix}}(J)$ connects solutions and gels of the same polymer–solvent system. In the model of ideal elastomeric gels, the function $\Pi_{\mathrm{mix}}(J)$ is independent of the density of crosslinks. In particular, when the density of crosslinks is so low that the free energy of stretching is negligible, the gel is indistinguishable from a solution, and eqn (6) reduces to $\sigma_1 = \sigma_2 = \sigma_3 = -\Pi_{\mathrm{mix}}(J) - \mu/\Omega$. The solution and the gel have the same chemistry because the dilute crosslinks negligibly affect the molecular interaction between the solvents and the polymer. The solution and the gel have different mechanics because the solution is a liquid that can sustain only hydrostatic stress in equilibrium, while the gel is a solid that can sustain non-hydrostatic stress in equilibrium—an attribute that significantly increases the number of distinct methods to determine experimentally the function $\Pi_{\mathrm{mix}}(J)$. In particular, $\Pi_{\mathrm{mix}}(J)$ can be determined by the free-swelling experiment of gels of different crosslink densities (Method 1 below), and by subjecting gels to a state of non-hydrostatic stresses (Methods 2 and 3 below). Furthermore, the function $\Pi_{\mathrm{mix}}(J)$ can be determined by allowing gels to swell under stretches of different types, such as uniaxial tension, uniaxial compression and equal biaxial tension.[16]

3. Experimental methods

We made polyacrylamide hydrogels by the following procedure. Acrylamide was dissolved in distilled water to 4.0 M in concentration, along with ammonium persulfate (0.012 × the weight of acrylamide) as polymerization initiators, N,N,N',N'-tetramethylethylenediamine (0.018 × the weight of acrylamide) as crosslinking accelerators, and N,N-methylenebisacrylamide (MBAA, 0.007, 0.012, 0.017, 0.024, 0.035 and 0.041 × the weight of acrylamide) as crosslinkers. The MBAA-to-acrylamide ratio was varied to form gels of different crosslink densities. For each MBAA-to-acrylamide ratio, three batches of gels were prepared. The gels were cured for 2 hours at room temperature. They were then submerged in distilled water, subject to no force, and kept at room temperature for a week, with a change of fresh distilled water every 48 hours.

We measured the swelling ratio J by using the gravimetric method. The gel was taken out of water, blotted with tissue paper to remove the water on the surface carefully. The gel was then immediately weighed on an analytical scale with an accuracy of 10^{-5} g to obtain the mass of the gel, m_{gel}. For the mass of the dry network m_{dry}, the gel was dehydrated by the freeze-drying technique. A piece of the gel was frozen under $-80\,^\circ\mathrm{C}$ and transferred to a freeze dry system (Labconco Corporation), whose collector was kept a temperature of $-50\,^\circ\mathrm{C}$ and a vapor pressure of 0.040 mbar. The freeze-drying process took 3 days. The dry network m_{dry} was weighed on an analytical scale. We calculated J from

$$J = 1 + \frac{(m_{\mathrm{gel}} - m_{\mathrm{dry}})/\rho_{\mathrm{water}}}{m_{\mathrm{dry}}/\rho_{\mathrm{PAAM}}}, \quad (7)$$

where the density of water is $\rho_{\mathrm{water}} = 1.000$ g cm^{-3} and that of polyacrylamide is $\rho_{\mathrm{PAAM}} = 1.443$ g cm^{-3}.[22] We measured the swelling ratio J after free swelling, as well as after the force–relaxation experiment described below.

We measured viscoelastic moduli of the gels with a Q800 dynamic mechanical analyzer (TA Instruments). Cylindrical samples were cut, 8 mm in diameter and 3 mm in thickness. The applied amplitude was 50 μm, and the frequency ranged 0.01–10 Hz.

We used an AR-G2 rheometer (TA Instrument) to perform uniaxial compression tests. A cylinder of the gel, 12 mm in diameter and 9 mm in thickness, was placed between the stage and plate made of steel, and submerged in distilled water (Fig. 3). The plate approached the gel at a slow speed of 5 μm s^{-1} till the force was detected to rise, indicating the contact between the plate and the gel. Upon contact, the plate was quickly loaded to a certain position within 90 s. During the loading process, both the force and height were recorded. The duration of this experiment was sufficiently short that the solvent had no time to redistribute in the gel, so that the gel behaved as an incompressible elastic material, and the experiment determined its stress–stretch curve.

We also performed force–relaxation experiments by using the AR-G2 rheometer. Cylindrical samples were cut, 3 mm in diameter and 0.5 mm in thickness. In each run of the experiment, a sample was placed between the stage and plate, and was submerged in distilled water (Fig. 3). The gel was slippery, and was free to expand laterally when compressed between the stage and the plate. The gap between the stage and the plate was sealed with mineral oil to prevent the evaporation of water surrounding the gel. The plate was programmed to approach the gel at a speed of 5 μm s^{-1}. Once the contact between the plate and the gel was detected as the force began to rise, the speed of the plate was switched to 50 μm s^{-1}. After a certain height was reached, the plate was held stationary, and the force applied on the plate was recorded as a function of time. After some time, the force–time curve approached a plateau, indicating that the gel had reached a state of equilibrium under the constraint of the plate. Using a single sample, several force–time curves were obtained by holding the plate at multiple positions. We labeled the direction of the applied force as direction *3*, and the two horizontal directions as *1* and *2*. The stretch in the vertical direction was $\lambda_3 = h/H$, where H was the thickness of the dry network, and h was the thickness of the gel set by the spacing between the plate and the stage. It was inconvenient to measure the diameter of the gel in the force–relaxation experiment. Consequently, we used the nominal stress s_3, defined as the applied force divided by the

Fig. 3 The setup for the force–relaxation experiment. A cylindrical sample of a gel is placed in water between a plate and a stage made of steel, and is sealed with mineral oil. While the plate is pressed on the gel and held at a fixed position, distance h above the stage, the force F applied on the plate is recorded as a function of time until the gel equilibrates with the force and the surrounding water. The experiment is run by adjusting the plate to several positions in succession.

area of the dry network. The nominal stress s_3 relates to the true stress σ_3 by $s_3 = \sigma_3 \lambda_1 \lambda_2 = \sigma_3 J/\lambda_3$.

4. Results and discussion

It is known that experimentally determined stress–stretch curves of polyacrylamide gels fit the Gaussian-chain model well.[16] The free energy derived from the Gaussian-chain model is[11]

$$W_{\text{stretch}}(\lambda_1, \lambda_2, \lambda_3) = \frac{1}{2}NkT\left[\lambda_1{}^2 + \lambda_2{}^2 + \lambda_3{}^2 - 3 - 2\log(\lambda_1\lambda_2\lambda_3)\right], \quad (8)$$

where N is the number of polymer chains per unit volume, and kT the temperature in the unit of energy. As stated previously, chemomechanical interaction is specific to the polymer and solvent, and can be very complex. For the time being we do not specify any form of the function $W_{\text{mix}}(J)$. Inserting eqn (8) into (6), one obtains

$$\sigma_1 = \frac{NkT}{J}\left(\lambda_1{}^2 - 1\right) - \Pi_{\text{mix}}(J) - \frac{\mu}{\Omega}, \quad (9a)$$

$$\sigma_2 = \frac{NkT}{J}\left(\lambda_2{}^2 - 1\right) - \Pi_{\text{mix}}(J) - \frac{\mu}{\Omega}, \quad (9b)$$

$$\sigma_3 = \frac{NkT}{J}\left(\lambda_3{}^2 - 1\right) - \Pi_{\text{mix}}(J) - \frac{\mu}{\Omega}, \quad (9c)$$

Thus, a gel is fully characterized by a scalar NkT and a single-variable function $\Pi_{\text{mix}}(J)$.[16] Once NkT and $\Pi_{\text{mix}}(J)$ are obtained, the four equations of state, (1), (9a), (9b) and (9c), connect the eight thermodynamic variables: λ_1, λ_2, λ_3, C, σ_1, σ_2, σ_3 and μ.

Submerged in pure water and subject to no applied forces, the gel attains a state of equilibrium—the free-swelling state—characterized by isotropic stretches, $\lambda_1 = \lambda_2 = \lambda_3 = \lambda_0$. When the gel is subject to a force, in a short time the solvent in the gel has no time to redistribute, so that the concentration of the solvent in the gel remains fixed, and the gel behaves like an incompressible material. The gel changes its shape to a state of stretches λ_1, λ_2, and λ_3, but the volume of the gel remains unchanged, so that $J_0 = \lambda_1\lambda_2\lambda_3 = \lambda_0{}^3$. Experimental data are often reported in terms of stretches relative to the free-swelling state, λ_1/λ_0, λ_2/λ_0 and λ_3/λ_0. In terms of these relative stretches, eqn (9) is written as

$$\sigma_3 - \sigma_1 = \frac{NkT}{\lambda_0}\left[\left(\frac{\lambda_3}{\lambda_0}\right)^2 - \left(\frac{\lambda_1}{\lambda_0}\right)^2\right], \quad (10a)$$

$$\sigma_3 - \sigma_2 = \frac{NkT}{\lambda_0}\left[\left(\frac{\lambda_3}{\lambda_0}\right)^2 - \left(\frac{\lambda_2}{\lambda_0}\right)^2\right]. \quad (10b)$$

These are the stress–stretch relations of a gel when the concentration of the solvent in the gel is fixed. The stress–stretch relations are the same as those of the neo-Hookean model commonly used for incompressible elastomers. The pre-factor in eqn (10) defines the shear modulus,

$$G = NkT/\lambda_0. \quad (11)$$

Fig. 4 illustrates the shear modulus G characterized with the dynamic mechanical analysis (DMA) and compression tests. Our
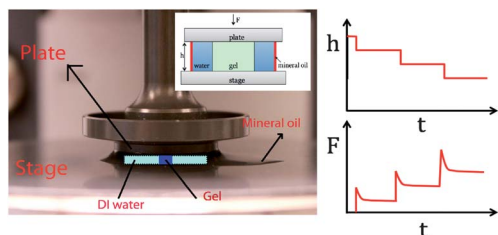
viscoelastic measurements show that the polyacrylamide gels are highly elastic, with small viscous damping (Fig. 4a and b). The storage modulus is denoted by G' and the loss modulus by G''. The magnitude $|G| = \sqrt{(G')^2 + (G'')^2}$ increases with the concentration of the crosslinkers. The modulus remains nearly a constant and the ratio of the loss modulus to the storage modulus G''/G' remains low over the range of low frequency (0.01 Hz < f < 1 Hz). The increase of the modulus and loss at high frequency may be due to the entanglement of the polymer chains. These increases do not concern us here because we will focus on the behavior of gels in equilibrium, so that only the modulus determined at low frequency will be used. The stress–stretch curves determined by the compression test fit the neo-Hookean model (eqn (10)) very well (Fig. 4c). Furthermore, the shear moduli measured by two techniques—dynamic mechanical analysis (DMA) and compression tests—match well over the entire range of the MBAA-to-acrylamide ratio (Fig. 4d).

As expected, the swelling ratio J_0 of the freely swollen gel, determined by the gravimetric method, decreases as the concentration of the crosslinker increases (Fig. 5a). We calculate the free-swelling stretch $\lambda_0 = J_0^{1/3}$, and the number of chains per unit volume of the dry network from eqn (11) using the storage modulus determined at low frequency (0.01 Hz < f < 1 Hz). As expected, the value of NkT rises with the increasing concentration of the crosslinkers (Fig. 5b).

In the force–relaxation experiment, once the plate is adjusted to a position, the force relaxes to attain a new state of equilibrium after some time (Fig. 6a). When the position of the plate is high, the gel is not much deformed from the free-swelling state, so that the force applied on the plate is small. In such a case, a certain

slope of the force–time is observed in the experiment, possibly due to drift of the equipment. The force–relaxation curves do become flat when the gel is compressed significantly. It takes about $t_D = 2$ h to reach the state of equilibrium. For a sample of radius $R = 1.5$ mm, the effective diffusivity of water in the polyacrylamide gel is estimated to be on the order of $D \approx R^2/t_D \approx 10^{-10}$ m^2 s^{-1}, which is consistent with the literature.[26] The measured nominal stresses in equilibrium are plotted against the stretches set by the positions of the plate (Fig. 6b).

As pointed out by Cai and Suo,[16] the function $\Pi_{mix}(J)$ can be determined by multiple distinct experimental methods. Here we illustrate several methods using our experimental data. To determine a function of a single variable, $\Pi_{mix}(J)$, one needs to run an experiment that contains at least one independent variable. In Method 1, the independent variable is chosen as the MBAA-to-acrylamide ratio. By a combination of the compression test, gravimetric experiment and free-swelling experiment, we have already obtained NkT and J_0 as functions of the MBAA-to-acrylamide ratio (Fig. 5). When a gel swells freely in pure water, the stresses and the chemical potential vanish, $\sigma_1 = \sigma_2 = \sigma_3 = 0$ and $\mu = 0$. In equilibrium the stretches are isotropic and homogeneous in the gel, $\lambda_1 = \lambda_2 = \lambda_3 = \lambda_0$. Eqn (9) reduces to

$$\Pi_{mix} = \frac{NkT}{\lambda_0^3}\left(\lambda_0^2 - 1\right). \tag{12}$$

This equation gives the osmotic pressure for a free-swelling gel. Consequently, we can determine pairs of the values (J, Π_{mix}) for gels of different values of the MBAA-to-acrylamide ratio.

In Method 2, the independent variable is chosen to be the position of the plate in the force–relaxation experiment. When
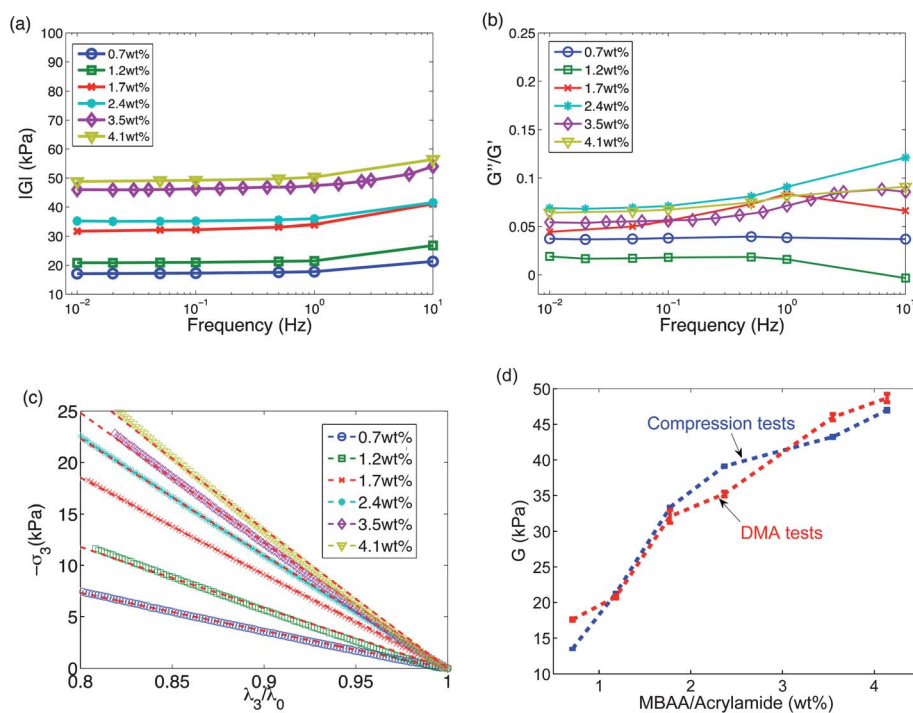

Fig. 4 (a) Viscoelastic moduli for gels of various values of the MBAA-to-acrylamide ratio over a range of frequency. The amplitude of the modulus, $|G| = \sqrt{G'^2 + G''^2}$. (b) The ratio of the loss modulus to the storage modulus, G''/G'. (c) The stress–stretch curve measured under unidirectional compression is fitted with eqn (10), as shown by red dashed lines. (d) Comparison of the modulus obtained from DMA and compression tests.
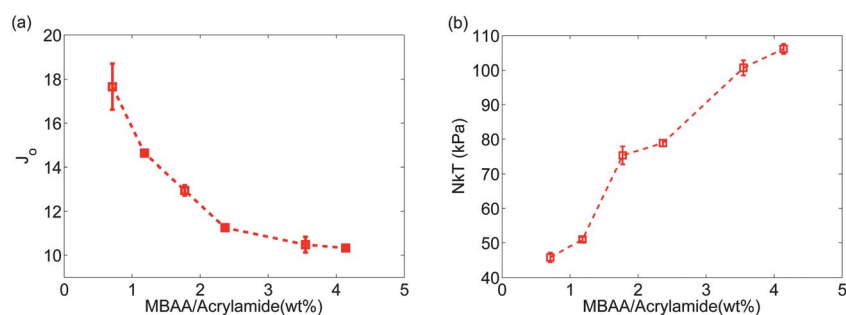
Fig. 5 Properties of freely swollen gels of several values of MBAA-to-acrylamide ratio. (a) The values of the swelling ratio J_0. (b) The values of NkT.

a disk of a gel reaches a state of equilibrium in distilled water and subject to the constraint of the plate and stage, J can be determined by the gravimetric experiment, and λ_3 can be determined by the position of the plate. The lateral stresses and the chemical potential vanish, $\sigma_1 = \sigma_2 = 0$ and $\mu = 0$. Recall that the lateral stretches are $\lambda_1 = \lambda_2 = \sqrt{J/\lambda_3}$. Eqn (9a) reduces to

$$\Pi_{\text{mix}} = \frac{NkT}{J}\left(\frac{J}{\lambda_3} - 1\right). \tag{13}$$

This equation gives the osmotic pressure in the gel in equilibrium with the pure solvent and subject to the constraint of the plate and the stage.

In Method 3, the independent variable is still chosen to be the position of the plate in the force–relaxation experiment, but we now use the measured stress in equilibrium. Subtracting eqn (9b) from (9c), and recalling that $\lambda_2^2 = J/\lambda_3$ and $s_3 = \sigma_1 J/\lambda_3$, we obtain that

$$J = \lambda_3^3 - \frac{s_3\lambda_3^2}{NkT}. \tag{14}$$

Once we determine NkT as before, and determine s_3 and λ_3 upon equilibrium from constrained swelling, we calculate J from eqn (14), and $\Pi_{\text{mix}}(J)$ from eqn (13).

The functions $\Pi_{\text{mix}}(J)$ determined by the three methods are indistinguishable (Fig. 7). This agreement supports the hypothesis that polyacrylamide hydrogels are ideal elastomeric gels. The osmotic pressure due to mixing, Π_{mix}, decreases as the swelling ratio J increases. Note that some data were obtained from the free-swelling gels, and others were obtained from the force–relaxation experiment. In the free-swelling experiment, the swelling ratio was varied by varying the crosslink density (i.e., by varying the MBAA-to-acrylamide ratio). In the force–relaxation

experiment, the swelling ratio is varied by both the crosslink density and the compression of the plate. The agreement indicates that the function $\Pi_{\text{mix}}(J)$ is independent of how the swelling ratio is varied.

Our data are plotted in Fig. 8 along with the data marked as Konda,[27] which was extracted by using Methods 2 and 3 from the tensile tests of polyacrylamide hydrogels. The two sets of data were for different ranges of the swelling ratio, but both were obtained by using more than one method to determine the osmotic pressure. Thus, the function $\Pi_{\text{mix}}(J)$ is independent of the methods of its determination over a range of swelling ratios typical in the applications of polyacrylamide gels.

These two sets of data are further compared with three other sets of data extracted from the literature (Fig. 9). The data marked as Day[22] and Livney[28] were obtained by measuring the osmotic pressure of polyacrylamide–water solutions enclosed in semipermeable membranes. Relatively mono-dispersed polyacrylamide chains were used in the two experiments with molecular weights 100 000 g mol^{-1} and 237 000 g mol^{-1} respectively. The data marked as Mallam[29] were measured by placing a polyacrylamide gel in a semipermeable bag submerged in certain polymer (e.g. polystyrene or polyvinyl acetate) solutions. By changing the concentration of the polymer in the aqueous solution outside the bag, the chemical potential of water in the external solution was changed. (The relation between the chemical potential of water and the concentration of the polymer was determined in a separate experiment.[25]) The semipermeable bag was only permeable to water. When the gel inside the bag and the solution outside the bag attain the equilibrium, the chemical potential of water inside equals that outside. Setting $\sigma_1 = \sigma_2 = \sigma_3 = 0$ in eqn (9), we obtain
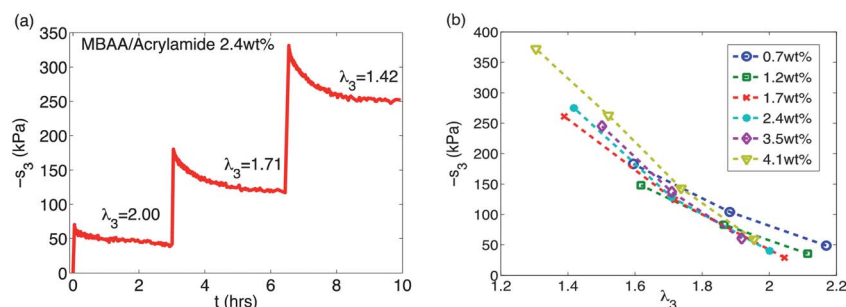

Fig. 6 Data obtained from force–relaxation experiment. (a) Three stress–relaxation curves for a gel with a MBAA-to-acrylamide ratio of 2.4 wt%. (b) For gels of various MBAA-to-acrylamide ratios, the nominal stress s_3 in equilibrium is plotted against the stretch λ_3.
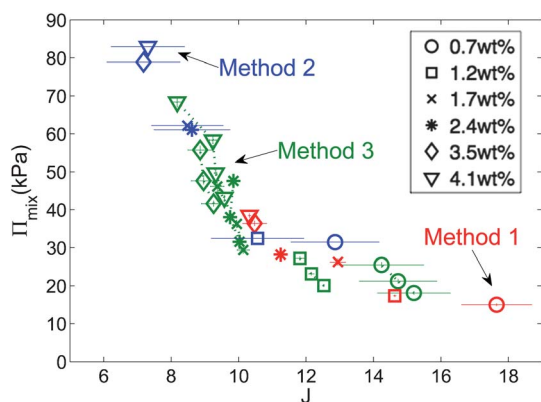
Fig. 7 The function $\Pi_{\mathrm{mix}}(J)$ determined by the three methods. Data points obtained with gels of different MBAA-to-acrylamide ratios are differentiated by symbols. Date points obtained by the three methods are differentiated by colors.
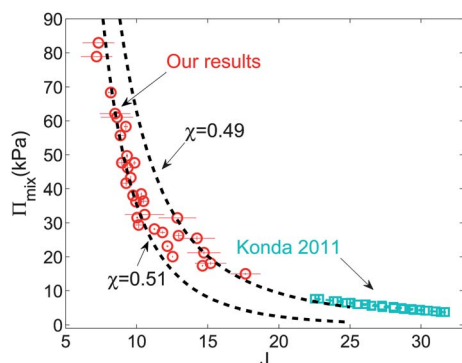

Fig. 8 To fit the experimentally determined osmotic pressure over a range of swelling ratios to the Flory–Huggins theory (dashed lines), different values of the Flory–Huggins parameter χ are required.
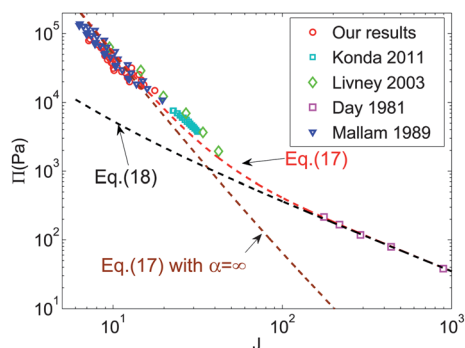

Fig. 9 Comparison of the function $\Pi_{\mathrm{mix}}(J)$ determined by various methods. The data are fitted to the Flory–Huggins theory. The fitting curves, as shown by dashed lines, are differentiated by colors, red for eqn (17), brown for eqn (17) with $\alpha = \infty$, and black for eqn (18).

$$\Pi_{\mathrm{mix}} = \frac{NkT}{\lambda^3}\left(\lambda^2 - 1\right) - \frac{\mu}{\Omega}. \qquad (15)$$

Mallam *et al.* used the gravimetric method to determine $J = \lambda^3$ for gels equilibrated with solutions of several values of the chemical potential of water, μ.[29] Meanwhile, they did uniaxial

compression measurements on the fully swollen gels for the shear modulus, where we can recalculate NkT with eqn (11). Once λ, NKT and μ are known, Π_{mix} can be calculated with eqn (15).

All the data overlap over a range of the swelling ratio, within which the osmotic pressures measured by various methods agree. This agreement indicates that the function $\Pi_{\mathrm{mix}}(J)$ is the same for polyacrylamide hydrogels and polyacrylamide–water solutions. The agreement further confirms that crosslinks negligibly affect the function $\Pi_{\mathrm{mix}}(J)$. The data of Day and Robb[22] were obtained for dilute solutions, and lie beyond the range of the four other sets of data.

Polyacrylamide gels are known to be temperature sensitive.[30] In this study we focus on isothermal processes. All the experiments were performed at room temperature, as well as those in the literature re-analyzed here to extract the function $\Pi_{\mathrm{mix}}(J)$.[22,27–29]

5. Comparison of experimental data with the Flory–Huggins model

To highlight the model of ideal elastomeric gels, we have so far avoided invoking the Flory–Huggins model of mixing. We now discuss how the Flory–Huggins model fits the experimental data of polyacrylamide hydrogels and polyacrylamide–water solutions. The free energy of mixing derived from the Flory–Huggins model is[12,13]

$$W_{\mathrm{mix}}(J) = \frac{kT}{\Omega}\left[(J-1)\log\left(1 - \frac{1}{J}\right) - \frac{1}{\alpha}\log J + \chi\left(1 - \frac{1}{J}\right)\right]. \qquad (16)$$

The first two terms in the bracket are due to the entropy of mixing, and the third term is due to the enthalpy of mixing. For uncrosslinked polymer chains, α is the volume per polymer chain divided by the volume per solvent molecule. The Flory–Huggins parameter χ is a dimensionless measure of the enthalpy of mixing. Inserting eqn (16) into (5), one obtains the osmotic pressure due to mixing:

$$\Pi_{\mathrm{mix}}(J) = -\frac{kT}{\Omega}\left[\frac{1}{J} + \log\left(1 - \frac{1}{J}\right) - \frac{1}{\alpha J} + \frac{\chi}{J^2}\right]. \qquad (17)$$

For a crosslinked polymer network, setting $\alpha = \infty$ leaves only a single parameter χ to fit experimental data. We plot eqn (17) with two values of χ, indicating that the Flory–Huggins theory does not fit the experimental data with any constant value of χ (Fig. 8). A common practice is to fit eqn (17) to experimental data by allowing χ to be a function of J, which will not be pursued here.

The Flory–Huggins model, however, does capture the trend of the large range of data on the log–log plot (Fig. 9). We use the Flory–Huggins eqn (17) to fit the five sets of data, giving $\chi = 0.4986$ and $\alpha = 3927$. This value of α may be compared with the following estimate. By definition, $\alpha = \Omega_{\mathrm{PAAM}}/\Omega$, where the volume per water molecule is $\Omega = 2.99 \times 10^{-29}$ m^3, and the volume per polyacrylamide chain is estimated by $\Omega_{\mathrm{PAAM}} = x\Omega_{\mathrm{AAM}}$, where $\Omega_{\mathrm{AAM}} = 8.21 \times 10^{-29}$ m^3 is the volume per acrylamide monomer,[22] and x is the number of acrylamide monomer per polyacrylamide chain ($x = 1400$ for the data of ref. 22). This estimate gives $\alpha = 3840$. Also plotted is eqn (17) with

$\chi = 0.49$ and $\alpha = \infty$, indicating that the finite value of α is needed to fit the data of dilute solutions.

The effect of the finite chain length of the polymer in a dilute solution is better appreciated as follows. Recall the Taylor series $\log(1 - x) = -x - 0.5x^2 - \dots$ and write eqn (17) as

$$\Pi_{\mathrm{mix}}(J) = \frac{kT}{\Omega}\left(\frac{1}{\alpha J} + \frac{0.5 - \chi}{J^2}\right). \qquad (18)$$

This approximation retains the leading terms of the power series. The term of J^{-1} comes from the entropy of mixing when the polymer chains are of finite length, and the term of J^{-2} comes from the entropy of mixing and enthalpy of mixing. In a gel, the polymers are crosslinked, $\alpha = \infty$, and the term of J^{-1} vanishes. In a solution, $\alpha < \infty$; for a dilute solution the term of J^{-1} can be significant compared to the term of J^{-2}. Eqn (18) represents the dilute solution well, but not for gels with small values of the swelling ratio (Fig. 9).

6.   Concluding remarks

For an ideal elastomeric gel, the stresses applied on the gel are balanced by the elasticity of the network, the osmosis due to mixing the polymer and the solvent, and the osmosis due to the solvent-containing environment outside the gel. The osmotic pressure due to mixing is a function of the swelling ratio, $\Pi_{\mathrm{mix}}(J)$. We show that this function obtained by several distinct experimental methods is consistent. Specifically, the function $\Pi_{\mathrm{mix}}(J)$ obtained from a gel under different states of applied stress is the same,[16] the function obtained from a free-swelling gel is the same as that obtained from the constrained-swelling gel, the function is independent of crosslink density, and the function obtained from the gels is similar to that obtained from the solutions. We further show that the Flory–Huggins model of polymer solutions with a constant Flory–Huggins parameter does not fit the experimental data well, but does capture the trend of the data over four orders of magnitude in the osmotic pressure. It is hoped that the other elastomeric gels will be examined to ascertain the range of applicability of the model of ideal elastomeric gels. It is also of great interest to extend this approach to gels sensitive to various stimuli, such as temperature, pH, and salt concentration.

Acknowledgements

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