Equations of state for ideal elastomeric gels

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Abstract – Submerged in a solvent-containing environment and subject to applied forces, a covalent polymer network absorbs the solvent and deforms, forming an elastomeric gel. The equations of state are derived under two assumptions. First, the amount of the solvent in the gel varies when the gel changes volume, but remains constant when the gel changes shape. Second, the Helmholtz free energy of the gel is separable into the contribution due to stretching the network and that due to mixing the polymer and the solvent. We demonstrate that these equations of state fit several sets of experimental data in the literature remarkably well.

Long, flexible polymers can be crosslinked by covalent bonds to form a three-dimensional network, an elastomer. Submerged in an environment containing solvent molecules, the network imbibes the solvent and swells, resulting in an elastomeric gel. Depending on functional groups along the polymers, the amount of swelling can be regulated by stimuli such as force [1], temperature [2,3], and pH value [4,5]. Elastomeric gels are being developed for diverse applications, including artificial muscles for actuators [6], self-regulated valves in microfluidics [7], and swellable packers in oil wells [8]. These applications have motivated the recent development of nonlinear field theories [9–12].

The field theories require the input that characterizes how mechanical constraints affect the amount of swelling, and how chemical processes generate forces. Elastomeric gels are often characterized by Flory-Rehner's model [13]. To compare theoretical predictions and experimental observations quantitatively, many fitting parameters have been added to the original model [2,3], and the original model has also been modified in many other ways [14,15]. In this paper, we explore an alternative approach. We develop a set of equations of state on the basis of two assumptions. First, the amount of the solvent in the gel varies when the gel changes volume, but remains constant when the gel changes shape. Second, the Helmholtz free energy of the gel is separable into the contributions of stretching the network and mixing the

polymer and the solvent. We demonstrate that these equations of state fit several sets of experimental data in the literature remarkably well.

Figure 1 illustrates a block of a network. In the reference state, the block is a unit cube of a dry network, containing no solvent and subject to no applied forces. In the current state, the network is submerged in a solvent-containing environment, and the six faces of the block are subject to applied forces. When the network, the solvent, and the applied forces equilibrate, the network absorbs C number of solvent molecules, and deforms homogeneously into the shape of a parallelepiped. The thermodynamic state of the block is invariant with respect to any rigid-body translation; we fix the position of one vertex of the block, O, to the origin of the coordinates. In the reference state, the three vectors **OA**, **OB** and **OC** are the edges of the unit cube. In the current state, the three vectors are the edges of the parallelepiped, with F_{i1} being the three components of the vector **OA**, F_{i2} the three components of the vector **OB**, and F_{i3} the three components of the vector **OC**. The nine components F_{iK} together define the tensor of the deformation gradient.

The ratio of the volume of the swollen gel and that of the dry network is determined as follows. The volume of the parallelepiped is $J = (\mathbf{OA} \times \mathbf{OB}) \cdot \mathbf{OC}$, namely, $J = \det \mathbf{F}$. The gel is a soft material. Subject to applied forces, the gel changes shape readily, but the volumes of individual polymer chains or solvent molecules remain nearly unchanged. As an idealization, we assume that the volume of the gel is a function of the concentration of the
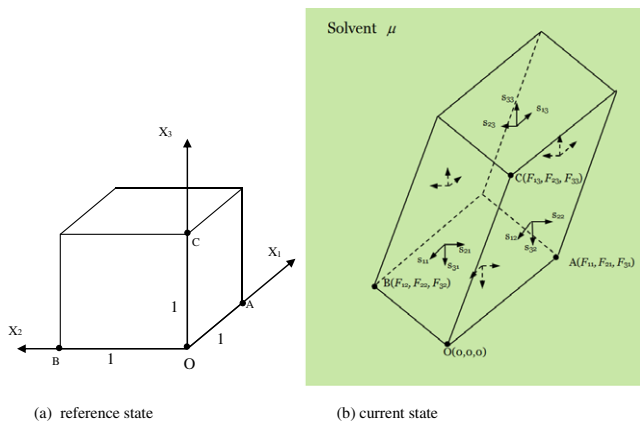
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Fig. 1: (Colour on-line) (a) In the reference state, a network of dry polymers is a unit cube, and contains no solvent and subject to no applied forces. (b) In the current state, the network is in equilibrium with applied forces and with an environment of a fixed chemical potential of solvent, μ; the network deforms homogeneously into a parallelepiped. The applied forces act on the six faces of the parallelepiped, and are indicated by the nominal stresses s_{iK}. The deformation is characterized by mapping the three vectors **OA**, **OB** and **OC** from the reference state to the current state. The components of the three vectors in the current state define the deformation gradient F_{iK}.

solvent:
$$J = f(C). \qquad (1)$$

That is, the amount of the solvent in the gel varies when the gel changes volume, but remains constant when the gel changes shape.

A more specific relation between J and C is commonly used in the literature. When two species of molecules mix, the volume of the mixture may differ from the sum of the volumes of the two pure components. This change in volume, however, is typically small compared to the change in volume during swelling [16–18]. It is commonly assumed that the volume of the gel equals the sum of the volume of the dry network and the volume of the absorbed solvent, $J = 1 + \Omega C$, where Ω is the volume per solvent molecule. This specific relation will not be used in this paper; rather, the more general assumption (1) is adopted.

The relation (1) determines the concentration of solvent, C, once the deformation gradient is known. Consequently, the nine components of the deformation gradient **F** specify the state of the gel. Attention is focused on isothermal processes, in which temperature is fixed and is not listed as a variable. Let W be the Helmholtz free energy of the gel in the current state. Under the constraint (1), the Helmholtz free energy of the gel is taken to be a function of the nine components of the deformation gradient, $W = W(\mathbf{F})$.

The density of crosslinks is typically very low; each polymer chain consists of a large number of monomers. Following Flory and Rehner, we assume that the crosslinks negligibly affect the interactions between the monomers

and the solvent molecules, so that the Helmholtz free energy of the gel is assumed to be separable into contributions from stretching the network and mixing the polymer and the solvent [13]:
$$W = W_{stretch}(\mathbf{F}) + W_{mix}(C). \qquad (2)$$

The free energy due to the stretching of the network, $W_{stretch}(\mathbf{F})$, is a function of the tensor of the deformation gradient, and depends on the density of crosslinks. The free energy due to the mixing of the polymer and the solvent, $W_{mix}(C)$, is a function of the concentration of the solvent in the gel, but is independent of the density of crosslinks.

Of course, assumption (2) is not always correct. For example, many biopolymers contain folded domains, which can unfold under applying stresses [19]. The interaction of the solvent with folded domains can significantly differ from that with unfolded domains. Consequently, W_{mix} in general depends on all the components of F_{iK}, rather than on a single variable, J. However, we will demonstrate that the relation (2) holds remarkably well for many gels.

The two assumptions, (1) and (2), form the basis for the model of ideal elastomeric gels. We next examine the consequences of the model.

As illustrated in fig. 1, s_{iK} is the force applied on the block in the current state, in direction i, on the face whose normal vector is in direction K when the block is in the reference state. Because the block in the reference state is a unit cube, by definition s_{iK} are the components of the nominal-stress tensor. The applied forces can be represented by hanging weights. In the current state, associated with a small change in the deformation gradient, $d\mathbf{F}$, the potential energy of the weights changes by $-s_{iK}dF_{iK}$. We adopt the convention that a repeating index implies the summation over 1, 2 and 3.

Let μ be the chemical potential of the solvent in the environment —that is, the increase of the Helmholtz free energy of the environment when the environment gains one solvent molecule. The chemical potential of solvent in a saturated mixture of liquid and vapor is set to be zero. Associated with the transfer of dC number of solvent molecules from the environment to the gel, the free energy of the environment changes by $-\mu dC$.

The gel, the hanging weights, and the solvent-containing environment together form a composite thermodynamic system. The composite exchanges energy with the rest of the world by heat, but not by work; the composite does not exchange matter with the rest of the world. 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:
$$dW - s_{iK}dF_{iK} - \mu dC = 0. \qquad (3)$$

The composite is capable of internal variations of two types: change in the deformation gradient and change in the number of solvent molecules inside the gel. The condition of equilibrium (3) holds for arbitrary small changes of $\mathbf{F}$ and C, subject to the constraint (1).

Inserting (1) and (2) into the condition of equilibrium (3), we obtain that

$$\left[\frac{\partial W_{stretch}(\mathbf{F})}{\partial F_{iK}} + \left(\frac{\mathrm{d}W_{mix}(C)}{\mathrm{d}C} - \mu \right) \frac{JH_{iK}}{\mathrm{d}f(C)/\mathrm{d}C} \right.$$
$$\left. -s_{iK} \right] \mathrm{d}F_{iK} = 0. \qquad (4)$$

We have used a mathematical identity $\mathrm{d}J = JH_{iK}\mathrm{d}F_{iK}$, where H_{iK} is the inverse of the deformation gradient, i.e., $H_{iK}F_{iL} = \delta_{KL}$ and $H_{iK}F_{jK} = \delta_{ij}$ [20]. The network, the solvent and the applied forces equilibrate when (4) holds for arbitrary small changes $\mathrm{d}F_{iK}$: a total of nine independent variables. Consequently, the term in the bracket in front of each of the nine terms in (4) must vanish individually, giving that

$$\sigma_{ij} = F_{jK}\frac{\partial W_{stretch}(\mathbf{F})}{J\partial F_{iK}} - \Pi(J)\delta_{ij}, \qquad (5)$$

with

$$\Pi(J) = \left(\mu - \frac{\mathrm{d}W_{mix}(C)}{\mathrm{d}C} \right) \frac{1}{\mathrm{d}f(C)/\mathrm{d}C}. \qquad (6)$$

We have expressed the equations of state (5) in terms of the true stress σ_{ij}, which is defined by imagining a small cube cut from the parallelepiped. The true stress is the force in the current state divided by the area in the current state, and relates to the nominal stress by $\sigma_{ij} = s_{iK}F_{jK}/J$ [20].

In the model of ideal elastomeric gels, the function $\Pi(J)$ 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 of the polymer and the solvent, and (5) reduces to $\sigma_{ij} = -\Pi(J)\delta_{ij}$. That is, the function $\Pi(J)$ is the osmotic pressure in the solution. For a solution in which polymers are not crosslinked, a semipermeable membrane is needed to prevent the polymers in the solution from escaping into the environment. In the solution, the osmosis is balanced by a state of applied hydrostatic stress. By contrast, in an elastomeric gel, the polymer chains are held together by crosslinks, so that no semipermeable membrane is needed to separate the gel and the environment. The osmotic pressure as a function of the concentration of polymer is the same for the solution and the gel. In the gel, the osmotic pressure is balanced by the elasticity of the network and by the applied stresses, eq. (5). The solution and the gel have the same chemistry because the dilute crosslinks negligibly affect the molecular interactions between the solvent 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.

Because the thermodynamic state of the parallelepiped is invariant with respect to any rigid-body rotation, the free energy can only depend on the lengths of, and the angles between, the three vectors $\mathbf{OA}$, $\mathbf{OB}$ and $\mathbf{OC}$. The six quantities are determined by a combination of the inner-products of the vectors, $F_{iK}F_{iL}$, known as the Green deformation tensor [20]. That is, the invariance associated with rigid-body rotation requires that W should depend on $\mathbf{F}$ through $F_{iK}F_{iL}$. Using this dependence in (5), one obtains that $s_{iK}F_{jK} = s_{jK}F_{iK}$ or $\sigma_{ij} = \sigma_{ji}$. These relations are also be interpreted as the balance of moments acting on the parallelepiped.

In the original Flory-Rehner model [13], specific functions are adopted for $W_{stretch}(\mathbf{F})$ and $W_{mix}(C)$. The free energy associated with stretching the network is given by the Gaussian-chain model [13]:

$$W_{stretch} = \frac{1}{2}NkT(F_{iK}F_{iK} - 3 - 2\log J), \qquad (7)$$

where N is the number of polymer chains per unit volume and kT is the temperature in the unit of energy. The free energy associated with mixing the polymer and the solvent is given by the Flory-Huggins model [13]:

$$W_{mix} = kT\left[C\log\frac{\Omega C}{1+\Omega C} + \frac{\chi C}{1+\Omega C} \right], \qquad (8)$$

where χ is a parameter describing the interaction between the solvent and the polymer. These functions have been used to interpret experimental data, and have been critiqued and modified in many ways. For example, many other models have been proposed to describe the stretching of the networks [21–23]. It has also been pointed out that the Flory-Huggins model often fails to match experiment data without extending the interaction parameter χ to a fitting function. For example, Hooper et al. [24] has pointed out that the Flory-Huggins model does not account for orientation-dependent interactions (e.g., hydrogen bonds), which can significantly affect the swelling behavior of a gel. Bawendi and Freed [25,26] have made systematic corrections to the mean-field theory of Flory and Huggins.

In this paper, we adopt the Gaussian-chain model, which characterizes the elasticity of a network by a single scalar, the number of polymer chains per unit volume, N. As stated previously, chemomechanical interactions are material-specific and can be very complex, and we do not make any assumption of the function $W_{mix}(C)$. Within this approach, a gel is fully characterized by a scalar, N, and a single-variable function, $\Pi(J)$. We show below that the function $\Pi(J)$ can be determined by several distinct experimental methods. Furthermore, we use existing experimental data to demonstrate that the function $\Pi(J)$ determined by one experimental method can be used to predict data obtained from another experimental method.

Inserting (7) into (5), we obtain that

$$\sigma_{ij} = \frac{NkT}{J}(F_{jK}F_{iK} - \delta_{ij}) - \Pi(J)\delta_{ij}. \qquad (9)$$

In relating the model to experiments, we often describe the deformation of the gel in the coordinates of principal stretches. Let $\lambda_1, \lambda_2, \lambda_3$ be the principal stretches of the gel, so that $\mathbf{F} = \mathrm{diag}(\lambda_1, \lambda_2, \lambda_3)$ and $J = \lambda_1 \lambda_2 \lambda_3$. Write (9) in terms of the principal stretches and the principal stresses:

$$\sigma_1 = \frac{NkT}{J} \left(\lambda_1^2 - 1 \right) - \Pi(J), \qquad (10a)$$

$$\sigma_2 = \frac{NkT}{J} \left(\lambda_2^2 - 1 \right) - \Pi(J), \qquad (10b)$$

$$\sigma_3 = \frac{NkT}{J} \left(\lambda_3^2 - 1 \right) - \Pi(J). \qquad (10c)$$

Submerged in the solvent-containing environment but subject to no applied forces, the gel attains a state of equilibrium, the free-swelling state, characterized by a isotropic swelling ratio $\lambda_1 = \lambda_2 = \lambda_3 = \lambda_0$. Setting $\sigma_1 = 0$ in (10a), we obtain that $\Pi(\lambda_0^3) = NkT(\lambda_0^{-1} - \lambda_0^{-3})$. This relation determines λ_0 once the scalar N and the function $\Pi(J)$ are known. When a gel in the free-swelling state 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 volume of the gel remains unchanged when the gel deforms to a state $(\lambda_1, \lambda_2, \lambda_3)$, so that $J = \lambda_1 \lambda_2 \lambda_3 = \lambda_0^3$. 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 the relative stretches, (10) is written as

$$\sigma_3 - \sigma_1 = \frac{NkT}{\lambda_0} \left[\left(\frac{\lambda_3}{\lambda_0} \right)^2 - \left(\frac{\lambda_1}{\lambda_0} \right)^2 \right], \qquad (11a)$$

$$\sigma_3 - \sigma_2 = \frac{NkT}{\lambda_0} \left[\left(\frac{\lambda_3}{\lambda_0} \right)^2 - \left(\frac{\lambda_2}{\lambda_0} \right)^2 \right]. \qquad (11b)$$

These are the stress-stretch relations of a gel when the concentration of the solvent 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 (11) defines the shear modulus, $G = NkT/\lambda_0$.

We next use the model of ideal elastomeric gels to analyze several sets of experimental data in the existing literature. Figure 2(a) illustrates an experiment in which a cylinder of a polyacrylamide hydrogel is subject to a uniaxial tensile force. The applied longitudinal stress is denoted as σ_3, and the transverse stresses are zero, $\sigma_1 = \sigma_2 = 0$. Denote the longitudinal stretch by λ_3, and the two transverse stretches are equal, $\lambda_1 = \lambda_2$. In ref. [27], the experiments are conducted with tensile forces applied at different rates. When the loading rate is so high that the amount of solvent in the gel remains unchanged, the deformation conserves the volume of the gel, $\lambda_3 \lambda_1^2 = \lambda_0^3$. Consequently, (11a) is specialized to the form

$$\sigma_3 = \frac{NkT}{\lambda_0} \left[\left(\frac{\lambda_3}{\lambda_0} \right)^2 - \left(\frac{\lambda_3}{\lambda_0} \right)^{-1} \right]. \qquad (12)$$
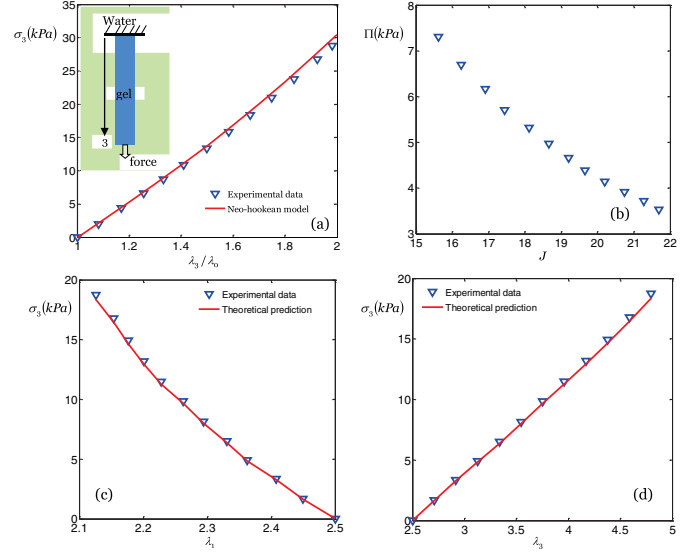

Fig. 2: (Colour on-line) (a) A cylinder of a gel is submerged in water and subject to a uniaxial tensile force. The stress-stretch curve measured under ultrafast tension is used to obtain the shear modulus. (b) The function $\Pi(J)$ is calculated from the measurements with ultraslow tension. The theoretical predictions are compared with experimental data for the $\sigma_3 - \lambda_1$ curve (c) and the $\sigma_3 - \lambda_3$ one (d). The experimental data are extracted from ref. [27].

This theoretical stress-stretch relation is plotted in fig. 2(a), along with the experimental data reported in [27]. The theoretical curve and the experimental data agree well once we fit the shear modulus as $NkT/\lambda_0 = 8.7\,\mathrm{kPa}$. The value of the free-swelling ratio λ_0 is unreported in [27]. However, the weight fraction of the polymer in the free swollen gel is reported as 6.2 wt%. Assuming the density of the polymer is the same as that of water, we estimate that the free-swelling ratio is $\lambda_0 = 2.5$. Consequently, we estimate that $NkT = 21.8\,\mathrm{kPa}$.

When the loading rate is so low that the gel equilibrates with the solvent and the applied stress, the tensile deformation causes the gel to absorb additional solvent, and the volume of the gel changes. Setting $\sigma_1 = 0$ in (10a), we obtain that

$$\Pi(J) = \frac{NkT}{J} \left(\lambda_1^2 - 1 \right). \qquad (13)$$

Under uniaxial tension, $\lambda_1 = \lambda_2$ and $J = \lambda_3 \lambda_1^2$. In [27], the relative stretches, λ_3/λ_0 and λ_1/λ_0, are measured at various values of the applied forces. These measured stretches, along with the values $\lambda_0 = 2.5$ and $NkT = 21.8\,\mathrm{kPa}$ estimated above, enable us to use (13) to plot the function $\Pi(J)$ in fig. 3(b).

In plotting (13), we do not need the values of the applied stress that maintain various states of stretches. As discussed above, the equations of state of the gel is fully characterized by the scalar N and the single-variable function $\Pi(J)$. Once determined, they predict the stress to maintain a state of stretches and in equilibrium with the external solvent. For a given value of J, we obtain
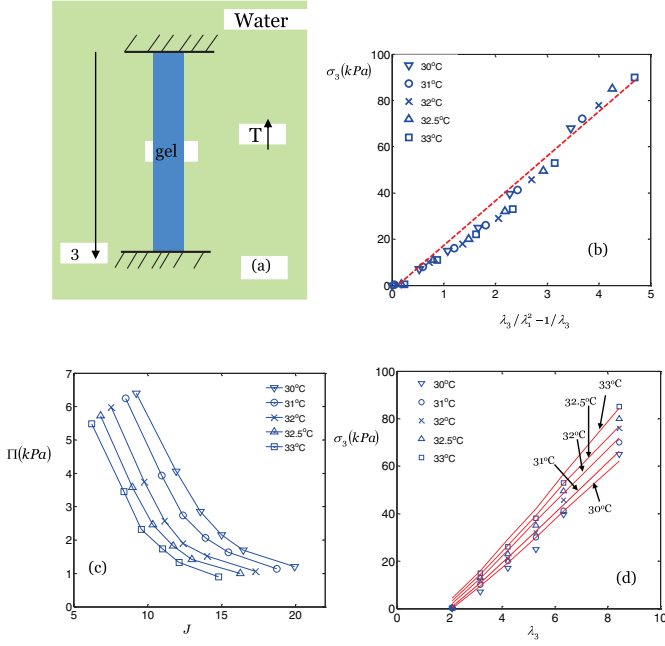
Fig. 3: (Colour on-line) (a) A bar of a hydrogel is submerged in water with a fixed length. Both the longitudinal stress and the lateral stretch change with temperature. (b) The longitudinal stress σ_3 is linearly related to $\lambda_3/\lambda_1^2 - 1/\lambda_3$ and the slope gives the shear modulus of the gel: $NkT = 18\,\mathrm{kPa}$. (c) The $\Pi(J)$ function is calculated for the gel from the experimental data at several temperatures. (d) The longitudinal stress-stretch relationship for PNIPAM gel at several temperatures. Different curves are calculated by using the shear modulus from (b) and the $\Pi(J)$ function from (c). The experiment data are extracted from ref. [28].
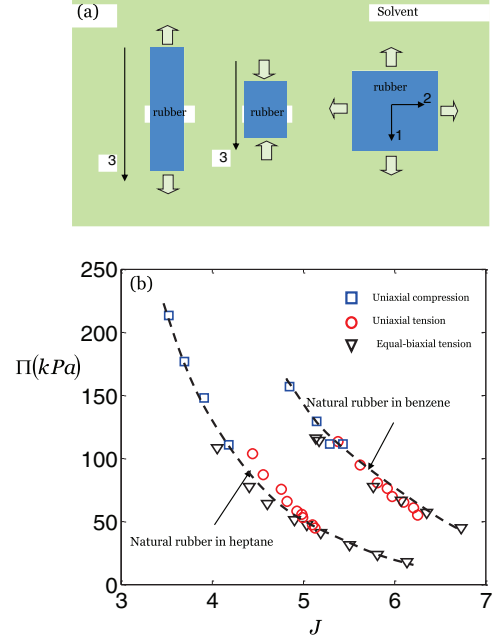

Fig. 4: (Colour on-line) (a) A natural rubber is submerged in a solvent, either heptane or benzene, and is subject to three types of load. (b) The function $\Pi(J)$ is calculated from the data obtained under the three types of loads. The experiment data are extracted from ref. [29].

λ_1 from (13), obtain λ_3 from $\lambda_3 = J/\lambda_1^2$, and obtain σ_3 from (10c). We plot the results as the $\sigma_3 - \lambda_1$ curve in fig. 2(c), and as the $\sigma_3 - \lambda_3$ curve in fig. 2(d). They both agree remarkably well with the experimental data reported in [27].

The next example concerns a poly (N-isopropylaryla-mide) hydrogel. The hydrophobicity of this hydrogel varies markedly with temperature, so that the $\Pi(J)$ function varies with temperature. According to the experiments carried out by Suzuki et al. [28], a bar of the hydrogel is first submerged in water at $30\,^\circ\mathrm{C}$ and reaches equilibrium with a homogenous and isotropic swelling ratio $\lambda_0 = 2.2$. Subsequently, the hydrogel is stretched in the longitudinal direction with fixed length, as illustrated in fig. 3(a). In the experiment, the stress in the longitudinal direction and the stretches in the lateral direction are carefully measured in equilibrated hydrogels at different temperatures. Write the stretch in the longitudinal direction by λ_3 and the stretch in the lateral direction by λ_1. With zero lateral stress, a combination of (10a) and (10c) eliminates the function $\Pi(J)$, giving that

$$\sigma_3 = NkT \left(\frac{\lambda_3}{\lambda_1^2} - \frac{1}{\lambda_3} \right). \tag{14}$$

Based on the experimental data reported in [28], in fig. 3(b), we plot σ_3 as a function of $\lambda_3/\lambda_1^2 - 1/\lambda_3$ for several stretches and temperatures. Since the temperature range in fig. 3(b) is relatively small, the variation of the parameter NkT is negligible: all the data points in fig. 3(b) approximately follows a single line, whose slope gives $NkT = 18\,\mathrm{kPa}$. Similarly, based on the stretches measured at different temperatures for the hydrogel and the shear modulus obtained above, $\Pi(J)$ is plotted at different temperatures for the hydrogel in fig. 3(c) by using eq. (13). With the shear modulus and $\Pi(J)$ for the hydrogel, we calculate the longitudinal stress-stretch as described before. The comparison between experimental data and theoretical prediction is plotted in fig. 3(d). Different samples are used in the experiments for different levels of longitudinal stretches. Given the variations of the samples, the theoretical predictions are also very good.

The last example is concerned with the experiments of Treloar [29]. A natural rubber is submerged in two types of solvent, heptane and benzene, and is subject to three types of loads: uniaxial tensile force, uniaxial compressive force, and equal biaxial tensile forces (fig. 4(a)). Both longitudinal stretch and lateral stretches are measured under very small loading rate, so that the rubber is in equilibrium with the solvent. Based on the average molecular weight between two crosslinks in ref. [29], we estimate that the shear modulus of the dry rubber is $NkT = 310\,\mathrm{kPa}$. For experimental data obtained under

uniaxial tensile or compressive forces, we use the measured stretches and (13) to plot the function $\Pi(J)$. For the rubber under equal biaxial tension, the vertical stress vanishes, $\sigma_3 = 0$, the lateral stretches are equal, $\lambda_1 = \lambda_2$, and $J = \lambda_1^2 \lambda_3$. Equation (10c) is specialized to the form

$$\Pi(J) = \frac{NkT}{J}\left(\lambda_3^2 - 1\right). \tag{15}$$

Using the above procedure, we plot the $\Pi(J)$ function in fig. 4(b). The functions $\Pi(J)$ determined by different types of load collapse to two curves, one for the rubber submerged in heptanes, and other for the rubber submerged in benzene. The plot demonstrates that the function $\Pi(J)$ is independent of the types of load. This observation supports the model of ideal elastomeric gels.

In summary, an ideal elastomeric gel is characterized by the number of polymer chains per unit volume, N, and the osmotic pressure as a function of the volumetric ratio, $\Pi(J)$. Experimental data in the literature allow the function $\Pi(J)$ to be determined in several ways. The agreement between the experiments and theoretical predictions is encouraging. It is hoped that the model of ideal elastomeric gels can be tested with other polymers, so that its scope of applicability can be defined.

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REFERENCES

[1] Doi M., *J. Phys. Soc. Jpn.*, **78** (2009) 052001.
[2] Shirota H., Endo N. and Horie K., *Chem. Phys.*, **238** (1998) 487.
[3] Cai S. Q. and Suo Z. G., *J. Mech. Phys. Solids*, **59** (2011) 2259.
[4] Brannon-Peppas L. and Peppas N. A., *Chem. Eng. Sci.*, **46** (1991) 715.
[5] Marcombe R., Cai S. Q., Hong W., Zhao X. H., Lapusta Y. and Suo Z. G., *Soft Matter*, **6** (2010) 784.
[6] Liu Z. and Clavert P., *Adv. Mater.*, **12** (2000) 288.
[7] Beebe D. J., Moore J. S., Bauer J. M., Yu Q., Liu R. H., Devadoss C. and Jo B. H., *Nature*, **404** (2000) 588.
[8] Cai S. Q., Lou Y. C., Ganguly P., Robisson A. and Suo Z. G., *J. Appl. Phys.*, **107** (2010) 103535.
[9] Hong W., Zhao X. H., Zhou J. X. and Suo Z. G., *J. Mech. Phys. Solids*, **56** (2008) 1779.
[10] An Y. H., Solis F. J. and Jiang H. Q., *J. Mech. Phys. Solids*, **58** (2010) 2083.
[11] Hui C. Y. and Muralidharan V., *J. Chem. Phys.*, **123** (2005) 154905.
[12] Chester S. A. and Anand L., *J. Mech. Phys. Solids*, **58** (2010) 1879.
[13] Flory P. J. and Rehner J., *J. Chem. Phys.*, **11** (1943) 521.
[14] Oh K. S., Oh J. S., Choi H. S. and Bae Y. C., *Macromolecules*, **31** (1998) 7328.
[15] Horkay F. and Mckenna G. B., *Physical Properties of Polymers Handbook* (AIP Press) 1996.
[16] Eichinger B. E. and Flory P. J., *Trans. Faraday Soc.*, **64** (1968) 2035.
[17] Sastry N. V. and Patel M. C., *J. Chem. Eng. Data*, **48** (2003) 1019.
[18] Zhong X., Wang Y. X. and Wang S. C., *Chem. Eng. Sci.*, **51** (1996) 3235.
[19] Dusek K., Duskova-Smrckova M., Llavsky M., Stewart R. and Kopecek J., *Biomacromolecules*, **4** (2003) 1818.
[20] Holzapfel G. A., *Nonlinear Solid Mechanics* (Wiley) 2000.
[21] Treloar L. R. G., *The Physics of Rubber Elasticity* (Oxford) 1975.
[22] Arruda E. M. and Boyce M. C., *J. Mech. Phys. Solids*, **41** (1993) 389.
[23] Gent A. N., *Rubber Chem. Technol.*, **69** (1996) 59.
[24] Hooper H. H., Baker J. P., Blanch H. W. and Prausnitz J. M., *Macromolecules*, **23** (1990) 1096.
[25] Bawendi M. G. and Freed K. F., *J. Chem. Phys.*, **88** (1988) 2741.
[26] Bawendi M. G., Freed K. F. and Mohanty U., *J. Chem. Phys.*, **84** (1986) 7036.
[27] Konda K., Urayama K. and Takigawa T., *Macromolecules*, **44** (2011) 3000.
[28] Suzuki A., Sanda K. and Omori Y., *J. Chem. Phys.*, **107** (1997) 5179.
[29] Treloar L. R. G., *Trans. Faraday Soc.*, **46** (1950) 787.