Bending a beam by a generalized ideal elastomeric gel

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A hybrid beam with a gel layer bonded on the top of an elastic non-swellable substrate has been commonly adopted to make various sensors and actuators. Usually, different models need to be developed for the hybrid beam when different gels are used in the system. In this article, based on the generalized ideal elastomeric gel model, we formulate a unified relationship between the swelling of hydrogels and the bending curvature of the elastic beam, which is independent of specific swelling mechanisms of gels. We further illustrate that the equations derived in the article can be used to validate the ideal elastomeric gel model and measure the elasticity of polymer networks of the gels.

1. Introduction

Gel is a network which can swell by absorbing solvent molecules. The amount of swelling can be affected by environmental humidity [1], temperature [2], pH value [3,4], light intensity [5], biological agents [6,7], etc. Thanks to this property, gels are being widely developed for a variety of sensors and actuators [8–10]. Among all the structures, a hybrid system with a gel layer on the top of an elastic non-swellable substrate has often been adopted [4,11]. For example, Bashir et al. [12] deposited a pH-sensitive hydrogel on the top of a microcantilever to measure the environmental pH value by detecting the deflection of the microcantilever. Similar structures with different hydrogels have been exploited to measure the concentrations of various ions or even glucose [7]. However, a theoretical formulation and analyses of such a hybrid system is limited, especially when considering the availability of all kinds of responsive gels.

To study the system with a gel layer bonded on an elastic non-swellable substrate, the swelling behaviours of constrained gels in different conditions need to be

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In the surrounding aqueous solution does work $\mu$ equals the sum of the volume of the dry network $\mu$ solutes, the applied forces and the work done by the chemical potential of water and different solutes: the change in the Helmholtz free energy of the block equals the sum of the work done by the when the hydrogel equilibrates with the applied forces and the surrounding aqueous solution, other particles and the dimensions of the block become $l_1, l_2$ and $l_3$. The Helmholtz free energy of the block in the current state is denoted as $F$.

When the block changes the dimensions by small amounts $\delta l_1, \delta l_2$ and $\delta l_3$, the applied forces do work $P_1 \delta l_1 + P_2 \delta l_2 + P_3 \delta l_3$. When the number of water molecules in the block increases by $\delta M_s$ and the number of other molecules in the block increases by $\delta M_i$, the chemical potential of water in the surrounding aqueous solution does work $\mu_s \delta M_s$ and $\mu_i \delta M_i$. At a constant temperature, when the hydrogel equilibrates with the applied forces and the surrounding aqueous solution, the change in the Helmholtz free energy of the block equals the sum of the work done by the applied forces and the work done by the chemical potential of water and different solutes:

$$\delta F = P_1 \delta l_1 + P_2 \delta l_2 + P_3 \delta l_3 + \mu_s \delta M_s + \sum_i \mu_i \delta M_i.$$  \hspace{1cm} (2.1)

The dimensions of the block, $l_1, l_2$ and $l_3$, can vary independently from the number of water molecules in the hydrogel, $M_s$, and the number of other solutes in the hydrogel, $M_i$. The condition of equilibrium (2.1) holds for arbitrary and independent small variations of the independent quantities: $l_1, l_2, l_3, M_s$ and $M_i$. However, these quantities are usually connected by the following considerations [14]. The volume of the block in the current state $l_1l_2l_3$, to a good approximation, equals the sum of the volume of the dry network $L_1L_2L_3$, the volume of the absorbed water $\Omega_s M_s$ and the volume of other solutes $\sum_i \Omega_i M_i$,

$$l_1l_2l_3 = L_1 L_2 L_3 + \Omega_s M_s + \sum_i \Omega_i M_i.$$  \hspace{1cm} (2.2)
This condition of equilibrium holds for arbitrary and independent variations \( \delta \lambda \) stretches by

\[
\text{we obtain that }
\]

\[
\sigma
\]

Inserting (2.3) into (2.1), we obtain that

\[
\delta F = \left( P_1 + \frac{l_2 l_3 \mu_3}{\Omega_s} \right) \delta l_1 + \left( P_2 + \frac{l_1 l_3 \mu_3}{\Omega_s} \right) \delta l_2 + \left( P_3 + \frac{l_1 l_2 \mu_3}{\Omega_s} \right) \delta l_3 + \sum_i \left( \mu_i - \frac{\Omega_i \mu_s}{\Omega_s} \right) \delta M_i. \tag{2.4}
\]

This condition of equilibrium holds for arbitrary and independent variations \( \delta l_1, \delta l_2, \delta l_3 \) and \( \delta M_i \).

Define the concentration of water and other solutes by \( \Omega_s c_s = M_s / l_1 l_2 l_3 \) and \( \Omega_i c_i = M_i / l_1 l_2 l_3 \), and stretches by \( \lambda_1 = l_1 / L_1, \lambda_2 = l_2 / L_2 \) and \( \lambda_3 = l_3 / L_3 \). Dividing both sides of (2.2) by the volume of the swollen elastomer, \( l_1 l_2 l_3 \), we obtain that

\[
\Omega_s c_s = 1 - \frac{1}{f} - \sum_i \Omega_i c_i, \tag{2.5}
\]

where \( f = \lambda_1 \lambda_2 \lambda_3 \). This expression places a constraint among the five variables: \( \lambda_1, \lambda_2, \lambda_3, c_s \) and \( c_i \).

Define the nominal density of the Helmholtz free energy by \( W = F / (L_1 L_2 L_3) \), true stresses by \( \sigma_1 = P_1 / (l_2 l_3), \sigma_2 = P_2 / (l_1 l_3) \) and \( \sigma_3 = P_3 / (l_1 l_2) \). Dividing both sides of equation (2.4) by \( L_1 L_2 L_3 \), we obtain that

\[
\delta W = \left( \sigma_1 + \frac{\mu_s}{\Omega_s} \right) \lambda_2 \lambda_3 \delta \lambda_1 + \left( \sigma_2 + \frac{\mu_s}{\Omega_s} \right) \lambda_1 \lambda_3 \delta \lambda_2 + \left( \sigma_3 + \frac{\mu_s}{\Omega_s} \right) \lambda_1 \lambda_2 \delta \lambda_3
\]

\[
+ \sum_i \left( \mu_i - \frac{\Omega_i \mu_s}{\Omega_s} \right) \lambda_1 \lambda_2 \lambda_3 \delta c_i. \tag{2.6}
\]

This condition of equilibrium holds for arbitrary and independent variations \( \delta \lambda_1, \delta \lambda_2, \delta \lambda_3 \) and \( \delta c_i \).
As a material model, the nominal density of the free energy is taken to be a function of independent variables:

\[ W = W(\lambda_1, \lambda_2, \lambda_3, c_i). \]  

(2.7)

Owing to the constraint (2.5), the concentration of water is excluded from the list of the independent variables in (2.7). At a fixed temperature, when the block deforms by small amounts, \( \delta \lambda_1, \delta \lambda_2 \) and \( \delta \lambda_3 \), and the number of solutes by small amounts, \( \delta c_i \), the free energy varies by

\[ \delta W = \frac{\partial W}{\partial \lambda_1} \delta \lambda_1 + \frac{\partial W}{\partial \lambda_2} \delta \lambda_2 + \frac{\partial W}{\partial \lambda_3} \delta \lambda_3 + \sum_i \frac{\partial W}{\partial c_i} \delta c_i. \]  

(2.8)

A combination of (2.6) and (2.8) gives that

\[ \left[ \frac{\partial W}{\partial \lambda_1} - \left( \sigma_1 + \frac{\mu_s}{\Omega_s} \right) \lambda_2 \lambda_3 \right] \delta \lambda_1 + \left[ \frac{\partial W}{\partial \lambda_2} - \left( \sigma_2 + \frac{\mu_s}{\Omega_s} \right) \lambda_1 \lambda_3 \right] \delta \lambda_2 + \left[ \frac{\partial W}{\partial \lambda_3} - \left( \sigma_3 + \frac{\mu_s}{\Omega_s} \right) \lambda_1 \lambda_2 \right] \delta \lambda_3 \]

\[ + \sum_i \left[ \frac{\partial W}{\partial c_i} - \left( \mu_i - \frac{\Omega_i}{\Omega_s} \right) \right] \delta c_i = 0. \]  

(2.9)

When the hydrogel equilibrates with the surrounding aqueous solution and the applied forces, (2.9) holds for arbitrary and independent variations \( \delta \lambda_1, \delta \lambda_2, \delta \lambda_3 \) and \( \delta c_i \). Consequently, the coefficient in front of each of the four variations in (2.9) must vanish, leading to four equations:

\[ \sigma_1 = -\frac{\partial W_s(\lambda_1, \lambda_2, \lambda_3)}{\lambda_2 \lambda_3 \partial \lambda_1} + \frac{\mu_s}{\Omega_s}, \]  

(2.10)

\[ \sigma_2 = -\frac{\partial W_s(\lambda_1, \lambda_2, \lambda_3)}{\lambda_1 \lambda_3 \partial \lambda_2} + \frac{\mu_s}{\Omega_s}, \]  

(2.11)

\[ \sigma_3 = -\frac{\partial W_s(\lambda_1, \lambda_2, \lambda_3)}{\lambda_1 \lambda_2 \partial \lambda_3} + \frac{\mu_s}{\Omega_s}, \]  

(2.12)

and

\[ \mu_i = -\frac{\Omega_i}{\Omega_s} \mu_s - \frac{\partial W_{\text{mix}}(c_s, c_i)}{\partial c_i}. \]  

(2.13)

In many gels, the density of the cross-links is very low. For example, each polymer chain may consist of over a thousand monomers. Consequently, to the first approximation, we may neglect the effect of the cross-links on solution, and simply write the free energy of the gel as the sum

\[ W = W_s(\lambda_1, \lambda_2, \lambda_3) + W_{\text{mix}}(c_s, c_i), \]  

(2.14)

where \( W_s \) is the free energy due to the stretching of the network, and \( W_{\text{mix}} \) is the free energy due to the mixing of the polymers and the solvent.

Inserting the above free energy function in (2.10)–(2.13), and using the constraint (2.5), we obtain that

\[ \sigma_1 = \frac{\partial W_s(\lambda_1, \lambda_2, \lambda_3)}{\lambda_2 \lambda_3 \partial \lambda_1} + \frac{\partial W_{\text{mix}}(c_s, c_i)}{f^2 \Omega_s \partial c_s} - \frac{\mu_s}{\Omega_s}, \]  

(2.15)

\[ \sigma_2 = \frac{\partial W_s(\lambda_1, \lambda_2, \lambda_3)}{\lambda_3 \lambda_1 \partial \lambda_2} + \frac{\partial W_{\text{mix}}(c_s, c_i)}{f^2 \Omega_s \partial c_s} - \frac{\mu_s}{\Omega_s}, \]  

(2.16)

\[ \sigma_3 = \frac{\partial W_s(\lambda_1, \lambda_2, \lambda_3)}{\lambda_1 \lambda_2 \partial \lambda_3} + \frac{\partial W_{\text{mix}}(c_s, c_i)}{f^2 \Omega_s \partial c_s} - \frac{\mu_s}{\Omega_s}, \]  

(2.17)

and

\[ \mu_i = -\frac{\Omega_i}{\Omega_s} \mu_s - \frac{\partial W_{\text{mix}}(c_s, c_i)}{f \partial c_i}. \]  

(2.18)

Equations (2.15)–(2.18), along with (2.5), constitute the equations of state of a hydrogel.
By using equation (2.18), the concentration of the solutes $c_i$ can be expressed as a function of the chemical potential $\mu_i$ and $\mu_s$, as well as the volume matrix change of the gel, $J$. As a result, equations (2.15)–(2.17) can be written as

$$\sigma_1 = \frac{\partial W_s(\lambda_1, \lambda_2, \lambda_3)}{\lambda_2 \lambda_3 \partial \lambda_1} - \Pi,$$

(2.19)

and

$$\sigma_2 = \frac{\partial W_s(\lambda_1, \lambda_2, \lambda_3)}{\lambda_3 \lambda_1 \partial \lambda_2} - \Pi,$$

(2.20)

with $\Pi = (\partial W_{\text{mix}}(c_s, c_i))/(J^2 \partial c_s) - \mu_s/\Omega_s$.

The equations of state (2.19)–(2.21) describe the mechano-chemical interaction of the hydrogels. In particular, the term $\Pi$ has the dimension of stress, and is known as osmotic pressure in a solution. $\Pi$ only depends on the volume of a gel as well as the chemical potential of all the solvent particles, but does not depend on the cross-link density and deformation of the polymer chain. Equations (2.19)–(2.21) also work for polymer solutions by letting the elasticity equal zero, and the stress corresponds to osmotic pressure. Therefore, $\Pi$ can be measured independently using a polymer solution.

### 3. Beam bending by an ideal elastomeric gel

Figure 2 shows a layer of hydrogel, with initial swelling ratio $\lambda_1 = \lambda_2 = \lambda_3 = \lambda_{\text{pre}}$, attached to an elastic and non-swellable substrate. With the swelling of the hydrogel, compressive stresses in lateral directions build up in the layer of hydrogel, which causes the bending of the hybrid beam. Usually, the bending of the substrate is small and the deformation of the hydrogel can be assumed approximately homogeneous. The stress in the vertical direction is zero, i.e.

$$\sigma_3 = 0.$$  

(3.1)

Inserting (3.1) into (2.21), we have that

$$\Pi = \frac{\partial W_s(\lambda_1, \lambda_2, \lambda_3)}{\lambda_1 \lambda_2 \partial \lambda_3}.$$  

(3.2)

Inserting (3.2) into (2.19) and (2.20), we can further obtain that

$$\sigma_1 = \frac{\partial W_s(\lambda_1, \lambda_2, \lambda_3)}{\lambda_2 \lambda_3 \partial \lambda_1} - \frac{\partial W_s(\lambda_1, \lambda_2, \lambda_3)}{\lambda_1 \lambda_2 \partial \lambda_3},$$  

(3.3)

and

$$\sigma_2 = \frac{\partial W_s(\lambda_1, \lambda_2, \lambda_3)}{\lambda_1 \lambda_3 \partial \lambda_2} - \frac{\partial W_s(\lambda_1, \lambda_2, \lambda_3)}{\lambda_1 \lambda_2 \partial \lambda_3}.$$  

(3.4)

Equations (3.3) and (3.4) indicate that the lateral stresses only depend on the swelling ratio in the vertical direction $\lambda_3$, but do not depend on the explicit form of $\Pi$. In other words, with fixed lateral stretches for a gel, the same deformation in the vertical direction will give rise to the same amount of lateral stresses, no matter what swelling mechanism is underlined (e.g. variation of humidity, pH, temperature). We would like to point out that if the lateral compressive stress is large enough, creases may develop on the surface of gel. The emergence of creases can change the magnitude of compressive stresses and bending moment, which is beyond the scope of the article.

Since the modulus of the gel is usually much smaller than the modulus of the substrate, the bending stiffness of the gel is negligible and the neutral plane for the hybrid beam sits on the middle plane of the elastic non-swellable substrate during the gel swelling. For instance, in one of our recent experiments [15], the modulus of the substrate is 2.5 GPa and the modulus of the hydrogel is only in the order of 1 kPa. In practice, the above assumption should be accurate enough if the modulus of the substrate is at least two orders of magnitude larger than the modulus.
of the gel. Therefore, the moment per unit length in the width direction applied to the substrate by the hydrogel is given by

$$ M = \frac{b_s}{2} \sigma_1 \lambda_3 H (\lambda_3 H + h_s), \quad (3.5) $$

where $b_s$, $h_s$ is the width and thickness of the non-swellable substrate, $H$ is the thickness of the gel layer in dry state.

The curvature can be calculated by using classic beam theory

$$ \Delta \kappa = \frac{M}{E_s I_s}, \quad (3.6) $$

where $E_s$ and $I_s$ are Young’s modulus and second moment of the transverse plane of the substrate, and $\Delta \kappa$ is the curvature change of the substrate due to the swelling of the hydrogel. As pointed out in Janssen et al. [16], the width of the substrate is usually much larger than its thickness. The elastic substrate should be viewed as a plate instead of a beam. Therefore, to be more precise, $E_s$ in (3.6) should be replaced by $E_s/(1 - \nu_s)$, where $\nu_s$ is Poisson’s ratio of the substrate. Such replacement is valid for all the following equations in the article.

A combination of (3.5) and (3.6) gives

$$ \Delta \kappa = \frac{6\sigma_1}{E_s h_s^3} (\lambda_3^2 H^2 + \lambda_3 H h_s), \quad (3.7) $$

which links the compressive stress in the equilibrium state to the change of the curvature of the beam. In (3.7), we assume the elastic substrate has a rectangular cross section with height $h_s$.

It was pointed out by one of the anonymous reviewers that equation (3.7) can be reduced to Stoney’s formula [17] when the thickness of the gel is much smaller than the thickness of the substrate, i.e. $\lambda_3 H \ll h_s$. In consequence, equation (3.7) can be viewed as an extension of Stoney’s
formula without assuming the gel thickness to be much smaller than the substrate thickness. A combination of (3.3) and (3.7) is the direct consequence of the generalized ideal elastomeric gel model, so the two equations can be used to validate the model.

4. Elasticity of cross-linked polymer network

To obtain the equations in §3, we made the following assumptions: (i) the system is in the equilibrium state; (ii) the gel is much softer than the elastic substrate; (iii) the deformation and deflections (more precisely, slope) of the elastic substrate is small; (iv) the generalized ideal elastomeric gel model is valid, which is independent of the specific type and swelling mechanisms of gels; and (v) no surface instabilities such as creases happen.

For the free energy of a specific gel, the expression for mixing free energy among polymer, solvent and different solutes is usually very complex and under intensive debates [18–21]. The elasticity of a polymer network, however, can often be well captured by several models, such as the neo-Hookean model [22], the Gent model [23], the Arruda–Boyce model [24], the Mooney–Rivilin model [25,26] and the Ogden model [27]. In this section, we use the neo-Hookean model and the Gent model to get explicit expressions between the swelling of gels and the bending of the beam.

(a) Neo-Hookean model

When the deformation of the polymer network is not very large, its elasticity can usually be modelled by the neo-Hookean model. Specifically, the free energy density of the stretching polymer network is given by

\[ W_s = \frac{1}{2}NkT\left(\frac{\lambda_3}{\lambda_1\lambda_2} - \frac{1}{\lambda_1\lambda_2\lambda_3}\right). \] (4.1)

Plugging (4.1) into (3.2)–(3.4), we have

\[ \Pi = NkT\left(\frac{\lambda_3}{\lambda_1\lambda_2} - \frac{1}{\lambda_1\lambda_2\lambda_3}\right), \] (4.2)

\[ \sigma_1 = NkT\frac{\lambda_1}{\lambda_2} \left(\frac{\lambda_3}{\lambda_3} - \frac{\lambda_1}{\lambda_1}\right) \] (4.3)

and

\[ \sigma_2 = NkT\frac{\lambda_2}{\lambda_1} \left(\frac{\lambda_3}{\lambda_3} - \frac{\lambda_2}{\lambda_2}\right). \] (4.4)

For equal-biaxial stretch, we have \( \lambda_1 = \lambda_2 = \lambda_{\text{pre}} \) and \( \sigma_1 = \sigma_2 = \sigma \); (4.2) and (4.3) become

\[ \Pi = \frac{NkT}{\lambda_{\text{pre}}^2} \left(\lambda_3 - \frac{1}{\lambda_3}\right) \] (4.5)

and

\[ \sigma = \frac{NkT}{\lambda_{\text{pre}}} \left(\frac{\lambda_{\text{pre}}}{\lambda_3} - \frac{\lambda_3}{\lambda_{\text{pre}}}\right). \] (4.6)

Plugging (4.6) into (3.7), we obtain that

\[ \Delta\kappa = \frac{NkT}{E_s h_s^2} \left(1 - \left(\frac{\lambda_3}{\lambda_{\text{pre}}}\right)^2\right) \left(\frac{\lambda_3 h_0}{\lambda_{\text{pre}} h_s} + 1\right), \] (4.7)

where \( h_0 = H\lambda_{\text{pre}} \). Equations (4.5)–(4.7) are valid for all kinds of hydrogel if the elasticity of the polymer network can be described by the neo-Hookean model. The lateral stress \( \sigma \) as a function of vertical stretch \( \lambda_3 \) is plotted in figure 3a. The change of curvature \( \Delta\kappa \) as a function of vertical stretch \( \lambda_3 \) is plotted in figure 3b. A combination of (4.2) and (4.7) can be used to experimentally measure the osmosis function \( \Pi \).
(b) Gent model

When the stretch of the polymer network is large, stiffening effects need to be considered. The Gent model is one of the models taking account of stiffening of polymer chains. The free energy density of the stretching polymer network is given by

\[ W_s = \frac{1}{2} NkT \left[ f_{\text{lim}} \log \left( 1 - \frac{\lambda_3^2}{f_{\text{lim}}} \right) + 2 \log J \right]. \]  

(4.8)

Similarly, for equal-biaxial stretch, the lateral stress and the change of the curvature of the beam are

\[ \sigma = \frac{NkT}{\lambda_{\text{pre}}} \left( \frac{\lambda_{\text{pre}}}{\lambda_3} - \frac{\lambda_3}{\lambda_{\text{pre}}} \right) \left( 1 - \left( \frac{2\lambda_{\text{pre}}^2 + 3}{f_{\text{lim}}} \right) \right) \]  

(4.9)

and

\[ \Delta \kappa = \frac{NkT}{\frac{6h_0}{E_s} \frac{h_0}{h_s}} \left( 1 - \left( \frac{\lambda_3}{\lambda_{\text{pre}}} \right)^2 \right) \left( \frac{\lambda_3}{\lambda_{\text{pre}}} \frac{h_0}{h_s} + 1 \right) \left( 1 - \left( \frac{2\lambda_{\text{pre}}^2 + 3}{f_{\text{lim}}} \right) \right). \]  

(4.10)

The lateral stress \( \sigma \) as a function of vertical stretch \( \lambda_3 \) is also plotted in figure 3a. The change of curvature \( \Delta \kappa \) as a function of vertical stretch \( \lambda_3 \) is plotted in figure 3b. In experiments, figure 3b can be used to determine the elasticity of the polymer network of hydrogels.

5. Conclusion

In summary, we investigated the bending of a beam with a gel layer bonded on top of an elastic non-swellable substrate. We adopted the generalized ideal elastomeric gel model to obtain the relationship between the swelling of the gel layer and the bending curvature of the substrate underneath. Since the obtained equations are only based on the ideal elastomeric gel model, they are valid for most gels and independent of specific swelling mechanisms of the gel. Finally, we also plugged specific models of the stretching polymer network to the generalized equations. Unfortunately, we cannot find any quantitative experimental measurement in the literature that can be directly compared with our predictions. We plan to conduct experiments by ourselves and use various gels in the beam bending system to validate the model proposed in the paper. We also expect the model developed in this article to be useful in characterizing different types of hydrogels and the design of gel actuators and sensors.

Data accessibility. Figure 3 is plotted using Matlab.
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