ELASTICITY OF RUBBER-LIKE MATERIALS

In the notes on the general theory of finite deformation (http://imechanica.org/node/538), we have left the free energy function unspecified. Here we fill this gap by describing free energy functions commonly used for rubber-like materials.

In the notes on the general theory of finite deformation, we have developed the model of elasticity in terms of tensors. Here we will begin with the development of the same model using stretches—we repeat the same ideas busing using simper algebra. The simpler algebra will help us focus on essential ideas. The expressions in terms of tensors are collected at the end of the notes.

THERMODYNAMICS OF ELASTICITY

Thermodynamics. Consider a rectangular block of a material. In the reference state, the edges of the block are of lengths L_1, L_2 and L_3. In a current state, the block is subject to forces P_1, P_2 and P_3 on its faces, and the edges of the block are of lengths l_1, l_2 and l_3. In the current state, when the lengths of edges of the block change by δl_1, δl_2 and δl_3, the forces do work

$$P_1 \delta l_1 + P_2 \delta l_2 + P_3 \delta l_3 .$$

The forces applied to the faces of the block are work-conjugate to the lengths of the edges of the block.

reference state   current state
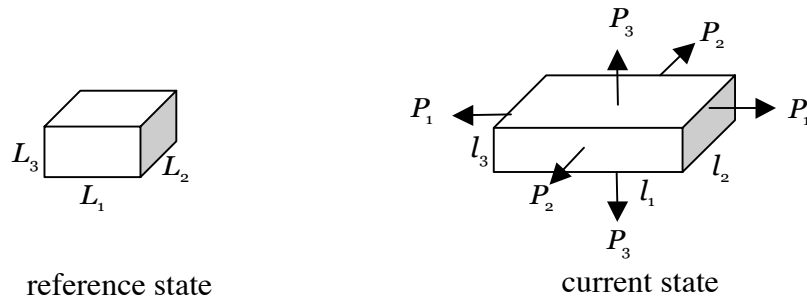
We will consider isothermal process—that is, during deformation the block is in thermal contact with a large reservoir of energy held at a fixed temperature. We will not list the temperature as a variable. Let F be the Helmholtz free energy of the block in the current state. Incidentally, we have just used F to stand for the Helmholtz free energy; this practice should not confuse free energy and deformation gradient.

Thermodynamics requires that during an isothermal process the increment of the Helmholtz free energy is no greater than the applied work:

$$\delta F \leq P_1 \delta l_1 + P_2 \delta l_2 + P_3 \delta l_3 .$$

The thermodynamic inequality holds for arbitrary and independent small

variations $\delta l_1, \delta l_2, \delta l_3$. The variation means the value of a quantity at a time minus that at a slightly earlier time. As usual in thermodynamics, this inequality involves the direction of time, but not the duration of time.

We next specialize the thermodynamic inequality to a model of elasticity. In the model of elasticity, we assume that the process of deformation is thermodynamically reversible. When the block and the forces are in a state of thermodynamic equilibrium, subject to a small variation of the edges of the block, the work done by the forces equals the change in the free energy:

$$\delta F = P_1 \delta l_1 + P_2 \delta l_2 + P_3 \delta l_3.$$

This condition of equilibrium holds for arbitrary and independent small variations $\delta l_1, \delta l_2, \delta l_3$.

Quantities per unit length, per unit area, and per unit volume. Once again consider the block of the material. The homogeneous deformation changes the block from a rectangular shape in the reference state to another rectangular shape in the current state.

Define the stretches by the lengths of the edges of the block in the current state divided by the lengths of the edges of the block in the reference state:

$$\lambda_1 = \frac{l_1}{L_1}, \lambda_2 = \frac{l_2}{L_2}, \lambda_3 = \frac{l_3}{L_3}.$$

Define the nominal stresses by the forces acting on the faces of the block in the current state divided by the areas of the faces in the reference state:

$$s_1 = \frac{P_1}{L_2 L_3}, s_2 = \frac{P_2}{L_3 L_1}, s_3 = \frac{P_3}{L_1 L_2}.$$

Define the nominal density of the Helmholtz free energy, W, by the Helmholtz free energy of the block in the current state divided by the volume of the block in the reference state:

$$W = \frac{F}{L_1 L_2 L_3}.$$

Dividing the condition of equilibrium by the volume of the block in the reference state, $L_1 L_2 L_3$, we obtain that

$$\delta W = s_1 \delta \lambda_1 + s_2 \delta \lambda_2 + s_3 \delta \lambda_3.$$

This condition of equilibrium holds for arbitrary and independent variations $\delta \lambda_1, \delta \lambda_2, \delta \lambda_3$. The left-hand side is the change in the Helmholtz of free energy, and the right-hand side is the work done by the applied forces. The nominal stresses are work-conjugate to the stretches.

Stress-stretch relations. As an additional assumption for the model of elasticity, we stipulate that the nominal density of the Helmholtz free energy is a function of the three stretches:

$$W = W(\lambda_1, \lambda_2, \lambda_3).$$

According to calculus, when the stretches change by $\delta\lambda_1, \delta\lambda_2, \delta\lambda_3$, the nominal density of the Helmholtz free energy changes by

$$\delta W = \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_1}\delta\lambda_1 + \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_2}\delta\lambda_2 + \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_3}\delta\lambda_3.$$

Comparing the two expressions for δW, we obtain that

$$\left[s_1 - \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_1}\right]\delta\lambda_1 + \left[s_2 - \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_2}\right]\delta\lambda_2 + \left[s_3 - \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_3}\right]\delta\lambda_3 = 0$$

This condition of equilibrium holds for arbitrary and independent variations $\delta\lambda_1, \delta\lambda_2, \delta\lambda_3$. Consequently, the stresses equal the partial derivatives:

$$s_1 = \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_1}, \quad s_2 = \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_2}, \quad s_3 = \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_3}.$$

True stress. The model of elasticity can be represented by any measures of stress and strain. As an example, consider the true stresses defined as

$$\sigma_1 = \frac{P_1}{l_2 l_3}, \quad \sigma_2 = \frac{P_2}{l_3 l_1}, \quad \sigma_3 = \frac{P_3}{l_1 l_2}.$$

In terms of the true stresses, the condition of equilibrium is

$$\delta W = \sigma_1 \lambda_2 \lambda_3 \delta\lambda_1 + \sigma_2 \lambda_3 \lambda_1 \delta\lambda_2 + \sigma_3 \lambda_1 \lambda_2 \delta\lambda_3.$$

This condition of equilibrium holds for arbitrary and independent variations $\delta\lambda_1, \delta\lambda_2, \delta\lambda_3$. The left-hand side is the change in the Helmholtz of free energy, and the right-hand side is the work done by the applied forces. The true stresses are not work-conjugate to the stretches.

Comparing the condition of equilibrium with the expression of δW in terms of partial derivatives, we obtain that

$$\left[\sigma_1 \lambda_2 \lambda_3 - \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_1}\right]\delta\lambda_1$$

$$+\left[\sigma_2 \lambda_3 \lambda_1 - \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_2}\right]\delta\lambda_2$$

$$+\left[\sigma_3 \lambda_1 \lambda_2 - \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_3}\right]\delta\lambda_3 = 0$$

This condition of equilibrium holds for arbitrary and independent variations $\delta\lambda_1, \delta\lambda_2, \delta\lambda_3$. Consequently, the condition of equilibrium requires that

$$\sigma_1 = \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\lambda_2 \lambda_3 \partial \lambda_1}, \quad \sigma_2 = \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\lambda_3 \lambda_1 \partial \lambda_2}, \quad \sigma_3 = \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\lambda_1 \lambda_2 \partial \lambda_3}.$$

Exercise. Assume the nominal density of the Helmholtz free energy is a function of the three principal Lagrange strains. Derive the expressions for the second Piola-Kirchhoff stresses in terms of the free energy function.

INCOMPRESSIBILITY

When a material undergoes large deformation, atoms and molecules rearrange. The relative change in volume is often small compared to the relative change in shape. It is a common practice to neglect the volumetric deformation, and assume that the material is *incompressible.*

Consider again the block of material. In the reference state, the block is rectangular, with edges of lengths L_1, L_2 and L_3. In the current state, the block is also rectangular, with edges of lengths l_1, l_2 and l_3. If the material is incompressible, the volume of the block must remain unchanged, namely, $L_1 L_2 L_3 = l_1 l_2 l_3$, or

$$\lambda_1 \lambda_2 \lambda_3 = 1.$$

In arriving at the stress-stretch relations above, we have assumed that the three stretches can vary independently. However, the condition of incompressibility, $\lambda_1 \lambda_2 \lambda_3 = 1$, places a constraint among the three stretches: they cannot vary independently. To enforce this constraint, we need to modify the previous derivation.

Free energy as a function of two stretches. We may regard λ_1 and λ_2 as independent variables, so that $\lambda_3 = (\lambda_1 \lambda_2)^{-1}$. Taking differential of the constraint $\lambda_3 = (\lambda_1 \lambda_2)^{-1}$, we obtain that

$$\delta \lambda_3 = \lambda_1^{-2} \lambda_2^{-1} \delta \lambda_1 + \lambda_1^{-1} \lambda_2^{-2} \delta \lambda_2.$$

Inserting the assumption of incompressibility into the condition of equilibrium, $\delta W = \sigma_1 \lambda_2 \lambda_3 \delta \lambda_1 + \sigma_2 \lambda_3 \lambda_1 \delta \lambda_2 + \sigma_3 \lambda_1 \lambda_2 \delta \lambda_3$, we obtain that

$$\delta W = \left(\frac{\sigma_1 - \sigma_3}{\lambda_1} \right) \delta \lambda_1 + \left(\frac{\sigma_2 - \sigma_3}{\lambda_2} \right) \delta \lambda_2.$$

This condition of equilibrium holds for arbitrary and independent variations $\delta \lambda_1$ and $\delta \lambda_2$.

As a material model, we assume that the nominal density of the Helmholtz free energy is a function of the two stretches:

$$W = W(\lambda_1, \lambda_2).$$

According calculus, when the stretches change by $\delta \lambda_1$ and $\delta \lambda_2$, the nominal

density of the Helmholtz free energy changes by

$$\delta W = \frac{\partial W(\lambda_1, \lambda_2)}{\partial \lambda_1} \delta \lambda_1 + \frac{\partial W(\lambda_1, \lambda_2)}{\partial \lambda_2} \delta \lambda_2 .$$

A comparison of the two expressions for δW, we obtain that

$$\left[\frac{\sigma_1 - \sigma_3}{\lambda_1} - \frac{\partial W(\lambda_1, \lambda_2)}{\partial \lambda_1} \right] \delta \lambda_1 + \left[\frac{\sigma_2 - \sigma_3}{\lambda_2} - \frac{\partial W(\lambda_1, \lambda_2)}{\partial \lambda_2} \right] \delta \lambda_2 = 0 .$$

This condition of equilibrium holds for arbitrary and independent variations $\delta \lambda_1, \delta \lambda_2$. Consequently, the two terms in front of $\delta \lambda_1$ and $\delta \lambda_2$ must individually vanish:

$$\sigma_1 - \sigma_3 = \lambda_1 \frac{\partial W(\lambda_1, \lambda_2)}{\partial \lambda_1} , \qquad \sigma_2 - \sigma_3 = \lambda_2 \frac{\partial W(\lambda_1, \lambda_2)}{\partial \lambda_2} .$$

These equations express the condition of thermodynamic equilibrium. Once the function $W(\lambda_1, \lambda_2)$ is given, these relations, together with the incompressibility condition $\lambda_1 \lambda_2 \lambda_3 = 1$, serve as the stress-strain relations for incompressible materials.

Because the material is incompressible, once the stretches are prescribed, the material model gives the combinations $\sigma_1 - \sigma_3$ and $\sigma_2 - \sigma_3$, but does not give all three stresses.

On the other hand, once all three stresses are prescribed, the material model determines the three stretches.

Exercise. For an incompressible material, derive the equations of state in terms of the nominal stress and the function $W(\lambda_1, \lambda_2)$.

triaxial stresses   hydrostatic stress   biaxial stresses
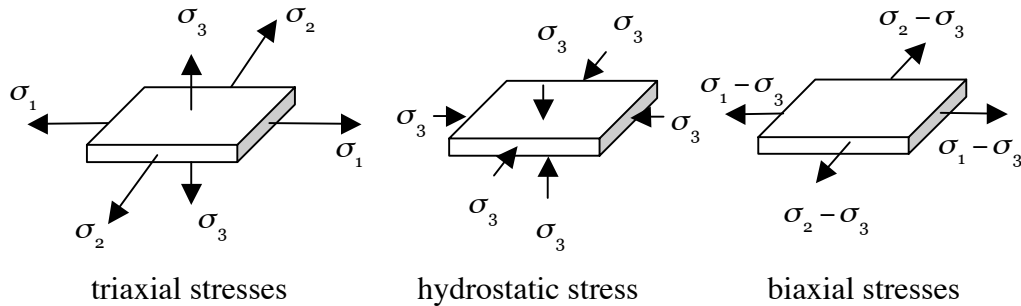
Physical interpretation. The material is in a state of triaxial stresses, $(\sigma_1, \sigma_2, \sigma_3)$. Because the material is incompressible, superposing a hydrostatic stress on the material will not change the state of deformation. For example, we can superimpose $(-\sigma_3, -\sigma_3, -\sigma_3)$, so that the material is in a state of biaxial

stresses $\left(\sigma_1 - \sigma_3, \sigma_2 - \sigma_3, 0\right)$.   The triaxial stresses $\left(\sigma_1, \sigma_2, \sigma_3\right)$ and the biaxial stresses $\left(\sigma_1 - \sigma_3, \sigma_2 - \sigma_3, 0\right)$ cause the same state of deformation. The work done by the biaxial stresses equal the change in free energy:

$$\delta W = \left(\sigma_1 - \sigma_3\right)\lambda_2\lambda_3\delta\lambda_1 + \left(\sigma_1 - \sigma_2\right)\lambda_1\lambda_3\delta\lambda_2 .$$

The material is also in a state of triaxial stretches, $\left(\lambda_1, \lambda_2, \lambda_3\right)$. Because the material is incompressible, $\lambda_1\lambda_2\lambda_3 = 1$, only two stretches are independent variables. We take λ_1, λ_2 as independent stretches, and write the free energy as a function of the two stretches,

$$W = W\left(\lambda_1, \lambda_2\right).$$

According to calculus, when the two stretches changes by small amounts, the free energy changes by

$$\delta W = \frac{\partial W\left(\lambda_1, \lambda_2\right)}{\partial \lambda_1}\delta\lambda_1 + \frac{\partial W\left(\lambda_1, \lambda_2\right)}{\partial \lambda_2}\delta\lambda_2$$

A comparison of the two expressions gives the stress-stretch relations:

$$\sigma_1 - \sigma_3 = \lambda_1 \frac{\partial W\left(\lambda_1, \lambda_2\right)}{\partial \lambda_1}, \quad \sigma_2 - \sigma_3 = \lambda_2 \frac{\partial W\left(\lambda_1, \lambda_2\right)}{\partial \lambda_2}.$$

Exercise. A thin sheet of an elastomer is sandwiched between two blocks of metal. The elastomer is taken to be incompressible, and the metal is taken to be rigid. The thickness of the elastomer is small compared to its lateral dimensions. When the two blocks of metal are compressed relative to each other by a force, what is the state of stress in the elastomer? (a) Assume that the elastomer sheet is well bonded to the blocks of metal. (b) Assume that the elastomer sheet is not bonded the blocks of metal, the elastomer can slide relative to the metal without friction.

Enforce incompressibility using a Lagrange multiplier. Before we introduce incompressibility, we have assumed that the three stretches can vary independently in arriving at the relation

$$\sigma_1 = \frac{\partial W\left(\lambda_1, \lambda_2, \lambda_3\right)}{\lambda_2\lambda_3\partial \lambda_1}, \quad \sigma_2 = \frac{\partial W\left(\lambda_1, \lambda_2, \lambda_3\right)}{\lambda_3\lambda_1\partial \lambda_2}, \quad \sigma_3 = \frac{\partial W\left(\lambda_1, \lambda_2, \lambda_3\right)}{\lambda_1\lambda_2\partial \lambda_3} .$$

Once we introduce incompressibility ($\lambda_1\lambda_2\lambda_3 = 1$), however, the three stretches cannot vary independently.

To enforce this constraint, we replace the free-energy function $W\left(\lambda_1, \lambda_2, \lambda_3\right)$ by a function

$$W\left(\lambda_1, \lambda_2, \lambda_3\right) - \left(\lambda_1\lambda_2\lambda_3 - 1\right)\Pi ,$$

with Π as a Lagrange multiplier. We then allow the three stretches to vary independently, and obtain the stress from

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

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

$$\sigma_3 = \lambda_3 \frac{\partial W(\lambda_1, \lambda_2, \lambda_3)}{\partial \lambda_3} - \Pi$$

These equations, along with the constraint $\lambda_1 \lambda_2 \lambda_3 = 1$, specify the model of incompressible elastic materials. The Lagrange multiplier Π acts like a hydrostatic pressure. The Lagrange multiplier is not a material parameter. Rather, Π is to be solved as a field for a given boundary-value problem. When the deformation of the body is inhomogeneous, Π is in general also inhomogeneous.

COMMONLY USED FREE ENERGY FUNCTIONS

The function $W(\lambda_1, \lambda_2)$ can be determined by subjecting a sheet of a rubber under various states of biaxial stress. The form of the function is sometimes inspired by theoretical considerations. Here are some commonly used forms.

Neo-Hookean model. This model is specified by the density of the Helmholtz free energy as a function of the stretches:

$$W = \frac{\mu}{2}\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\right).$$

The material is also taken to be incompressible, $\lambda_1 \lambda_2 \lambda_3 = 1$.

Recall that

$$\sigma_1 - \sigma_3 = \lambda_1 \frac{\partial W(\lambda_1, \lambda_2)}{\partial \lambda_1}.$$

Inserting the constraint $\lambda_3 = (\lambda_1 \lambda_2)^{-1}$, we obtain the stress-stretch relation:

$$\sigma_1 - \sigma_3 = \mu\left(\lambda_1^2 - \lambda_3^2\right).$$

Similarly, we obtain that

$$\sigma_2 - \sigma_3 = \mu\left(\lambda_2^2 - \lambda_3^2\right).$$

These two equations, along with $\lambda_1 \lambda_2 \lambda_3 = 1$, constitute the equations of state.

A neo-Hookean material is characterized by a single parameter, μ. The parameter is specific to a given material, and can be determined experimentally. For example, consider a bar in a state of uniaxial stress:

$$\sigma_1 = \sigma, \quad \sigma_2 = \sigma_3 = 0 .$$

Let the stretch along the axis of loading be $\lambda_1 = \lambda$. Incompressibility dictates that the stretches in the directions transverse to the loading axis be $\lambda_2 = \lambda_3 = \lambda^{-1/2}$. Inserting into the above stress-stretch relation, we obtain the relation under the uniaxial stress:

$$\sigma = \mu\left(\lambda^2 - \lambda^{-1}\right) .$$

Recall that stretch relates to the engineering strain as

$$\lambda = l / L = 1 + e .$$

When the strain is small, namely, $|e| \ll 1$, the above stress-stretch relation reduces to

$$\sigma = 3\mu e .$$

Thus, we interpret 3μ as Young's modulus and μ the shear modulus.

The neo-Hookean model can also be derived from a model in statistical mechanics. The model gives

$$\mu = NkT ,$$

where N is the number of polymer chains per unit volume, and kT the temperature in the unit of energy. This model assumes that stretch is small compared the extension limit, and uses Gaussian distribution.

- L.R.G. Treloar, The Physics of Rubber Elasticity, Third Edition, Oxford University Press, 1975.

Exercise. A rubber band is modeled as an incompressible, neo-Hookean material. The band is stretched by a force. Plot the force as a function of the stretch in two ways as follows. (a) Normalize the force by the shear modulus and the cross-sectional area in the reference state. (b) Normalize the force by the shear modulus and the cross-sectional area in the current state. Comment on the difference of the two plots.

Exercise. A rubber is modeled as an incompressible, neo-Hookean material with shear modulus μ. The rubber is subject to triaxial nominal stresses: $s_1 = 0.5\mu$, $s_2 = 1.0\mu$, and $s_3 = 1.5\mu$. Calculate the stretches of the block.

Gent model. In an elastomer, each individual polymer chain has a finite contour length. When the elastomer is subject no loads, the polymer chains are coiled, allowing a large number of conformations. Subject to loads, the polymer chains become less coiled. As the loads increase, the end-to-end distance of each polymer chain approaches the finite contour length, and the elastomer approaches a limiting stretch. On approaching the limiting stretch, the elastomer stiffens steeply. This strain-stiffening effect is absent in the neo-Hookean model, but is represented by the *Gent model*:

$$W = -\frac{\mu J_{\lim}}{2} \log\left(1 - \frac{\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3}{J_{\lim}}\right).$$

The Gent model contains two material constants: μ is the small-stress shear modulus, and $J_{\lim}$ is a constant related to the limiting stretch. The stretches are restricted as $0 \le \left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\right)/J_{\lim} < 1$.

In the limit $\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\right)/J_{\lim} \to 0$, the Taylor expansion of the Gent model recovers the neo-Hookean model. In the limit $\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\right)/J_{\lim} \to 1$, the free energy diverges, and the elastomer approaches the limiting stretch.

The material is also taken to be incompressible. The stress-stretch relations are

$$\sigma_1 - \sigma_3 = \frac{\mu\left(\lambda_1^2 - \lambda_3^2\right)}{1 - \dfrac{\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3}{J_{\lim}}},$$

$$\sigma_2 - \sigma_3 = \frac{\mu\left(\lambda_2^2 - \lambda_3^2\right)}{1 - \dfrac{\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3}{J_{\lim}}}.$$

These two equations, along with $\lambda_1 \lambda_2 \lambda_3 = 1$, constitute the equations of state.

- Gent, A. N., A new constitutive relation for rubber. Rubber Chemistry and Technology, 1996, 69: 59-61.

Exercise. A rubber obeys the Gent model. When a rod made of the rubber is stretched by a force, the limiting stretch is found to be 6.   (a) Plot the true stress normalized by the shear modulus as a function of the stretch. (b) Compare this plot with the plot if the rubber were modeled as a neo-Hookean material. (c) The same rubber is now made into a sheet, and is subject to equal-biaxial stresses in the plane of the sheet. Repeat (a) and (b) above.

Mooney model. In this model, the free energy is fit to the expression
$$W = c_1\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\right) + c_2\left(\lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} - 3\right).$$
The two material constants c_1 and c_2 are used to fit experimental data.

- M. Mooney (1940) A theory of large elastic deformation, Journal of Applied Physics 11, 582-592.

Ogden model. In this model, the free energy density is fit to a series of more terms

$$W = \sum_n \frac{\mu_n}{\alpha_n}\left(\lambda_1^{\alpha_n} + \lambda_2^{\alpha_n} + \lambda_3^{\alpha_n} - 3\right),$$

where α_n may have any values, positive or negative, and are not necessarily

integers, and μ_n are constants. The stress-stretch relations are

$$\sigma_1 - \sigma_3 = \sum_n \mu_n \left(\lambda_1^{\alpha_n} - \lambda_3^{\alpha_n}\right),$$

$$\sigma_2 - \sigma_3 = \sum_n \mu_n \left(\lambda_2^{\alpha_n} - \lambda_3^{\alpha_n}\right).$$

- R.W. Ogden (1972) Large deformation isotropic elasticity – on the correlation of theory and experiment for incompressible rubberlike solids. Proceedings of the Royal Society of London A326, 567-583.

Valanis-Landel model. The model is taken to be of the form

$$W = w\left(\lambda_1\right) + w\left(\lambda_2\right) + w\left(\lambda_3\right).$$

The function of one variable $w(.)$ is used to fit experimentally measured stress-strain curves. This model generalizes Neo-Hookean model, the Mooney model, and the Ogden model.

- K.C. Valanis and R.F. Landel, The strain energy function of a hyperelastic material in terms of the extension ratios. Journal of Applied Physics 38, 2997 (1967)

ARRUDA-BOYCE MODEL

Model a single strand of polymer as a freely jointed chain. See notes on freely jointed chain (http://imechanica.org/node/14216). Here we list the key results. In this model, a polymer chain is modeled by a sequence of links capable of free rotation relative to each other. At a finite temperature, the relative rotations of the links allow the polymer chain to fluctuate among a large number of conformations. The statistics of the conformations gives the force-displacement relation of the polymer chain

$$r = nb\left(\frac{1}{\tanh\beta} - \frac{1}{\beta}\right),$$

where r is the mean value of the displacement in the direction of the force, n is the number of links per polymer chain, and $\beta = fb/kT$ the normalized force in the polymer chain. The Helmholtz free energy of the single strand of polymer is

$$w = nkT\left(\frac{\beta}{\tanh\beta} + \log\frac{\beta}{\sinh\beta}\right).$$

Model a polymer network with eight chains. Let Λ be the stretch of a single strand of polymer, namely, the end-to-end length of the stretched polymer r divided by that of the undeformed polymer r_0, namely,

$$\Lambda = \frac{r}{r_0}.$$

The Helmholtz free energy of the polymer, w, is a function of the stretch, namely,

$$w = w(\Lambda).$$

Next we consider a network of polymers, crosslinked by covalent bonds. Many models exist in the literature to derive the behavior of the network from that of the individual polymers. In the Arruda-Boyce model, the network is represented by many cells, each cell by a rectangle, and the polymers in the cell by the eight half diagonals. When the network is unstressed, the cell is a unit cube, and the length of a half diagonal is $\sqrt{3}/2$. When the network is stretched, the cell is a rectangle with sides λ_1, λ_2 and λ_3, and the length of a half diagonal is $\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2\right)^{1/2}/2$. Consequently, the end-to-end length of each chain is

$$\Lambda = \frac{1}{\sqrt{3}}\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2\right)^{1/2}.$$

Let v be the volume per link, and nv be the volume per chain. The free energy per unit volume of the network is

$$W = \frac{w(\Lambda)}{nv}.$$

The eight-chain model is described by a free energy function of the form $W(\Lambda)$.

- E.M. Arruda and M.C. Boyce, A three dimensional constitutive model for the large stretch behavior of rubber elastic materials. Journal of the Mechanics and Physics of Solids 41, 389-412 (1993).

Combing the freely joined chain model and the eight-chain model. A combination of the two models gives

$$\Lambda = \frac{1}{\sqrt{3}}\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2\right)^{1/2},$$

$$\Lambda = \frac{nb}{r_o}\left(\frac{1}{\tanh\beta} - \frac{1}{\beta}\right),$$

$$W = \frac{kT}{v}\left(\frac{\beta}{\tanh\beta} + \log\frac{\beta}{\sinh\beta}\right).$$

These equations define the function $W(\lambda_1, \lambda_2)$ using two intermediate parameters: the stretch Λ in each chain and the normalized force β in each chain.

The polymer network is also taken to be incompressible:

$$\lambda_1\lambda_2\lambda_3 = 1.$$

Incidentally, it is often suggested that a particular choice for r_o is $r_o = b\sqrt{n}$, the root-mean-square value of the end-to-end distance of a freely joined chain when the chain is subject to no force. This choice is unnecessary so long we regard the Arruda-Boyce model as a two-parameter model.

Liming behavior of the Arruda-Boyce model. In the limit $\beta \to \infty$, the chain approaches the limiting stretch:

$$\Lambda \to \frac{nb}{r_\mathrm{o}}.$$

In the limit $\beta \to 0$, the chain coils much below the limiting stretch, and the model reduces to

$$\Lambda = \frac{nb}{3r_\mathrm{o}} \beta,$$

$$W = \frac{kT}{6v} \beta^2.$$

Eliminating β from the above expressions, we recover the neo-Hookean model:

$$W = \frac{\mu}{2}\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2\right)$$

with

$$\mu = \frac{kT}{v}\left(\frac{r_\mathrm{o}}{nb}\right)^2.$$

Stress-stretch relations of the Arruda-Boyce model. The material is also taken to be incompressible, $\lambda_1 \lambda_2 \lambda_3 = 1$. Recall that

$$\sigma_1 - \sigma_3 = \lambda_1 \frac{\partial W(\lambda_1, \lambda_2)}{\partial \lambda_1}.$$

According to calculus, we write

$$\sigma_1 - \sigma_3 = \lambda_1 \frac{dW(\beta)}{d\beta}\left(\frac{d\Lambda(\beta)}{d\beta}\right)^{-1} \frac{\partial \Lambda(\lambda_1, \lambda_2)}{\partial \lambda_1}.$$

A direct calculation gives that

$$\sigma_1 - \sigma_3 = \left(\frac{kT}{v}\right)\left(\frac{r_\mathrm{o}}{nb}\right)\frac{\beta\left(\lambda_1^2 - \lambda_3^2\right)}{3\Lambda}.$$

We can similarly obtain that

$$\sigma_2 - \sigma_3 = \left(\frac{kT}{v}\right)\left(\frac{r_\mathrm{o}}{nb}\right)\frac{\beta\left(\lambda_2^2 - \lambda_3^2\right)}{3\Lambda}.$$

Exercise. A material obeys the Arruda-Boyce model, with $\mu = 1\mathrm{MPa}$ and the limiting stretch $nb/r_\mathrm{o} = 10$. Plot the stress-stretch relation when the material is subject to a uniaxial force. Include both tensile force and compressive force.

Comparing the Gent model and the Arruda-Boyce model. Both models recover the neo-Hookean model at small strains, and both models represent the extension limit. The Gent model was proposed as a phenomenological model, without invoking any statistical mechanics. The Arruda-Boyce model represents individual polymer chain as a freely jointed chain, and represents a polymer network by using eight chains. The Gent model has a simpler mathematical expression, and the Arruda-Boyce model connects individual polymer chains, polymer network and macroscopic behavior.

In the Gent model, the free energy depends on stretches through a single combination, $\lambda_1^2 + \lambda_2^2 + \lambda_3^2$. The same is true for the Arruda-Boyce model, regarding β as an intermediate variable.

Each model contains two material parameters: μ and $J_{\lim}$ for the gent model, and kT/v and nb/r_o for the Arruda-Boyce model. For the two models to have the same shear modulus at small strains, we require that

$$\mu = \frac{kT}{v}\left(\frac{r_o}{nb}\right)^2 .$$

For the two models to have the same extension limit, we require that

$$J_{\lim} + 3 = 3\left(\frac{nb}{r_o}\right)^2 .$$

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- Boyce, M.C., Direct comparison of the Gent and the Arruda-Boyce constitutive models of rubber elasticity. Rubber Chemistry and Technology, 1996, 69: 781-785.

Exercise. Both the Arruda-Boyce model and the Gent model are neo-Hookean when the applied force is small, and both models can describe the extension limit. Compare the two models by plotting them on the same stress-stretch diagram, given the same shear modulus and the same extension limit. Assume the sample is subject to uniaxial tensile force and the limiting stretch is 10.

ELASTICITY IN TERMS OF TENSORS

Synopsis of the general theory of elasticity. Let us recall key results from the notes on the general theory of elasticity (http://imechanica.org/node/538). A homogeneous deformation is specified by the deformation gradient **F**, a linear operator that maps a straight segment in the reference state to a straight segment in the current state. The homogeneous deformation causes the straight segment to stretch and rotate. The deformation gradient generalizes the definition of stretch, and is a measure of deformation.

An elastic material is specified by the Helmholtz free energy as a function of the deformation gradient:

$$W = W(\mathbf{F}).$$

Once this function is known, the nominal stress is given by

$$s_{iK} = \frac{\partial W(\mathbf{F})}{\partial F_{iK}}.$$

This equation relates the stress and deformation gradient, and is known as the equation of state.

The free energy is invariant when the block undergoing a rigid-body rotation. Thus, the free energy depends on $\mathbf{F}$ through the deformation tensor

$$C_{KL} = F_{iK}F_{iL}.$$

The tensor $\mathbf{C}$ is positive-definite and symmetric. In three dimensions, this tensor has six independent components. Thus, to specify an elastic material model, we need to specify the free energy as a function of the six variables:

$$W = W(\mathbf{C}).$$

For a given material, such a function is specified by a combination of experimental measurements and theoretical considerations. Trade off is made between the amount of effort and the need for accuracy.

A combination of the above expressions gives that

$$s_{iK} = 2F_{iL}\frac{\partial W(\mathbf{C})}{\partial C_{KL}}.$$

The true stress relates to the nominal stress as

$$J\sigma_{ij} = s_{iK}F_{jK}.$$

A combination of the above two equations gives that

$$\sigma_{ij} = 2F_{iL}F_{jK}\frac{\partial W(\mathbf{C})}{\partial C_{KL}}.$$

The true stress is symmetric, $\sigma_{ij} = \sigma_{ji}$.

Invariants of a tensor. Let $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ be an orthonormal basis of a Euclidean space. Any vector $\mathbf{u}$ in the Euclidean space is a linear combination of the base vectors:

$$\mathbf{u} = u_1\mathbf{e}_1 + u_2\mathbf{e}_2 + u_3\mathbf{e}_3.$$

We say that u_1, u_2, u_3 are the components of the vector $\mathbf{u}$ relative to the basis $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$. We are familiar with the geometric interpretations of these ideas. The vector $\mathbf{u}$ is an arrow in the space. The basis $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$ consists of three unit vectors normal to one another. The components u_1, u_2, u_3 are the projection of

the vector **u** on to the three unit vectors $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$.

Once a vector **u** is given in the Euclidean space, the vector itself does not change if we use another basis. However, the components u_1, u_2, u_3 do change if we use another basis. We are familiar the rule of the transformation of the components.

The length of the vector **u** is invariant with the choice of the basis. The sum

$$u_i u_i$$

does not have any free index, and is a scalar. When a new basis is used, the components u_1, u_2, u_3 change, but the scalar $u_i u_i$ remains invariant.

The idea of invariant can be readily generalized. For any symmetric second-rank tensor **C**, the six components of the tensor form three scalars:

$$\alpha = C_{KK},$$

$$\beta = C_{KL} C_{KL},$$

$$\gamma = C_{KL} C_{LJ} C_{JK}.$$

These scalars are formed by combining the individual components of the tensor in ways that make all indices dummy. The three scalars remain unchanged when the coordinates rotate, and are known as the invariants of the tensor **C**.

Exercise. A body undergoes a homogeneous deformation specified by a deformation gradient. This deformation maps material particles in a unit cube in the reference state to a parallelepiped in the current state. The shape of the parallelepiped depends on the orientation of the unit cube. Let the lengths of the three edges of the parallelepiped be l_1, l_2 and l_3. Show that the sum $l_1^2 + l_2^2 + l_3^3$ is independent of the orientation of the unit cube.

An alternative way to write invariants. Invariants of a symmetric second-rank tensor can be written in many forms. In many textbooks, the invariants are introduced as follows. An eigenvalue ξ of the tensor **C** obeys

$$\det(\mathbf{C} - \xi \mathbf{I}) = 0.$$

The left-hand side of this equation corresponds to a third order polynomial of ξ. We can verify that

$$\det(\mathbf{C} - \xi \mathbf{I}) = -\xi^3 + I_1 \xi^2 - I_2 \xi + I_3,$$

where the coefficients of the polynomial are given by

$$I_1 = C_{KK},$$

$$I_2 = \frac{1}{2}\left(C_{KK} C_{LL} - C_{KL} C_{KL}\right),$$

$$I_3 = \det \mathbf{C}.$$

These three coefficients are invariants of the tensor $\mathbf{C}$.

The three roots of the polynomial, ξ_1, ξ_2, ξ_3, are the eigenvalues of the tensor $\mathbf{C}$. The three invariants can be expressed in terms of the eigenvalues:

$$I_1 = \xi_1 + \xi_2 + \xi_3 ,$$

$$I_2 = \xi_1\xi_2 + \xi_2\xi_3 + \xi_3\xi_1 ,$$

$$I_3 = \xi_1\xi_2\xi_3 .$$

Exercise. Confirm that the two sets of invariants (α, β, γ) and (I_1, I_2, I_3) are related as

$$I_1 = \alpha$$

$$I_2 = \frac{1}{2}\left(\alpha^2 - \beta\right)$$

$$I_3 = \frac{1}{6}\left(\alpha^3 - 3\alpha\beta + \gamma\right)$$

Isotropy. For an isotropic material, the free-energy density is unchanged when the coordinates rotate in the reference state. When the coordinates rotate, however, the individual components of the tensor $\mathbf{C}$ will change. How do we write the function $W(\mathbf{C})$ for an isotropic material?

To specify a model of an isotropic elastic material, we need to prescribe the free-energy density as a function of the three invariants of the Green deformation tensor:

$$W = W\left(I_1, I_2, I_3\right).$$

Once this function is specified, we can derive the stress by using the chain rule:

$$s_{iK} = \frac{\partial W(\mathbf{F})}{\partial F_{iK}} = \frac{\partial W\left(I_1, I_2, I_3\right)}{\partial I_1}\frac{\partial I_1}{\partial F_{iK}} + \frac{\partial W\left(I_1, I_2, I_3\right)}{\partial I_2}\frac{\partial I_2}{\partial F_{iK}} + \frac{\partial W\left(I_1, I_2, I_3\right)}{\partial I_3}\frac{\partial I_3}{\partial F_{iK}} .$$

Derivatives of this kind are recorded in many textbooks on continuum mechanics.

Incompressibility. Subject to external forces, elastomers can undergo large change in shape, but very small change in volume. A commonly used idealization is to assume that such materials are incompressible, namely,

$$\det \mathbf{F} = 1 .$$

In arriving at the relation $s_{iK} = \partial W(\mathbf{F})/\partial F_{iK}$, we have assumed that each component of F_{iK} can vary independently. However, the condition of incompressibility places a constraint among the components. To enforce this constraint, we replace the free-energy function $W(\mathbf{F})$ by a function

$$W(\mathbf{F}) - (\det \mathbf{F} - 1)\Pi,$$

with Π as a Lagrange multiplier. We then allow each component of F_{iK} to vary independently, and obtain the stress from

$$s_{iK} = \frac{\partial}{\partial F_{iK}}\left[W(\mathbf{F}) - (\det \mathbf{F} - 1)\Pi\right].$$

Recall an identity in the calculus of matrix:

$$\frac{\partial \det \mathbf{F}}{\partial F_{iK}} = H_{iK}\det \mathbf{F},$$

where $\mathbf{H}$ is defined by $H_{iK}F_{iL} = \delta_{KL}$ and $H_{iK}F_{jK} = \delta_{ij}$. For a proof see p. 41 of Holzapfel.

Thus, for an incompressible material, the stress relates to the deformation gradient as

$$s_{iK} = \frac{\partial W(\mathbf{F})}{\partial F_{iK}} - \Pi H_{iK}.$$

This equation, along with the constraint $\det \mathbf{F} = 1$, specifies a material model for incompressible elastic materials. The Lagrange multiplier Π is not a material parameter. Rather, Π is to be solved as a field for a given boundary-value problem. When the deformation of the body is inhomogeneous, Π is in general also inhomogeneous.

Recall that the true stress relates to the nominal stress as $\sigma_{ij} = s_{iK}F_{jK}/J$. In terms of the true stress, the equation of state is

$$\sigma_{ij} = F_{jK}\frac{\partial W(\mathbf{F})}{\partial F_{iK}} - \Pi\delta_{ij}.$$

The Lagrange multiplier acts like a hydrostatic pressure.

Neo-Hookean model expressed in terms of tensors. The neo-Hookean model is defined by the free-energy function:

$$W = \frac{\mu}{2}\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\right),$$

along with the condition of incompressibility, $\lambda_1 \lambda_2 \lambda_3 = 1$. We now express the model in terms of tensors.

The three stretches enter the free energy function in the combination $\lambda_1^2 + \lambda_2^2 + \lambda_3^2$. This combination is an invariant of the Green deformation tensor:

$$C_{KK} = \lambda_1^2 + \lambda_2^2 + \lambda_3^2.$$

Also recall that $C_{KK} = F_{iK}F_{iK}$. Consequently, the free energy function can be written in the form

$$W = \frac{\mu}{2}\left(F_{iK}F_{iK} - 3\right).$$

The condition of incompressible can be written as

$$\det \mathbf{F} = 1.$$

In terms of the nominal stress, the neo-Hookean model takes the form

$$s_{iK} = \mu F_{iK} - \Pi H_{iK}.$$

In terms of the true stress, the neo-Hookean model takes the form

$$\sigma_{ij} = \mu F_{iK}F_{jK} - \Pi \delta_{ij}.$$

Exercise. A body undergoes a shear deformation. Mark a set of material particles in the body. When the body is in the reference state, the set of material particles forms a unit cube. When the body is in the current state, the same set of material particle forms a parallelepiped, as shown in the figure. The dimension normal to the paper (not shown) remains unchanged. Write the deformation gradient for this deformation. Assume the material is neo-Hookean. Calculate all components of the true stress tensor.

reference state   current state
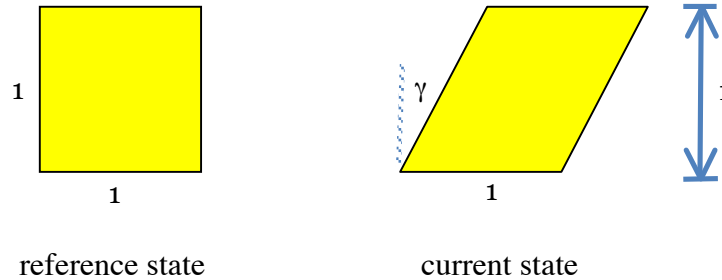
Exercise. In the above, several forms of free energy function are given in terms of the principal stretches. They can be rewritten in terms of deformation gradient, following the same procedure outlined above.   Go through this procedure for the Gent model and the Arruda-Boyce model.

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