Lecture 11:
Rubber elasticity

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1 Suggested reading

- *Polymer Physics* – Rubinstein and Colby: Chapter 7

2 Thermodynamics of rubber

In the last section, we considered cross-linking and gelation reactions that formed polymer networks and gels. As reaction proceeds sufficiently far beyond the gel point, p_c, most of the polymer content will be included in the gel as a single macroscopic network polymer ($P_{gel} \approx 1$). These soft solids are a broadly useful class of materials and as engineers we are interested in understanding their mechanical properties. A class of soft, polymer networks that have been studied in detail are rubbers, which comprise many commodity products such as rubber bands, car tires, gaskets, and adhesives. These materials can undergo large elastic deformations without breaking; here, we explore the physics that enable these extremely useful properties. As we will see, entropic elasticity of polymer chains is the origin of these fascinating mechanical properties.

Let us consider a polymer network. Thermodynamics describes the change in internal energy of this system as the sum of all changes in energy. This includes the heat added to the system TdS, the work done to change the volume of the polymer network $-pdV$, and work done to deform the polymer network fdL, where f is the force of deformation and L is the deformation length.

$$dU = TdS - pdV + fdL. \tag{1}$$

This differential form describes the change in internal energy of the polymer network with a corresponding entropy change dS, volume change dV, or change in network length dL and is a thermodynamic state function of S, V, and L. We can transform this to the Helmholtz free energy F

$$F = U - TS. \tag{2}$$

and consider the differential form

$$dF = dU - d(TS) = dU - TdS - SdT \tag{3}$$
$$= -SdT - pdV + fdL \tag{4}$$
$$= \left(\frac{\partial F}{\partial T}\right)_{V,L} dT + \left(\frac{\partial F}{\partial V}\right)_{T,L} dV + \left(\frac{\partial F}{\partial L}\right)_{T,V} dL. \tag{5}$$

This implies that

$$\left(\frac{\partial F}{\partial T}\right)_{V,L} = -S \; ; \left(\frac{\partial F}{\partial V}\right)_{T,L} = -p \; ; \left(\frac{\partial F}{\partial L}\right)_{T,V} = f. \tag{6}$$

The Helmholtz free energy is a thermodynamic state function of T, V, and L. Thus, a second derivative of the Helmholtz free energy does not depend on the order of differentiation.

$$\frac{\partial^2 F}{\partial T \partial L} = \frac{\partial^2 F}{\partial L \partial T} \tag{7}$$

Combining Equation 6 and 7, we can define a Maxwell relation:

$$-\left(\frac{\partial S}{\partial L}\right)_{T,V} = \left(\frac{\partial f}{\partial T}\right)_{V,L}. \tag{8}$$

We then consider the force f that is required to deform the polymer network, which is comprised of two contributions one related to the change in internal energy with a change in length and one related to the change in entropy with a change in length.

$$f = \left(\frac{\partial F}{\partial L}\right)_{T,V} = \left[\frac{\partial (U - TS)}{\partial L}\right]_{T,V} = \left(\frac{\partial U}{\partial L}\right)_{T,V} - T\left(\frac{\partial S}{\partial L}\right)_{T,V}. \tag{9}$$

The entropic term can be rewritten using the Maxwell relation from Equation 8:

$$f = \left(\frac{\partial U}{\partial L}\right)_{T,V} + T\left(\frac{\partial f}{\partial T}\right)_{V,L} = f_E + f_S. \tag{10}$$

where f_E is the energetic contribution to the force and f_S is the entropic contribution to the force.

As discussed earlier in the course, the force required for deformation in typical crystalline solids is heavily dominated by the energetic contribution. This is caused by the increase in internal energy when the crystalline lattice is distorted from its equilibrium conformation. However, in polymer networks, we generally take an ideal assumption that there is no energetic contribution to elasticity, $f_E = 0$. For small deformations and most polymer networks this is a fair assumption, the interactions of the monomers along the backbone do not alter significantly with deformation as the local molecular environment is basically indistinguishable between the at rest and deformed states. Therefore, as was the case for individual chains, the elasticity of polymer networks is driven by entropy.

In addition, the entropic nature of elasticity in polymer networks imparts thermoelastic behavior whereby the force at constant extension increases with increasing temperature. This is the opposite behavior as for typical crystalline solids where the force at constant extension decreases weakly with increasing temperature. In polymer networks, each network strand loses conformation entropy upon stretching meaning that $\partial S/\partial L < 0$ and so the entropic contribution to the forces increases with increasing temperature.

$$f_S = T\left(\frac{\partial f}{\partial T}\right)_{V,L} = -T\left(\frac{\partial S}{\partial L}\right)_{T,V}. \tag{11}$$

The theory of **rubber elasticity** has been developed to describe the elastic properties of polymer networks and is a molecular view of the network behavior. Below we describe rubber elasticity in one of its most common forms, known as the **affine network model**. The affine network model describes well the mechanical behavior of polymer networks but does not account for all aspects of the systems, such as entanglements, loops, cross-link fluctuations, and dangling ends. As such other models have been applied, e.g., phantom network model, entangled rubber elasticity, real elastic network theory, and others. In this discussion, we describe the affine network model in detail to provide physical insight into the entropic nature of rubber elasticity. In future lectures, we will present the phantom network model and real elastic network theory but not derive them.

3 Affine network theory

One of the most attractive properties of polymer networks and gels is their ability to deform reversibly up to several times their size and over many cycles. The elastic behavior of polymer networks is caused by the entropic elasticity of the individual polymer chains that comprise the network, the network strands. A simple model that describes the rubber elasticity of polymer networks is the **affine network model**, described originally by Kuhn. The central assumption of the affine network model is that the deformation of each network strand is identical to the macroscopic deformation of the network. That is chain deformation is affine with network deformation. In addition, it is assumed that the network is composed of Gaussian chains, that the network is ideal $f_E = 0$, that the volume of the network is constant, that the chains are flexible ($T > T_g$), and that there is no chain slip or strain-induced crystallization.

Let us consider a polymer network that has dimensions L_{x0}, L_{y0}, and L_{z0} in the undeformed state. If the network is deformed in the x, y, and z dimensions by the factors λ_x, λ_y, and λ_z, the dimensions of the deformed network will be

$$L_x = \lambda_x L_{x0}, \quad L_y = \lambda_y L_{y0}, \quad L_z = \lambda_z L_{z0}. \tag{12}$$

We assume that each network strand is composed of N monomers. If we zoom in on a given network strand in the undeformed case, we can decompose the end-to-end vector $\vec{R}_0$ into its projections along the x, y, and z directions of R_{x0}, R_{y0}, and R_{z0}. In this model, the junction points or the ends of the network strands do not fluctuate in space and are deformed along with the macroscopic deformation of the network. This implies that the chain in the deformed state $\vec{R}$ has projections

$$R_x = \lambda_x R_{x0}, \quad R_y = \lambda_y R_{y0}, \quad R_z = \lambda_z R_{z0}. \tag{13}$$

Recall, from the Lecture Notes, the entropy of a polymer chain of N Kuhn monomers each of length b with end-to-end vector $\vec{R}$

$$S(\vec{R}, N) = -\frac{3}{2}k_B \frac{\vec{R}^2}{Nb^2} + S(0, N) = -\frac{3}{2}k_B \frac{R_x^2 + R_y^2 + R_z^2}{Nb^2} + S(0, N). \tag{14}$$

Therefore, the entropy change of the individual chain upon deformation is the difference in entropy between the deformed and non-deformed states:

$$S(\vec{R}, N) - S(\vec{R}_0, N) = -\frac{3}{2}k_B \frac{R_x^2 + R_y^2 + R_z^2}{Nb^2} + \frac{3}{2}k_B \frac{R_{x0}^2 + R_{y0}^2 + R_{z0}^2}{Nb^2} \tag{15}$$

$$= -\frac{3}{2}k_B \frac{(\lambda_x^2 - 1)R_{x0}^2 + (\lambda_y^2 - 1)R_{y0}^2 + (\lambda_z^2 - 1)R_{z0}^2}{Nb^2}. \tag{16}$$

The entropy change for the whole network upon deformation is the sum of the entropy changes for the individual network strands over all n network strands:

$$\Delta S_{net} = -\frac{3}{2}\frac{k_B}{Nb^2}\left[(\lambda_x^2 - 1)\sum_{i=1}^{n}(R_{x0})_i^2 + (\lambda_y^2 - 1)\sum_{i=1}^{n}(R_{y0})_i^2 + (\lambda_z^2 - 1)\sum_{i=1}^{n}(R_{z0})_i^2\right]. \tag{17}$$

Assuming that the polymer network was formed by cross-linking chains in the ideal state, then we can compute the components of the mean-square end-to-end distance in the undeformed state

$$\langle R_{x0}^2 \rangle = \frac{1}{n}\sum_{i=1}^{n}(R_{x0})_i^2 = \frac{Nb^2}{3} = \langle R_{y0}^2 \rangle = \langle R_{z0}^2 \rangle. \tag{18}$$

Therefore,

$$\sum_{i=1}^{n}(R_{x0})_i^2 = \sum_{i=1}^{n}(R_{y0})_i^2 = \sum_{i=1}^{n}(R_{z0})_i^2 = \frac{n}{3}Nb^2. \tag{19}$$

Combining Equation 17 and 19, we can write the total entropy change upon deformation of the network:

$$\Delta S_{net} = -\frac{3}{2}\frac{k_B}{Nb^2}\left[(\lambda_x^2 - 1)\frac{n}{3}Nb^2 + (\lambda_y^2 - 1)\frac{n}{3}Nb^2 + (\lambda_z^2 - 1)\frac{n}{3}Nb^2\right] \tag{20}$$

$$= -\frac{nk_B}{2}(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3). \tag{21}$$

As stated in the assumptions, the main contribution to the free energy change in the network upon deformation comes from this entropic term.

$$\Delta F_{net} = -T\Delta S_{net} = \frac{nk_B T}{2}(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3). \tag{22}$$

Polymer networks, in the dry state, or gels swollen in an incompressible fluid, are often considered to be incompressible so that the volume does not change significantly upon deformation:

$$V = L_{x0}L_{y0}L_{z0} = L_x L_y L_z = \lambda_x L_{x0}\lambda_y Ly0\lambda_z L_{z0} = \lambda_x\lambda_y\lambda_z V. \tag{23}$$

This implies that $\lambda_x\lambda_y\lambda_z = 1$. In reality, there is a small volume change upon deformation but this is quite small and negligible.

To predict the modulus of elasticity for the model polymer network, we consider a uniaxial deformation. The non-deformed dimensions of the network adjust to maintain a constant volume

$$\lambda_x = \lambda, \quad \lambda_y = \lambda_z = \frac{1}{\sqrt{\lambda}}. \tag{24}$$

These can be combined with Equation 22 to calculate the free energy change upon uniaxial deformation at constant volume

$$\Delta F_{net} = \frac{nk_B T}{2}(\lambda^2 + \frac{2}{\lambda} - 3). \tag{25}$$

The force required to induce the uniaxial deformation λ can thus be calculated from Equation 6

$$f_x = \frac{\partial \Delta F_{net}}{\partial L_x} = \frac{\partial \Delta F_{net}}{\partial \lambda L_{x0}} = \frac{1}{L_{x0}} \frac{\partial \Delta F_{net}}{\partial \lambda} \tag{26}$$

$$= \frac{nk_B T}{L_{x0}} \left(\lambda - \frac{1}{\lambda^2} \right). \tag{27}$$

As the sample volume is increased, this force would naturally increase and we generally normalize the force f_x to the cross-sectional area to obtain a stress

$$\sigma_{xx} = \frac{f_x}{L_y L_z} = \frac{nk_B T}{L_{x0} L_y L_z} \left(\lambda - \frac{1}{\lambda^2} \right) = \frac{nk_B T}{L_{x0} L_{y0} L_{z0}} \lambda \left(\lambda - \frac{1}{\lambda^2} \right) \tag{28}$$

$$= \frac{nk_B T}{V} \left(\lambda^2 - \frac{1}{\lambda} \right). \tag{29}$$

This stress is the true stress in the network. Since it can be difficult to measure the cross-sectional area of the sample in situ during deformation, we often use the engineering stress, which is normalized to the original cross-sectional area $L_{y0} L_{z0}$

$$\sigma_{eng} = \frac{f_x}{L_{y0} L_{z0}} = \frac{nk_B T}{L_{x0} L_{y0} L_{z0}} \left(\lambda - \frac{1}{\lambda^2} \right) = \frac{nk_B T}{V} \left(\lambda - \frac{1}{\lambda^2} \right) = \frac{\sigma_{true}}{\lambda}. \tag{30}$$

The **shear modulus** G relates the stress and the deformation. Equation 30 shows that

$$\boxed{G = \frac{nk_B T}{V} = \nu k_B T = \frac{\rho \Re T}{M_s}} \tag{31}$$

Where ν is the number density of network strands $\nu = n/V$, ρ is the network density (mass per unit volume), M_s is the number-average molar mass of the network strands, and $\Re$ is the gas constant. This derivation arises from the entropic elasticity from the individual Gaussian network strands and shows that the modulus scales linearly with network strand density. More precisely, the modulus of a polymer network is $k_B T$ per network strand. Further, the modulus increases directly with temperature owing to this entropic driving force that is the basis of rubber elasticity.

Rubber elasticity provides a simple physical framework to calculate the mechanical properties of networks and gels and is also instrumental in predicting gel swelling.