Chapter 3 Polymer Physics
Polymer Gels and Elastomers

An ideal rubber responds to stress through changes in the entropy of the chains making up the network. The ideal rubber displays a Hookean spring constant, $3kT/Nb^2$ (pp. 46).

The elastic free energy, A, of a chain, under the assumption of a Gaussian coil distribution and affine deformation of crosslink sites yields,

$$A = n_c kT(E_{\alpha\beta})^2/2 + A_0(V,T)$$

where n_c is the number of chains in the rubber, $E_{\alpha\beta}$ is the deformation gradient tensor (modulus tensor), and A_0 is the free energy in the unstretched state. This equation for the free energy allows the calculation of the mechanical response of an ideal rubber.

For example, the shear modulus, G, is given by,

$$G = v_c kT$$

where v_c is the number density of crosslinked chains.

Under uniaxial extension the stress, s, is given by,

$$\sigma = v_c\, kT\, (\lambda^2 - 1/\lambda)$$

under the assumption of incompressibility. λ is the strain.

The ideal rubber model of Kuhn lacks a description of finite extension and non-affine behavior of crosslink sites.

Stress Optical Law:

When we consider dynamic behavior, optical birefringence will be used as a basis for a number of phenomena. Some of these phenomena are based in the stress optical law for networks and for this reason Doi introduces the stress optical law in chapter 3.

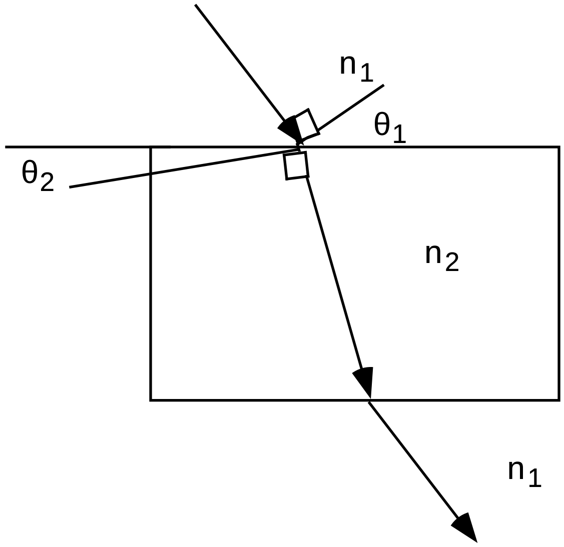
The index of refraction of a material is a measure of the bending of light as it passes through a sample. If polarized light is used the index can vary with direction of polarization depending on the degree of orientation of the sample. An oriented sample will have a stretching direction, SD, and a normal direction, ND. The birefringence, Δn, is defined as,

$$\Delta n = n_{SD} - n_{ND}$$

Birefringence can occur as a direct, linear result of orientation leading to a linear stress optical rule,

$$\Delta n = C_{opt}\, (\sigma_{zz} - \sigma_{xx})$$

where C_{opt} is the stress-optical coefficient. Birefringence in polymers is a measure of the conformational distribution of chains since it is based on the birefringence of the chain's



$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

substructural components. The development of a molecular scale basis for birefringence in polymers is based on the Rouse model for a chain, that is, a polymer chain can be viewed as a sequence of identical elastic springs (composed of a number of Gaussian segments giving rise to an elastic constant, b_{Rouse},

$$b_{Rouse} = 3kT/a_{Rouse}^{2}$$

where a_{Rouse} is the end-to-end distance of a Gaussian Rouse segment. The tensile stress, σ_{zz}, is given by,

$$\sigma_{zz} = b_{Rouse}\Sigma\{z_i z_i\}/V = b_{Rouse}\ c_{spr} <z_i^2>$$

where c_{spr} is the number density of Rouse springs and $<z_i^2>$ is the average mean-square extensions in the z-direction. Similarly,

$$\sigma_{zz} - \sigma_{xx} = b_{Rouse}\ c_{spr}\ \{<z_i^2> - <x_i^2>)$$

The total extension of the chain, r_i, is related to the x and z extensions by the direction cosines,

$$z_i = r_i \cos\theta^i_z$$

$$x_i = r_i \cos\theta^i_x$$

so,

$$\sigma_{zz} - \sigma_{xx} = b_{Rouse}\ c_{spr}\ \{<\cos^2\theta^i_z> - <\cos^2\theta^i_x>)< r_i^2>$$

The sum of all direction cosine squares equals 1,

$$<\cos^2\theta^i_x> + <\cos^2\theta^i_y> + <\cos^2\theta^i_z> = 1$$

and,

$<\cos^2\theta^i_y> = <\cos^2\theta^i_x>$

so,

$<\cos^2\theta^i_x> = 1/2 \{1 - <\cos^2\theta^i_z>\}$

and

$\sigma_{zz} - \sigma_{xx} = b_{Rouse}\ c_{spr} < r_i^2> \{3<\cos^2\theta^i_z> - 1\}/2$

The expression to the right of $< r_i^2>$ is called the **orientational order parameter** for the Rouse segments, S^{spr}_{or}.

$\sigma_{zz} - \sigma_{xx} = c_{spr}\ 3kT < r_i^2> S^{spr}_{or}/a_{Rouse}^2$

The Rouse element, or a spring element, has internal optical birefringence which is related to the birefringence of a chains base unit, a statistical segment or mer unit. The birefringence of a perfectly oriented, $S_{or} = 1$, bulk sample is related to the asymmetry in polarizability of molecular units, $\Delta\beta$, through the Lorentz-Lorenz equation,

$$\Delta n = \frac{\bar{n}^2 + 2}{\bar{n}} \frac{1}{6\varepsilon_0} c_m \Delta\beta$$

c_m is the density of molecular units, ε_0 is the dielectric constant for vacuum and n bar is the mean index of refraction. The anisotropy of the polarizability per Rouse spring, $\Delta\beta_{spr}$, is related to the anisotropy of the polarizability of a chain unit, $\Delta\beta$, by the function,

$\Delta\beta_{spr} = n_m \Delta\beta <\Phi(f)>$

where f is the tensile force on the spring and $\Phi(f)$ is a function which is even, i.e. +f and -f have the same resulting value and as f->0, $\Phi(f)$->0; as f->∞, $\Phi(f)$->1. The simplest form is,

$\Phi(f) = \Phi_2 f^2$

where Φ_2 is a constant. The stress-optical ratio, $C_{opt} = \Delta n/ \sigma_{zz} - \sigma_{xx}$, is given by,

$$C_{opt} = \frac{\bar{n}^2 + 2}{\bar{n}} \frac{1}{6\varepsilon_0} \frac{n_m \Delta\beta a_R^2}{3kT} \frac{\langle f^2 \rangle}{\langle r_i^2 \rangle} \Phi_2$$

also,

$f = 3kT\, r_i/a_R^{\,2}$

and,

$a_R^{\,2} = n_m\, a_0^{\,2}$

so,

$$C_{opt} = \frac{\bar{n}^2 + 2}{\bar{n}} \frac{1}{2\varepsilon_0} \frac{kT\Delta\beta}{a_0^2} \Phi_2$$

predicting a constant stress-optical coefficient on a molecular basis for a rubber or a polymer melt which can be described using the Rouse chain model, i.e. an entangled melt. The stress-optical coefficient depends on the size of a monomer, a_0, the optical anisotropy per monomer, $\Delta\beta$, and the coefficient Φ_2 which is related to the orientation of chain elements within a Rouse element (the elastic restoring forces).

Figure 3.4 pp. 55 demonstrates that the stress optical law, that is the ratio of optical birefringence and stress remains constant even under nonlinear deformation, holds not only for rubbers, but also for polymer solutions and melts. The lines reflect the optical birefringence divided by the stress-optical coefficient and the points the stress as measured in polystyrene solutions. Both the shear stress and the normal stresses are represented very will by this model. **This indicates that the basis of stress in an elastomer and in polymer melts and solutions is segmental orientation.**

Interaction Between Chain Elements in a Gel:

The Rouse model does not consider chain interactions such as those considered in the excluded volume interaction or entanglement effects. Additionally, Doi discusses "nematic" ordering issues which are certainly not considered in Kuhn networks using a Rouse model. Nematic interactions on the stress optical coefficient are a fairly unusual treatment and are of no real importance.

Excluded Volume:

We have already stated that a polymer in a single component melt is in a Gaussian state due to screening of interactions. This would appear to be completely applicable to a rubber which is essentially a single phase melt if the crosslink sites are small. The Rouse /Kuhn model would appear to have some problems for good-solvent gels in terms of excluded volume, i.e. the entire theory is based on Gaussian scaling starting with the calculation of the free energy for a network and all the way through the use of the Rouse spring constant. There is no formal resolution of this problem, however, the data in figure 3.4, pp. 55, appears to be in good solvent conditions so it would appear that at least the gross behavior of the stress optical coefficient is met for excluded volume coils. Doi makes the argument that the Stress optical law holds for all systems where the volume fraction is constant since the excluded volume term in the Flory-Huggins approach appears with a volume fraction prefactor. This doesn't seem to resolve the issue of Gaussian statistics which are assumed throughout the derivation of the stress optical law. A scaling approach to the stress-optical law would appear to be possible and has probably been pursued

Entanglement Interactions (Deviation from Phantom Chains):

The Kuhn/Rouse model assumes that chain response is not effected by entanglements. For instance the Rouse model predicts a zero shear viscosity which follows a linear power of molecular weight. This is only observed below the entanglement molecular weight. Where entanglements are important the zero shear viscosity follows a 3.4 power of molecular weight, so the effect of entanglements are dramatic, especially on kinetic features. In a gel or elastomer undergoing deformation entanglements are expected to contribute to the modulus and are expected to modify the segmental orientation function.

Figure 3.6 of Doi shows the tube-model for an entangled rubber. The presence of other chains serves to form an oddly shaped "tube" in which the polymer chain is confined, especially at a single snapshot of time. The tube diameter, a, is related to the inverse of the linear density of chains in the system.

If a polymer is assumed to be trapped in a tube of diameter "a", the entropy of the chain will be significantly reduced since the number of possible configurations will be limited by the tube. The total number of configurations, W, for the chain can be broken into two terms which describe a random configuration along the path of the tube, W_1(L,N), and a confined configurations normal to the path of the tube, W_2(a,N),

$W = W_1(L,N)\ W_2(a,N)$

W_1(L,N) corresponds to a 1-dimensional random walk,

$$W_1(L,N) = z_1^N \left(\frac{3}{2\pi N b^2}\right)^{3/2} \exp\left(\frac{-3L^2}{2Nb^2}\right)$$

and W_2(a,N) reflects the number of random walks in a tube of diameter a,

$W_2(a,N) = z_2(a)^N$

W_2(a,N) is a function of the tube diameter alone for a fixed molecular weight. If a fixed tube diameter is assumed then W_2(a,N) is a constant.

If affine deformation is assumed then the tube length changes in proportion to the bulk strain. The change in free energy on deformation from a length L to a length L' is given by,

$$A'_{chain} - A_{chain} = kT(\ln W' - \ln W) = \frac{3kT}{2Nb^2}(L'^2 - L^2)$$

The undeformed chain can be described as a series of subunits of length "a", the tube diameter" which are randomly arranged in space. The unit vector, $\mathbf{u}_i$, describes the direction of each segment of length "a". When a strain tensor, E, is applied to the sample the direction of element "i" becomes E dot $\mathbf{u}_{i.}$ The length of element "i" becomes a |E dot $\mathbf{u}_i$|. The deformed length, L', is the sum of these deformed segments,

$$L' = \sum_{i=1}^{Z} a\left|E\cdot\ u_i\right| = Za\left\langle \left|E\cdot\ u_i\right|\right\rangle_0$$

where Z is the number of segments of length "a" in the undeformed state. Then,

$$\left[A'_{chain} - A_{chain}\right]_{Tube\_Model} = n_c \frac{3kT}{2Nb^2} Z^2 a^2 \left(\left\langle \left| E \cdot u_i \right| \right\rangle_0^2 - 1\right)$$

In the absence of entanglements, Kuhn Theory, this result is,

$$\left[A'_{chain} - A_{chain}\right]_{Kuhn\_Model} = n_c \frac{3kT}{2} \left(\left\langle \left| E \cdot u_i \right| \right\rangle_0^2 - 1\right)$$

where n_c is the number of crosslinked chains. The entangled chain under the tube model shows an enhanced change in free energy on strain, and a corresponding enhanced modulus, by the factor Z^2a^2/Nb^2. This has been experimentally verified.

Equilibrium Gel Swelling:

Consider a rubber which is placed in and excess of what would be a good solvent for the base polymer, polydimethylsiloxane (PDMS) in benzene at room temperature for instance. The elasticity of the network opposes dissolution of the network while specific (local) enthalpic interactions and the increase in entropy drive swelling of the elastomer. A thermodynamic balance is reached between elasticity and decrease in free energy for mixing which leads to a fixed, equilibrium amount of swelling which depends on the system and temperature. The degree of equilibrium swelling is a measure of the interaction parameter, χ, and the molecular weight between crosslinks, M_c. By summing the elastic and mixing free energies and setting the derivative with respect to composition to zero, the following equation can be obtained,

$$\varphi + \ln(1 - \varphi) + \chi\varphi^2 + \frac{\rho V_c}{M_c} \varphi_c^{1/3} = 0$$

Doi equation 3.74 pp. 63. The logarithm term can be expanded as $\ln(1-\varphi) = -[\varphi + \varphi^2/2 + \varphi^3/3 + \varphi^4/4 + \ldots]$. Retaining only second order terms (for φ less than 1) this yields,

$$(\chi - 1/2)\,\varphi^2 + \rho V_c\, \varphi^{1/3}/M_c = 0$$

or

$$\varphi = (\rho V_c / \{(1/2 - \chi)\, M_c\})^{3/5}$$

Problems with this Equilibrium Swelling Model:

Although the equilibrium swelling law given above, has been widely used and verified experimentally we should consider certain problems in the derivation in the context of coil scaling behavior which was discussed in chapter's 1 and 2.

First, the swelling law is based on Gaussian statistics which are not correct if the volume fraction of a good solvent exceeds about 1%. This is certainly the case for a swollen elastomer in a good solvent where the solvent volume fraction might be about 50%.

Secondly, we have seen previously that coil expansion in a good solvent usually involves transitions in scaling, i.e. blobs. That is, one might expect good solvent scaling at small sizes of observation to occur first as the solvent enters the rubber followed by expansion of good solvent blobs which is counteracted by mechanical elasticity operating at the size scale of the chain between crosslinks. Observation of coil scaling in swollen elastomers is a fairly trivial task using SANS and deuterated solvents. These results contradict the simple view used to describe equilibrium swelling. A major unanswered question is how do these structural observations correlate with bulk observations of equilibrium swelling which seem to follow the equation given above.