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Rubber Elasticity

1. Conditions of Rubber Elasticity

The elasticity of glassy and semi-crystalline polymers is primarily determined by their cohesive energy E_{coh} and shows little dependence on time scale for small deformations. Beyond the elastic regime, these materials exhibit plastic flow or fracture, leading to permanent deformation.

In contrast, **rubbers and elastomers can sustain large, reversible deformations**, often exceeding several hundred percent in strain. This remarkable behavior is fundamentally **entropic** rather than energetic in origin. It requires:

- **long and flexible chains**, enabling large conformational rearrangements and implying a low glass transition temperature T_g.
- **weak intermolecular forces**, ensuring that deformation relies on conformational changes rather than cohesive interactions.
- **local anchoring points**, either chemical cross-links or physical entanglements, which prevent viscous flow and ensure macroscopic reversibility.

Rubber elasticity is therefore a phenomenon **unique to organic polymers above T_g.** Materials exhibiting rubbery behavior at ambient temperature typically have low-T_g, non-crystallizable backbones, such as random aliphatic copolymers, natural rubber (*cis*-1,4-polyisoprene) or silicones (–Si–O–).

2. Thermodynamics of Elastomer Deformation

Rubbers are effectively incompressible materials, since their bulk modulus K is several orders of magnitude larger than Young's modulus E. Thus, volume changes during deformation are negligible. The most appropriate thermodynamic potential for describing such processes is the **Helmholtz free energy**,

$$A = U - TS \quad , \tag{1}$$

where U is the internal energy and S the entropy.

The **first law of thermodynamics** expresses the **conversation of energy**: any change in the internal energy U equals the sum of the heat Q supplied and the work W done on the system.

For a deformable solid, this work has two contributions: the **volumetric work** associated with pressure and volume changes, and the **tensile work** arising from an applied force f acting over a length change dl:

$$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W = T\mathrm{d}S - p\mathrm{d}V + f\mathrm{d}l \quad . \tag{2}$$

Here, p is the pressure, V the volume, f the uniaxial tensile force, and l the sample length.

According to the **second law of thermodynamics**, for a reversible process: $\mathrm{d}Q = T\mathrm{d}S$. This defines the thermodynamic temperature T as the proportionality factor between heat and entropy change. Physically, it expresses that adding heat increases the system's disorder, but less so at higher temperatures (since a given amount of heat produces a smaller entropy increase).

The term $f\mathrm{d}l$ in Equation 2 represents the **mechanical work needed to stretch the polymer network**, i.e. the energy required to collectively extend all chains by $\mathrm{d}l$ against the elastic restoring force.

Substituting Equation 2 into Equation 1 gives the differential form of the Helmholtz free energy:

$$\mathrm{d}A = \mathrm{d}U - \mathrm{d}(TS) = -S\mathrm{dT} - p\mathrm{d}V + f\mathrm{d}l \quad . \tag{3}$$

Thus, A is a thermodynamic state function of T, V, and l, whose total differential is:

$$\mathrm{d}A = \left(\frac{\partial \mathrm{A}}{\partial T}\right)_{V,l}\mathrm{d}T + \left(\frac{\partial \mathrm{A}}{\partial V}\right)_{T,l}\mathrm{d}V + \left(\frac{\partial \mathrm{A}}{\partial l}\right)_{T,V}\mathrm{d}l \quad . \tag{4}$$

Comparison of Equations 3 and 4 identifies the corresponding partial derivatives:

$$\left(\frac{\partial \mathrm{A}}{\partial T}\right)_{V,l} = -S\,, \quad \left(\frac{\partial \mathrm{A}}{\partial V}\right)_{T,l} = -p\,, \quad \left(\frac{\partial \mathrm{A}}{\partial l}\right)_{T,V} = f \quad . \tag{5}$$

For incompressible rubbers (d$V \approx 0$), the volume term can be neglected.

Because **A is state function**, its mixed derivatives commute (i.e. the order of differentiation does not matter):

$$\frac{\partial^2 \mathrm{A}}{\partial T \partial l} = \frac{\partial^2 \mathrm{A}}{\partial l \partial T} \quad \to \quad -\left(\frac{\partial \mathrm{S}}{\partial l}\right)_{T,V} = \left(\frac{\partial f}{\partial T}\right)_{V,l} \quad . \tag{6}$$

This relation links the temperature dependence of the restoring force to the entropy change associated with deformation. Finally, the total force can be written as:

$$f = \left(\frac{\partial \mathrm{A}}{\partial l}\right)_{T,V} = \left(\frac{\partial (U - TS)}{\partial l}\right)_{T,V} = \left(\frac{\partial \mathrm{U}}{\partial l}\right)_{T,V} - T\left(\frac{\partial \mathrm{S}}{\partial l}\right)_{T,V} = \left(\frac{\partial \mathrm{U}}{\partial l}\right)_{T,V} + T\left(\frac{\partial \mathrm{f}}{\partial T}\right)_{V,l} \equiv f_U + f_E \quad . \tag{7}$$

Here, $f_U = (\partial U/\partial l)_{T,V}$ and $f_E = T(\partial f/\partial T)_{V,l}$ are the **energetic** and **entropic** contributions, respectively.

Under typical rubbery conditions (well above T_g), **internal energy changes are negligible, and the entropic term dominates.** Stretching a rubber constrains chain conformations, thereby reducing entropy. **The system resists this loss by generating a restoring force that increases with temperature, a hallmark of entropy-driven elasticity.**

3. Molecular Theory of Rubber Elasticity

To calculate the elastic restoring force, we first determine the entropy of a single ideal chain, then extend this to a network of many such chains. The **affine network model** used in this context assumes:

- the network consists of many subchains between crosslinks.
- each subchain is sufficiently long to behave as a **freely jointed chain** with n bonds of length a. The mean-square end-to-end distance in the unstretched state is $\langle {R_n}^2 \rangle = na^2$.
- the **deformation is affine**: the macroscopic deformation is transmitted directly to each chain's end-to-end vector.
- the network behaves as an **ideal rubber**: internal energy changes during deformation are negligible, so **elasticity is purely entropic.**

Conformational Entropy of a Single Chain

The probability density that a chain has an end-to-end vector of magnitude R_n is given by a three-dimensional Gaussian distribution:

$$P = \left(\frac{3}{2\pi n a^2}\right)^{3/2} \exp\left(-\frac{3{R_n}^2}{2na^2}\right) \quad , \tag{8}$$

This expression gives the **probability per unit volume** in configuration space for finding a chain with end-to-end vector $\vec{R}_n$. Multiplying P by the infinitesimal volume element $\mathrm{d}\tau$ yields the probability that one chain end lies within the small region $\mathrm{d}\tau$ around R_n. This probability is proportional to $P\mathrm{d}\tau$.

The function P has its maximum at $R_n = 0$, corresponding to a randomly coiled chain in which the segment orientations are uncorrelated and the average end-to-end distance vanishes. As R_n increases, the exponential term suppresses P, reflecting that fewer conformations exist that produce a large end-to-end distance. In other words, **the most probable state of a polymer chain is a random coil, while stretched conformations are exponentially less probable**.

According to statistical thermodynamics, entropy is proportional to the logarithm of the number of accessible microstates:

$$S^c = \mathrm{k} \ln \Omega = \mathrm{k} \ln(P\mathrm{d}\tau) = \mathrm{C} + \mathrm{k} \ln P \quad , \tag{9}$$

where k is Boltzmann's constant. Since $\mathrm{d}\tau$ is independent of R_n, it is absorbed into the constant C. Substituting Equation 8 gives:

$$S^c = \mathrm{C} + \mathrm{k}\ln\left[\left(\frac{3}{2\pi n a^2}\right)^{3/2} \exp\left(-\frac{3{R_n}^2}{2na^2}\right)\right] \quad . \tag{10}$$

Grouping all terms that are independent of R_n into a new constant S_0 yields:

$$S^c = \mathrm{S}_0 - \frac{3\mathrm{k}{R_n}^2}{2na^2} \quad , \tag{11}$$

Thus, the **conformational entropy decreases quadratically** with the chain extension R_n. At $R_n = 0$, the chain adopts the most disordered coil configuration with maximal entropy. Stretching the chain (R_n increases) reduces conformational freedom and entropy, which produces a restoring force upon release.

Network Elasticity

For a macroscopic deformation characterized by principal stretch ratios $\lambda_1, \lambda_2, \lambda_3$, each chain's end-to-end vector $\vec{R}_n = (x, y, z)$ is **affinely** deformed and becomes $\vec{R}_n(\lambda) = (\lambda_1 x, \lambda_2 y, \lambda_3 z)$.

The corresponding entropy change is:

$$\Delta S^c = -\frac{3\mathrm{k}}{2na^2}\left[R_n(\lambda)^2 - {R_n}^2\right] = -\frac{3\mathrm{k}}{2na^2}\left[\left({\lambda_1}^2 - 1\right)x^2 + \left({\lambda_2}^2 - 1\right)y^2 + \left({\lambda_3}^2 - 1\right)z^2\right] \quad . \tag{12}$$

Since the internal energy U is assumed constant (purely entropic elasticity), the Helmholtz free energy change per chain is:

$$\Delta A^c = -T\Delta S^c = -\frac{3\mathrm{k}T}{2na^2}\left[\left({\lambda_1}^2 - 1\right)x^2 + \left({\lambda_2}^2 - 1\right)y^2 + \left({\lambda_3}^2 - 1\right)z^2\right] \quad . \tag{13}$$

For a network of N chains (or network strands) per unit volume, the isotropic orientation gives:

$$\langle {R_n}^2 \rangle = \langle {x_n}^2 \rangle + \langle {y_n}^2 \rangle + \langle {z_n}^2 \rangle = na^2 \quad , \tag{14}$$

Here, we average over all chain orientations in the isotropic undeformed state and replace the individual chain coordinates $x^2, y^2, z^2$by their ensemble averages:

$$\langle {x_n}^2 \rangle = \langle {y_n}^2 \rangle = \langle {z_n}^2 \rangle = \frac{na^2}{3} \quad . \tag{15}$$

Substituting Equation 15 into Equation 13 gives the **average free-energy change per chain**:

$$\langle \Delta A^c \rangle = \frac{\mathrm{k}T}{2}\left[\left({\lambda_1}^2 - 1\right) + \left({\lambda_2}^2 - 1\right) + \left({\lambda_3}^2 - 1\right)\right] \quad , \tag{16}$$

and for N chains per unit volume:

$$\Delta A = N\langle \Delta A^c \rangle = \frac{NkT}{2}\left[{\lambda_1}^2 + {\lambda_2}^2 + {\lambda_3}^2 - 3\right] \quad . \tag{17}$$

For **uniaxial deformation** and assuming incompressibility ($\lambda_1\lambda_2\lambda_3 = 1$):

$$\lambda_1 = \lambda\,, \qquad \text{and} \qquad \lambda_2 = \lambda_3 = \frac{1}{\sqrt{\lambda}} \quad . \tag{18}$$

Substituting into Equation 17 yields:

$$\Delta A = N\langle \Delta A^c \rangle = \frac{NkT}{2}\left[\lambda^2 + 2\lambda^{-1} - 3\right] \quad . \tag{19}$$

Stress-Strain Relation and Modulus

The tensile stress follows from differentiation of the free energy with respect to the sample length l (Equation 5). Since $\lambda = l/l_0$, differentiation with respect to l is equivalent to differentiation with respect to λ:

$$\sigma = f = \left(\frac{\partial A}{\partial l}\right)_T = \left(\frac{\partial A}{\partial \lambda}\right)_T = \frac{\partial}{\partial \lambda}\left(\frac{NkT}{2}(\lambda^2 + 2\lambda^{-1} - 3)\right) = NkT(\lambda - \lambda^{-2}) \quad . \tag{20}$$

The stretch factor can be expressed in terms of the **engineering strain** ε

$$\varepsilon = \frac{l - l_0}{l_0} = \frac{l}{l_0} - 1 = \lambda - 1 \quad , \tag{21}$$

which can be inserted into Equation 19 in order to find a **relation between stress and strain**:

$$\sigma = NkT\left(\varepsilon + 1 - \frac{1}{(\varepsilon + 1)^2}\right) = NkT\frac{(\varepsilon + 1)^3 - 1}{(\varepsilon + 1)^2} = NkT\frac{\varepsilon^3 + 3\varepsilon^2 + 3\varepsilon}{(\varepsilon + 1)^2} \quad . \tag{22}$$

For small strains ($\varepsilon \ll 1$), higher-order terms can be neglected, yielding a linear relationship:

$$\sigma \approx 3NkT\varepsilon \quad . \tag{23}$$

Hence, the **Young's modulus** is:

$$E = \frac{\varepsilon}{\sigma} = 3NkT \quad , \tag{24}$$

and, for an incompressible material, the **shear modulus** is:

$$G = \frac{E}{3} = NkT \quad . \tag{25}$$

This result is remarkable:

- the **elastic response of a rubber network arises entirely from entropy changes**, not from internal energy changes.
- **when chains are stretched, the number of accessible conformations decreases**, which reduces entropy.
- **the restoring force is entropic in nature**, driving the system back toward maximal disorder (random coil configurations).
- The **modulus increases linearly with temperature** and with the **network chain density *N***, explaining why rubbers become stiffer when heated and why vulcanization (which increases *N*) enhances elasticity.
- **Microscopic details vanish**: In the Gaussian chain model, the na^2 factor cancels in the free-energy change. As a result, the modulus depends only on the strand density, not on their individual length n or segment size a.

4. Limitations

While powerful at small strains and conceptually elegant, the ideal Gaussian network model has several limitations:

- **Finite extensibility**: The Gaussian assumption breaks down as R_n approaches the contour length na. This can be corrected by the **Langevin function**, which predicts the characteristic stiffening at large extension.
- **High crosslinking density**: when network strands become very short, the Gaussian approximation fails because chain statistics deviate from ideal random walks.
- **Network topology**: the affine network model assumes all strands deform identically with the macroscopic strain. Real networks exhibit non-affine deformations, especially near defects or dangling ends.
- **Energetic contributions**: at large deformations or for stiff chains, changes in internal energy become non-negligible compared to the entropic term.
- **Incompressibility assumption**: valid for most rubbers, but must be relaxed for foams or highly compressible elastomers.