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Rubber elasticity: a scaling approach

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Summary

A scaling analysis of the rubber-like elastic behavior of a cross-linked polymer network is presented which incorporates the two most salient contributions to the free energy of deformation: the chain connectivity of the segments and the restrictions on the chain configurations due to entanglements. The affine deformation of the junction points is assumed and a tube model is used to discuss the deformation dependence of the entanglement constraint parameter.

Introduction

A minimal statistical mechanical model of rubber elasticity must incorporate the two main features of the network chains; the connectivity of the chain segments on a global scale and the topological entanglement constraints on the chain segments on a local scale. The essential physics of these contributions can be determined from a scaling type argument.

The Free Energy of an Entangled Network Chain

A network chain is comprised of N segments and has its ends attached to separated junction points in the network. The first term in the chain free energy is due to the connectivity of the segments and is given in units of k_BT, by the usual Gaussian contribution

$$F_{connectivity} \sim R^2/N \qquad (1)$$

where R is the chain end-to-end separation. We note that eq. 1 is separable into its cartesian components. The ~ notation indicates that there is a nonuniversal constant of proportionality which is neglected.

The second term in the chain free energy arises from the confinement of the chain by other chains in the network (1). This can be modelled using restoring potentials (1-3), various types of tubes (4-10) or obstacle nets. Regardless of the specific model of the entanglement constraint, the resulting free energy term takes a universal scaling form for strong confinement. The length scales involved are the average chain dimension, $\langle \underset{\sim}{R}^2 \rangle_0^{1/2}$, which varies as $N^{1/2}$ in a dense system and the confinement parameter, ξ, which in specific models represents the tube diameter, the obstacle net spacing or the mean segment fluctuation. The main effect of topological constraints is to decrease the effective local degrees of freedom of the chain which results in an extensive free energy change proportional to N. Since the free energy is a function of the dimensionless variable $\langle \underset{\sim}{R}^2 \rangle_0 / \xi^2$ the confinement contribution to the free energy equals

$$F_{\text{topological}} \sim N/\xi^2 \qquad (2)$$

We note that this expression also holds for a chain between close parallel plates and a chain strongly adsorbed on a surface. If the confinement occurs in more than one direction, as in a box, then there will be a term having the form of eq. 2 for each direction of confinement. The ~ notation indicates the neglect of a nonuniversal constant which depends on the details of the confinement model, such as the tube geometry or the restoring potential form.

The free energy of the entangled network chain can be written as the sum of the connectivity and topological constraint contributions

$$F_{\substack{\text{entangled}\\ \text{chain}}} \sim (1/N) \sum_{i=x,y,z} R_i^2 + N \sum_{i=x,y,z} \xi_i^{-2} \qquad (3)$$

where x, y, z are the macroscopic axes of deformation, R_i are the corresponding components of $\underset{\sim}{R}$ and ξ_i is the confinement parameter normal to the ith axis and R_i.

The Network Free Energy of Deformation

The total free energy of the network can be written by multiplying eq. 3 by ν, the number of network chains. The calculation of the mechanical response of the network requires assumptions about the deformation properties of R_i and ξ_i. For a network that is initially isotropic we assume that the chain vector deforms affinely

$$R_i = \lambda_i \cdot R_o \qquad (4)$$

We further assume that under deformation the confinement parameter changes in a 'scaled affine' manner

$$\xi_i = \lambda_i^{\beta} \cdot \xi_o \qquad (5)$$

Eq. 5 is introduced by analogy to eq. 4 and presumes that the local topological constraints remain symmetric about the macroscopic deformation axes.

The network free energy change of deformation is

$$\Delta F_{network} \sim (\nu R_o^2/N) \sum_{i=x,y,z} [\lambda_i^2-1] + (\nu N/\xi_o^2) \sum_{i=x,y,z} [\lambda_i^{-2\beta}-1] \qquad (6)$$

It should be noted that eq. 6 supports the empirically successful Valanis-Landel form, $F(\lambda_x,\lambda_y,\lambda_z) = \sum_{i=x,y,z} f(\lambda_i)$. Furthermore, eq. 6 is a constituitive free energy expression consistent with continuum mechanics arguments (11). We now turn to considering the value of β.

Discussion

Determination of the variation of the confinement parameter with deformation is a delicate matter. The basic difficulty is that ξ depends on the local properties of the chain, which cannot be adequately represented using the Gaussian chain model. For example, if the network chains are treated as purely Gaussian random walks, then by dimensional analysis (12) ξ varies with density as $\xi \sim \rho^{-1}$ and using the analysis in ref. 2, the modulus varies with density as $E \sim \rho^3$. The problem is that a Gaussian chain is volumeless, whereas a real chain has a hard core volume. This basic property should be incorporated into a minimal model of rubber elasticity.

Edwards (1) and deGennes (2) envision a chain in the bulk as being enclosed in a randomly shaped tube, which is depicted schematically in Figure 1. Edwards has shown that if the total space occupied by the tubes surrounding the network chains $\nu \cdot (d^2 \cdot L)$ [L is the chain contour length which is proportional to the tube length and d is the tube diameter] is taken to completely fill the macroscopic volume of the network, then $d \sim \rho^{-1/2}$ and using the analysis in ref. 2, $E \sim \rho^2$, which is physically reasonable. The idea of space filling tubes is especially plausible in a dense system where the confinement scale is not very different from the actual cross-sectional dimension of the chain so that the space filling by the tubes derives from the volume occupied by the

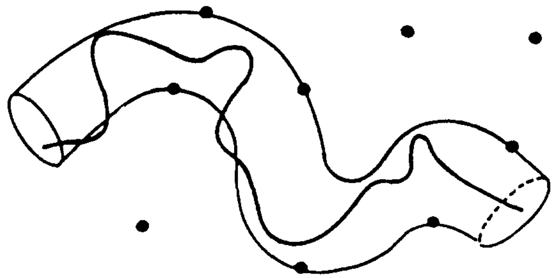

Figure 1. A polymer chain in a random tube.

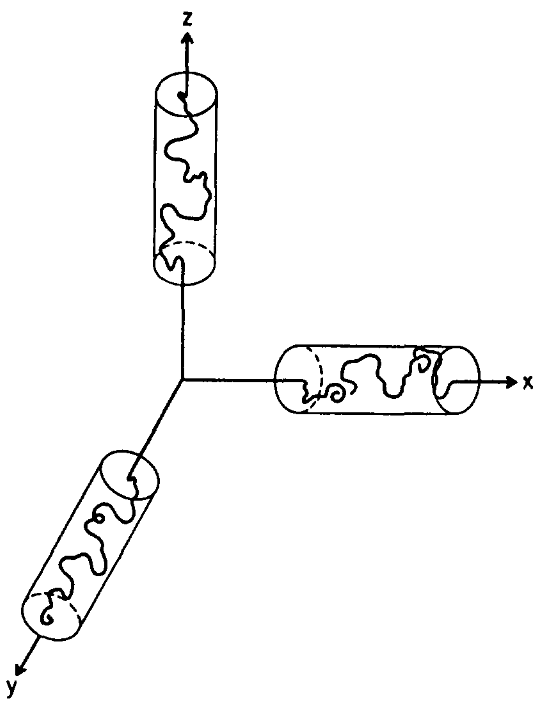

Figure 2. The three-tube model.

physical chains. Using this assumption with ξ equal to d in eq. 6 results in the prediction that the equilibrium modulus depends on both the plateau modulus and the number of network chains.

This heuristic modelling with the random tube picture can also be used to obtain an estimate of β. Imagine decomposing the random tube into sections lying along the axes of deformation. A tube section is specified by a position vector parallel to an axis. One-third of the sections lie along a given deformation axis. In the undeformed state, the tube sections have length L_0 and diameter d_0. The resulting 'three-tube' picture is illustrated in Figure 2, which depicts the main characteristics of the model: connectivity, confinement and cartesian separability. Under deformation, each tube section is taken to deform independently so that the length of a tube section along the ith axis, L_i, deforms affinely. The total lengths of the tubes deform according to the same relation. Furthermore, as the length of a section changes, its diameter, d_i, is assumed to change so as to preserve the confining volume of the tube so that

$$[L_i \cdot d_i^2]/[L_0 \cdot d_0^2] = \lambda_i^{1 + 2\beta} = 1 \qquad (7)$$

It follows that $\beta = -1/2$. The motivation for using the 'constant tube volume' assumption is to model the macroscopic incompressibility of the network and the physical volume of the chains. Figures 3 and 4 show the fit of eq. 6 with $\beta = -1/2$ to experimental data (13,14) which seems quite satisfactory, especially in view of the simplicity of the model.

Other values of β are possible if the constant tube volume requirement is not imposed on the model. As a case in point, the affine tube deformation model corresponding to $\beta = 1$, produces the Mooney-Rivlin equation which has some empirical success (13,14). Since our derivation of eq. 6 is based on scaling arguments, rather than tubes, other confinement models of entangled networks, such as chains on an obstacle array, will also show Mooney-Rivlin behavior if the constraint parameter, such as the obstacle net spacing, is taken to deform affinely. It should be pointed out that the $\beta = 0$ condition which produces the classical phantom chain network result, does not imply the absence of entanglements, but only that the global deformation of the network does not, on average, alter the local environment. There is also a possibility that β is not universal for all network structures.

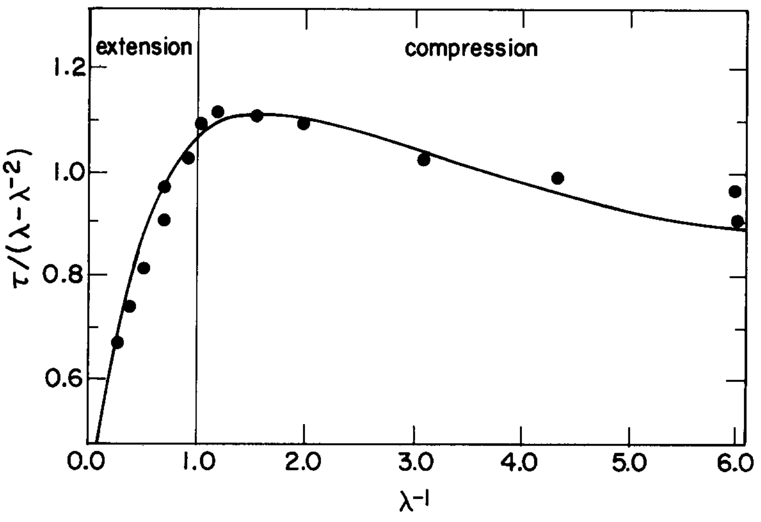

Figure 3. Uniaxial extension-compression deformation. Circles are experimental data and the solid line is calculated using eq. 6 with β = -1/2.

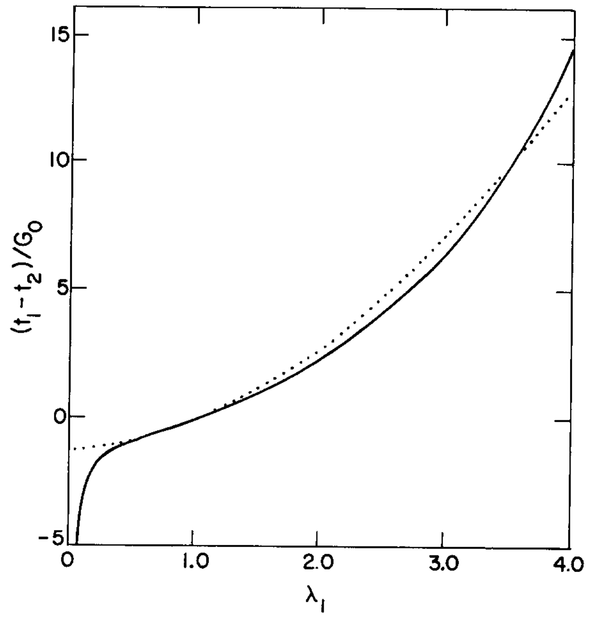

Figure 4. Biaxial extension deformation. The solid line is obtained from experimental data and the dotted line is calculated using eq. 6 with β = -1/2.

In conclusion, we have developed an expression for the free energy of deformation of a cross-linked polymer network using scaling arguments to account for global chain connectivity and local entanglement effects. This expression contains a parameter β indicating the deformation behavior of the topological constraint parameter. The use of a space filling tube model with a constant tube volume deformation condition gives $\beta = -1/2$. It would be very desirable to treat β as an empirical parameter and to determine its value by fitting eq. 6 to data for a variety of network systems, each under several constant volume deformation conditions.

Finally, it should be pointed out that the chain confinement concept has also been implicitly used in reptation and retracing models of the non-equilibrium mechanical response of cross-linked networks (15,16). Two recent reviews of tube concepts in rubber elasticity (17,18) complement our discussion here.

Acknowledgements

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