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The localisation model of rubber elasticity. II

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Summary

The effect of the spatial localization of a network chain by surrounding chains is incorporated into the chain probability distribution function and the network free energy is then calculated using the statistical mechanical formalism for constrained systems. In addition to a term having the classical 'Gaussian' form, the resulting expression contains another term which depends on both the cross-link density of the network and the plateau modulus of the uncross-linked melt.

Introduction

Classical theories of rubber elasticity [see Deam and Edwards (1)] assume the network free energy per unit volume is proportional to the number of effective network chains per unit volume $\bar{v}$,

$$\Delta F_{network} \sim \bar{v} \bullet \Delta F_{chain} \qquad (1)$$

This assumption is consistent with the model of a Gaussian chain network system comprised of non-interacting, volumeless 'phantom' chains. When a network of real interacting chains is considered, eq. 1 can only be used if each network chain sees an effective mean-field arising from its interaction with surrounding chains.

We recently presented a mean-field model of rubber elasticity (2) in which the elastic free energy of an individual network chain was written as the sum of two terms. One term, F_{con}, represented the connectivity of the chain and was obtained from the Gaussian end-to-end vector probability distribution function. The other term, F_{loc}, represented the spatial localization of the chain by surrounding chains and this contribution was estimated using a scaling analysis. Here we incorporate the localization effect into the chain probability distribution function and calculate the network free energy using the Edwards statistical mechanical formalism for systems with constraints (3).

The Free Energy of a Constrained Network Chain

The entropy of deformation of a network chain is given by Edwards (3) as

$$\Delta S_{chain} / k_B = \int G(\underset{\sim}{R}) \ln[G(\{\lambda_i\},\underset{\sim}{R})/G(\underset{\sim}{R})]d\underset{\sim}{R} \qquad (2)$$

where $G(\underset{\sim}{R})$ is the end-to-end vector distribution function of the constrained network chain and λ_i is the macroscopic deformation ratio in the ith direction.

In the classical theory of rubber elasticity, $G(\underset{\sim}{R})$ is the Gaussian end-to-end vector distribution function

$$G(\underset{\sim}{R}, <\underset{\sim}{R}^2>_0) = \prod_{i=x,y,z} G(R_i , <\underset{\sim}{R}^2>_0) \qquad (3)$$

where

$$G(R_i , <\underset{\sim}{R}^2>_0) = (3/2\pi <\underset{\sim}{R}^2>_0)^{1/2} \exp\{-3R_i^2/ 2 <\underset{\sim}{R}^2>_0\} \qquad (4)$$

R_i is the component of the end-to-end vector $\underset{\sim}{R}$ along the ith macroscopic deformation axis and $<\underset{\sim}{R}^2>_0$ is the unperturbed mean square value of $\underset{\sim}{R}$. Using eqs. 3 and 4 in eq. 1 and assuming the affine deformation of the vector components, $R_i \rightarrow \lambda_i R_i$, Edwards (3) obtained the classical connectivity (or 'Gaussian') contribution to the network free energy, as well as a logarithmic term. The log term makes no contribution to a constant volume deformation which is the case we are considering here.

A primitive model which emphasizes that a network chain is "hemmed in" by surrounding chains and which neglects the network structure is based on an analysis of a polymer confined to a central harmonic potential. The free energy of a strongly-confined chain is rather insensitive to the precise details of the confining potential (8) and we can write

$$G(\underset{\sim}{R} , <\underset{\sim}{R}^2>_o , \{\xi_{oi}\}) = \prod_{i=x,y,z} G(R_i , <\underset{\sim}{R}^2>_o , \xi_{oi}) \qquad (5a)$$

$$G(R_i , <\underset{\sim}{R}^2>_o , \xi_{oi}) \sim (3/2\pi \xi_{oi}^2)^{1/2} \exp(-3R_i / 2 \xi_{oi}^2) \exp(-b <\underset{\sim}{R}^2>_o /\xi_{oi}^2) \qquad (5b)$$

The length scale ξ_{oi} defines the range over which the chain is "localized" by a central harmonic potential along the ith macroscopic deformation coordinate R_i. $G(\underset{\sim}{R})$ factors into a product of $G(R_i)$ in eq. 5a as a consequence of the separability of the harmonic potential.

The $G(R_i)$ simplify to the asymptotic form in eq. 5b in the limit $\xi_{oi}^2 << \langle \underset{\sim}{R}^2 \rangle_o$, corresponding to the network chain being strongly "hemmed in" by surrounding chains.

A more sophisticated model than the one above would incorporate both chain connectivity <u>and</u> chain localization effects. Edwards (3) introduced a mean-field model of a polymer network chain subject to a harmonic potential along the chain contour. This "random tube" model can be analyzed in stages.

We first consider a polymer in a straight "tube" defined by a harmonic pseudo-potential in the "tube coordinates" $\{L_i\}$ normal to the tube axis coordinate Z. The end-to-end distribution function $G(Z, \{L_i\}, \langle \underset{\sim}{R}^2 \rangle_o, \xi_{oi})$ for a chain strongly confined along the Z axis, $(\xi_{oi} << \langle \underset{\sim}{R}^2 \rangle_o)$, equals

$$G(Z , \{L_i\}, \langle \underset{\sim}{R}^2 \rangle_o , \xi_{oi}) = G_{\|}(Z , \langle \underset{\sim}{R}^2 \rangle_o) \bullet G_{\perp}(\{L_i\}, \langle \underset{\sim}{R}^2 \rangle_o , \xi_{oi}) \tag{6a}$$

$$G_{\|}(Z, \langle \underset{\sim}{R}^2 \rangle_o) = (3/2\,\pi \langle \underset{\sim}{R}^2 \rangle_o)^{1/2} \exp(-3Z^2/\,2 \langle \underset{\sim}{R}^2 \rangle_o) \tag{6b}$$

$$G_{\perp}(\{L_i\}, \langle \underset{\sim}{R}^2 \rangle_o , \xi_{oi}) \sim \prod_{i=x,y,z} (3/2\,\pi\, \xi_{oi}^2)^{1/2} \exp(-3\, L_i^2/\xi_{oi}) \exp(-b \langle \underset{\sim}{R}^2 \rangle_o/\xi_{oi}^2) \tag{6c}$$

The random tube model can now be constructed by viewing the random tube as consisting of various straight tube sections lying along the macroscopic deformation axes. G_r for the random tube is then approximated as a product of connectivity and confinement contributions

$$G_r(R_i , L_i , \langle \underset{\sim}{R}^2 \rangle_o , \xi_{oi}) \approx G_{con}(R_i , \langle \underset{\sim}{R}^2 \rangle_o)\, G_{loc}(L_i , \langle \underset{\sim}{R}^2 \rangle_o , \xi_{oi}) \tag{7a}$$

$$G_{con}(R_i , \langle \underset{\sim}{R}^2 \rangle_o) = \prod_{i=x,y,z} (3/2\,\pi \langle \underset{\sim}{R}^2 \rangle_o)^{1/2} \exp(-3\, R_i^2/\,2 \langle \underset{\sim}{R}^2 \rangle_o) \tag{7b}$$

$$G_{loc}(L_i , \langle \underset{\sim}{R}^2 \rangle_o , \xi_{oi}) \sim \prod_{i=x,y,z} (3/2\,\pi\, \xi_{oi}^2)^{1/2} \exp(-3\, L_i^2/\,2\, \xi_{oi}^2) \exp(-b \langle \underset{\sim}{R}^2 \rangle_o/\xi_{oi}^2) \tag{7c}$$

The connectivity contribution G_{con} in eq. 7b equals $G(\underset{\sim}{R}, \langle \underset{\sim}{R}^2 \rangle_o)$ in eq. 3 so that G_r reduces to the classical theory in the absence of localization interactions. When the localization effect dominates we have $G_r \approx G_{loc}$ which has the form of eq. 5. Upon straightening the random tube eq. 7 reduces to eq. 6.

The free energy of deformation of a network chain can be calculated using eq. 7 once the deformation dependences of R_i, L_i and ξ_i are specified.

The variation of R_i is taken to be affine $R_i \rightarrow \lambda_i R_{oi}$, as in the classical theory. This seems reasonable since the dimensions of the junction separation, R_i, should be large on *average* (3). The "tube coordinates" L_i are not fixed by network cross-linking and are thus unaffected by deformation. However, the extent of localization ξ_i as measured in the local coordinates L_i may change with deformation. It might be assumed that the ξ_i vary in an affine manner which would yield a reduced stress expression having the infamous Mooney-Rivlin form (2). However, the strong confinement of the network chain implies that the dimensions of ξ_{oi}^2 are small compared to $<\underset{\sim}{R}^2>_o$ so that the affine assumption is not particularly reasonable. A determination of the variation of ξ_i with deformation can be made by recalling that the precise nature of the potential in the strong confinement limit is not important and so we can replace the harmonic potential by an infinite wall potential. This is equivalent to confining the chain in a "tube" of radius ξ. We have argued (2) that the volume of this tube should approximate the hard-core volume of the chain. In this case, since the physical volume of the chain does not change with deformation, the 'localization' volume $R_i \bullet \xi_i^2$ should also remain unchanged. Since R_i transforms affinely, it follows (2) that
$\xi_i \rightarrow \lambda_i^{-1/2} \xi_o$.

The Network Free Energy

For a constant volume deformation we combine eqs. 1, 2 and 7 and we integrate over both the chain coordinates R_i and the tube coordinates L_i to obtain

$$\Delta F(\{\lambda_i\})_{\text{network}} = (G_v/2) \sum_{i=x,y,z} (\lambda_i^2 - 1) + G_{loc} \sum_{i=x,y,z} (\lambda_i - 1) \tag{8a}$$

where

$$G_v \cong \bar{v}\, k_B T/2 \cong \rho RT/M_c \tag{8b}$$

$$G_{loc} = \gamma\, G_v + G_N \tag{8c}$$

$$G_N = \bar{v} <R^2>_o\ k_B T/\xi_o^2 \propto \rho^2\, k_B T \tag{8d}$$

γ is an unspecified constant. In obtaining the expression for G_N, we have used the relationship $\xi_o \sim \rho^{-1/2}$ where ρ is the density, based on the volume filling argument of Edwards (3) [see also (2)]. This argument is consistent with our localization volume analysis. G_N can be identified with the plateau modulus of the uncross-linked melt (2). We note that since $\xi^2{}_0$ is identified with the hard-core cross-sectional area of the polymer chain, it is expected that G_N will vary inversely with the cross-sectional area of the chain.

Result

The general functional form of the network free energy of deformation in eq. 8 is unchanged from our previous scaling analysis (2). However, the contribution of the localization portion of the network free energy now depends on the cross-link density of the network as well as on the plateau modulus of the uncross-linked melt.

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