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Origins of Entanglement Effects in Rubber Elasticity†

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ABSTRACT: The effects of entanglements on a network chain with fixed ends are modeled as hoops through which the chain must pass. This model differs from the tube models which allow no "chain leakage" from the tube and from the slip-link models which do not conserve monomer along the chain. The strain-dependent portion of the free energy as the chain ends are displaced is shown to arise from three factors: the entropy of the strained unentangled subchains spanning the hoops, the distortion of the hoops with strain, and the narrowing of the distribution of segments required to reach a hoop with increasing extension ratio. An analytical expression for the free energy of the chain can be derived that takes the $M - 1$ hoops per chain to be of infinitesimal diameter thereby neglecting this second factor. The resulting free energy for a network of these chains is of the form

$$A = (\xi/2)[M\sum_1^3 \lambda_i^2 + (M-1)\ln \sum_1^3 \lambda_i^2]$$

where ξ is the cycle rank of the network and λ_i is the extension ratio along the ith axis.

The early theories of rubber elasticity due to Flory[1] and James and Guth[2] allowed network chains to pass through each other freely and gave expressions for the force in response to a uniaxial deformation of the form

$$f \sim (\lambda - 1/\lambda_2) \quad (1)$$

where λ is the extension ratio. However, it is well-known[3] that the reduced force

$$[f^*] = f/(\lambda - 1/\lambda^2) \quad (2)$$

is not independent of the uniaxial extension ratio. Recent molecular theories have attributed this effect to the conservation of network topology via entanglements but have modeled the entanglements in several different ways. The constrained junction theories of Floy and Erman[4,5] and Ronca and Allegra[6] assume that the major effect of entanglements is to modify the strain dependence of the network junction fluctuations. The tube models of Gaylord[7] and Marrucci[8] assume that the network chains are confined to virtual tubes by the entanglements. Finally, the theories of Edwards and co-workers[9,10] model the entanglements by slip-links that preserve network topology. In the present model, entanglements acting on a single polymer chain are envisioned simply as hoops through which the chain must pass. This view is not as restrictive as confining the chain to a tube and, as shown later, differs from the slip-link model in that it does not consider subchains connecting sliplinks to be individual entities each with a prescribed length distribution.

Theory

A simple version of this model is shown in Figure 1 where the chain endpoints are located at (0,0,0) and (0,0,z) and the $M - 1$ hoops are equally spaced squares perpendicular to and centered about the z axis. The partition function for the chain can be expressed as

$$Q = \int_0^N dn_1 \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dy_1 \, F(x_1)F(y_1)G(x_1-x_0,y_1-y_0,H,n_1) \int_0^{N-n_1} dn_2 \int_{-\infty}^{\infty} dx_2 \int_{-\infty}^{\infty} dy_2 \, F(x_2)F(y_2)G(x_2-x_1,y_2-y_1,H,n_2) \ldots \quad (3)$$

where $G(x,y,H,n)$ is the probability that a subchain connecting two entanglements (hoops) and starting at the origin will end at (x,y,H) in n segments. The partition function is an M-fold convolution in the chain-length variable which results from the fact that each of the subchains requires n_i segments to reach the next hoop and $\sum_1^M n_i$ must equal N, the total number of segments of length l on the chain. If the chain statistics are assumed to be Gaussian, then G is given by

$$G = (3/2\pi n l^2)^{3/2} \exp[-3(x^2 + y^2 + H^2)/2nl^2] \quad (4)$$

$F(x)$ defines the size of the hoop along the x axis and may be, for example, a repulsive hard core or a harmonic potential. For the case of a hard core potential, $F(x) = 1$ for $-a \le x \le a$ and 0 elsewhere for a square hoop of width $2a$.

Mathematically, the simplest function for $F(x)$ is the Dirac δ function, $\delta(x)$, for which the hoop diameter vanishes. Using this, the spatial integrations are easily evaluated and the partition function can be evaluated by Laplace transformation of the convolution in N and subsequent inversion. The resulting expression for the partition function is in this case

$$Q = \frac{K(M,l,N)}{H^{M-1}} \exp(-3M^2H^2/2Nl^2) \quad (5)$$

where K is a function independent of the extension ratio. If we make the assumption that the position of an entanglement (hoop) deforms affinely when the chain end is moved from z to λz, then $H = \lambda H_0$. Using the formula f

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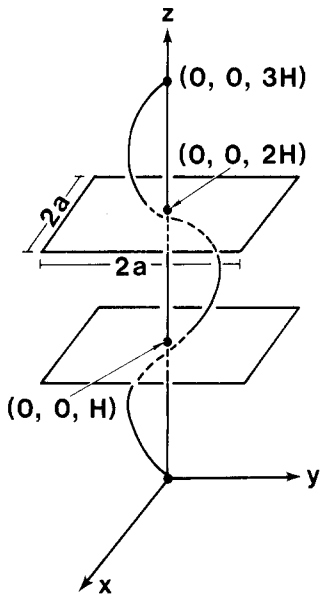

Figure 1. Simple view of an entangled network chain. The entanglements are modeled as $M - 1$ hoops (therefore, M subchains) perpendicular to and centered about the z axis through which the chain must pass. Here, $M = 3$.

$= -\partial \ln Q/\partial\lambda$ for the force on the chain in uniaxial extension and noticing that $MH_0 = R_0$ (the end-to-end distance), we can obtain the following expression

$$f = 3(R_0^2/\langle R_0^2\rangle)\lambda + (M-1)/\lambda \tag{6}$$

where $\langle R_0^2\rangle = Nl^2$.

The above derivation can be made more general to account for arbitrary placement of the δ-function hoops. The resulting expression for the strain-dependent portion of the partition function is

$$\ln Q = \ln (\sum_1^M t_i) - \sum_1^M \ln t_i - (3/2Nl^2)(\sum_1^M t_i)^2 \tag{7}$$

where $t_i = (\lambda_1^2 H_{1i}^2 + \lambda_2^2 H_{2i}^2 + \lambda_3^2 H_{3i}^2)^{1/2}$ and H_{ki} is the displacement of the ith entanglement from the $(i-1)$th entanglement along the kth axis in the unstrained state. We have again assumed that the entanglements and chain ends deform affinely with strain. If we also assume that $H_{ki}^2 = H_{1i}^2$ for all k (a preaveraging assumption), then the strain-dependent portion of the chain free energy for arbitrary deformation is

$$A = \frac{1}{2}\frac{L_0^2}{\langle R_0^2\rangle}(\sum_1^3 \lambda_i^2) + \frac{M-1}{2}\ln(\sum_1^3 \lambda_i^2) \tag{8}$$

where $L_0 = \sum_1^M (3H_{1i}^2)^{1/2}$ is the contour length of the random walk of steps connecting entanglements in the unstrained state.

To calculate the free energy of a network of ν entangled chains, we integrate over the Gaussian distribution of unstrained end-to-end vectors (which is here equivalent to assuming a Gaussian distribution for H_{1i} with $\langle H_{1i}^2\rangle = Nl^2/3M$) which results in

$$A = \nu\left[\frac{M}{2}\sum_1^3 \lambda_i^2 + \frac{M-1}{2}\ln\sum_1^3 \lambda_i^2\right] \tag{9}$$

where $\langle L_0^2\rangle = M\langle R_0^2\rangle$. We have assumed here, as in the tube models, that the network junctions deform affinely with the strain which is exact only at large M. In addition, not all network chains are elastically effective. Both of these effects are accounted for in networks composed of chains which can freely pass through each other by simply replacing ν by ξ, the cycle rank.[11] The constrained junction theories, on the other hand, assume that the junction fluctuations are suppressed by entanglements in a strain-dependent manner and this simple substitution is not sufficient. A thorough consideration of junction fluctuations in the present model is difficult. By simple replacement of ν with ξ, as done in the slip-link models, in eq 9 and differentiation with respect to λ, the force of the entangled network in response to a uniaxial deformation is found to be

$$f = \xi\left[M(\lambda - 1/\lambda^2) + (M-1)\frac{(\lambda - 1/\lambda^2)}{(\lambda^2 + 2/\lambda)}\right] \tag{10}$$

In the above, M should be linearly dependent on N/N_e where N_e is the average entanglement molecular weight of the network chains.

In order to understand the physical origins of the terms in eq 9, it is useful to return to the version of this model shown in Figure 1 and calculate the partition function exactly for $M = 2$ by using eq 3. If we examine a uniaxial deformation and assume that the hoop dimensions deform affinely (i.e., $a^2 = a_0^2/\lambda$), the partition function is given by

$$Q = \int_0^1 ds \frac{\exp(-3\lambda^2 H_0^2/2gNl^2)}{g^{1/2}}[\text{erf}\,(3a_0^2/2g\lambda Nl^2)^{1/2}]^2 \tag{11}$$

where $g(s) = s(1-s)$. The force can be found by using the expression $f = -Q^{-1}\partial Q/\partial\lambda$ and inverting the order of integration and differentiating which result in

$$f = 3(H_0^2/Nl^2)\lambda\langle g^{-1}\rangle + (6a_0/\pi\lambda^3 Nl^2)^{1/2}\langle (g^{1/2}\,\text{erf}\,K\,\exp K^2)^{-1}\rangle \tag{12}$$

where the quantities in brackets depend on λ and represent

$$\langle u^{-1}\rangle = Q^{-1}\int_0^1 ds\,\frac{1}{u}\frac{\exp(-3\lambda^2 H_0^2/2gNl^2)}{g^{1/2}}[\text{erf}\,(3a_0^2/2g\lambda Nl^2)^{1/2}]^2 \tag{13}$$

with u either g or $g^{1/2}$ erf K exp K^2 and $K = (3a_0/2g\lambda Nl^2)^{1/2}$. Note that the second term in eq 12 vanishes as a_0 vanishes (i.e., as the hoop diameter becomes infinitesimal). We will discuss the physical origin of these terms in the following section.

Discussion

The physical origin of the first term in eq 9 is due to the entropy of the unentangled subchains connecting entanglements. Therefore, the primary effect of a hoop is to act as an additional cross-link. The origin of the second term arising from the entanglements is more subtle and describes the deviation from viewing the hoops as simply cross-links. It does not have the same origin as the corresponding term in the tube models of Gaylord[7] and Marrucci.[8] The free energy of the chain confined to a tube undergoing uniaxial deformation is given, for example,[8] by

$$A = \frac{1}{2}\frac{R_0^2}{\langle R_0^2\rangle}\sum_1^3 \lambda_i + \frac{N}{3^{1/2}N_e}(\sum_1^3 \lambda_i^2)^{1/2} = T1 + T2 \tag{14}$$

and the second term, $T2$, is due to the fact that the tube deforms as the network is strained. In the derivation of eq 9, the hoops have been taken to be of infinitesimal diameter independent of extension ratio. We can see, however, in eq 12 that the present model does produce a term (the second term in eq 12 that corresponds to $T2$ of the tube models if the hoops are taken to be of finite width.

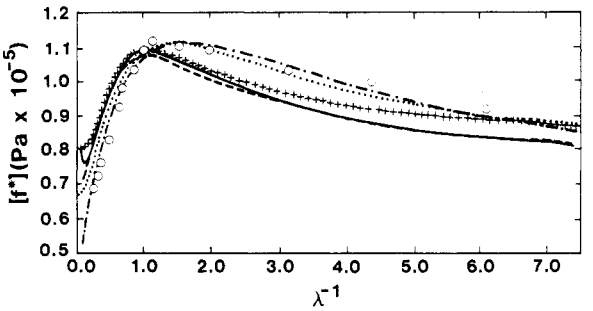

Figure 2. Reduced force versus inverse uniaxial extension ratio:[13] (O) experimental data;[12] (- - -) Marrucci tube model;[8] (—) Ball et al. slip-link model;[9] (-·-) Gaylord tube model;[7] (···) Flory constrained junction theory;[4] (+) the present model with $\xi = 0.104 \times 10^5$ and $M = 8$.

Unfortunately, the evaluation of this term for arbitrary placement of $M - 1$ hoops is difficult.

The origin of the second term in eq 9 is instead due to the fact that the distribution of segments required to reach a hoop narrows as the extension ratio increases thus reducing the number of configurations available as λ increases. This is more closely related to the slip-link models.[9,10] Although interpretation of the physical origin of the corresponding term in the original slip-link paper of Ball et al.[9] is difficult due to the replica formalism and approximations required to solve the problem, a later investigation by Edwards and Vilgis[10] does present an approximate derivation of the replica formalism results which is shown to be equivalent to order $(\lambda_i - 1)^2$. Here, the distribution of segments between slip-links is prescribed in the problem statement; that is, the number of segments required for a subchain to reach a slip-link is uniformly distributed between $n - a$ and $n + a$ where n is the average number of segments required to reach a slip-link. This introduces a slippage parameter, η, that is related to a. In addition, the slip-link procedure cannot obey the conservation law $\sum n_i = N$ since the entropy of each subchain spanning slip-links is considered individually. The resulting free energy of the network is given by

$$A = \frac{N_c}{2}\sum_1^3 \lambda_i^2 + \frac{N_s}{2}\sum_1^3 \left[\frac{\lambda_i^2(1+\eta)}{1+\eta\lambda_i^2} + \ln\,(1+\eta\lambda_i^2) \right] \quad (15)$$

where N_c is the number of cross-links and N_s is the number of slip-links. In the present model, the distribution of segments between hoops is exact due to the problem formulation and monomers along a chain are conserved. This influences the calculations as seen in that eq 9 and 15 are not equivalent.

We now compare the uniaxial force calculated by eq 10 to the uniaxial extension–compression data of Pak and Flory[12] on well-entangled PDMS networks. These data were chosen since Gottlieb and Gaylord[13] have previously used them to compare the predictions of tube, slip-link, and constrained junction theories. Figure 2 plots the reduced experimental force against inverse uniaxial extension ratio as well as the predictions by the Gaylord and Marrucci tube models, Ball et al. slip-link model, Flory constrained junction theory, and the present model. As we can see, the present model results in agreement with experimental data comparable to that obtained by the marrucci and slip-link models; that is, the theory underestimates the reduced force for $\lambda < 1$ and overestimates it for $\lambda > 1$. In addition, the experimental data seem to peak at approximately $\lambda \approx 1.2$ whereas the present theory predicts a maximum at $\lambda = 1$, as do the Marrucci and slip-link theories.

Conclusions

We have shown that the entanglements, modeled as hoops through which a polymer chain must pass, affect the free energy in two ways. First, a term that softens with increasing uniaxial extension arises from the deformation of the hoops with strain. The evaluation of this term is difficult in the present formalism for arbitrary hoop placement whereas the tube models can derive a term of this type much more easily. The second effect of entanglements in the hoop model results from the narrowing of the distribution of segments required for a subchain to reach a hoop as the strain increases. As stated previously, this effect is absent in the tube models but is accounted for in an approximate fashion in the slip-link models which seems to neglect the conservation of monomers along a chain. The present model accounts for this effect exactly and, therefore, results in a different expression for the elastic free energy.

The comparison of the predictions of eq 10 and experimental data meets with the same moderate level of success as do the Marrucci tube[8] and slip-link[9] models. The constrained junction theory[4] and the Gaylord tube model[7] seem to fit the experimental data well. Perhaps what this tells us is that either it is necessary to account for the deformation of the hoops with strain or to account more accurately for the nonaffine deformation of network junctions. The latter seems formidable for an infinite network but may be feasible for micronetwork calculations.

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