# Comparison of the Constrained Junction and the Slip-Link Models of Rubber Elasticity

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*Received May 5, 1993*

## Introduction

The classical theories of rubber elasticity are based on the hypothetical phantom-like chain which may pass freely through its neighbors and itself. In a real chain, the volume of a segment is excluded to other segments belonging either to the same chain or to others in the network. Consequently, the uncrossability of chain contours by those occupying the same volume becomes an important factor. Departures from phantom-like behavior due to entanglements are introduced in several recent models of rubber elasticity. Among these, the constrained junction (CJ) model[1-3] and the slip-link (SL) model[4,5] have shown remarkable success in describing the behavior of networks in the presence of entanglements.[6-10]

In the CJ model, intermolecular correlations are assumed to suppress the fluctuations of junctions. The extension of this model to involve constraints suppressing the fluctuations of chain mass centers rather than the junctions did not introduce substantial differences to the original description.[11,12] In the SL model, the constraining action is of topological nature and the entanglements restrict the chain along the entire contour, which yields an additional contribution to the elastic free energy. Application of the entanglements to junctions in one model and to the chain contour in the other has led to serious disagreement among various workers in interpreting experimental data on amorphous networks. The source of this disagreement may be traced back to the definition of an entanglement. According to the constrained junction model, the excess elastic free energy due to entanglements is proportional to the number of *covalent junctions*. According to the slip-link model, the excess elastic free energy is proportional to the number of *slip-links* operating along the chain contour. This number may be substantially larger than the number of covalent junctions. Obviously, the resolution of this controversial issue is beyond the capabilities of any analytical model, and one should seek help either from careful experiments on well-defined networks or from extensive numerical simulations. At present, neither of the two seems to supply the solution.

A closer examination of the two models shows, however, significant similarities as to their mathematical structure and especially as to the definition of the constraint parameters. In the present Note, we compare the elastic free energies of the two models and interpret the similarities and differences of the two models. The basic result will be that both models contain similar physics although they look very different from their starting point of view and their treatment of the topological constraints.

## The Elastic Free Energies

The elastic free energy, $\Delta A_{el}$, for both the CJ and SL models is assumed to be of the following additive form:

$$\Delta A_{el} = \Delta A_{ph} + \Delta A_c \tag{1}$$

where $\Delta A_{ph}$ is the elastic free energy of the phantom network and $\Delta A_c$ is that of the entanglements. This is indeed a convenient assumption in most of the models developed in rubber elasticity as can be seen later. In the context of the slip-link model this is very similar, since the slip-links and the cross-links can be treated as independent parameters in the beginning although a simple relationship between both can be established.[13] The elastic free energy of the pure cross-link contribution is given as

$$\Delta A_{el} = \frac{1}{2}\xi kT\sum_t(\lambda_t^2 - 1) \tag{2}$$

Here, $\xi$ is the cycle rank of the network, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\lambda_t$ is the extension ratio along the $t$th principal coordinate direction.

**(i) Contribution of Entanglements in the CJ Model.** $\Delta A_c$ is given by the CJ model as

$$\Delta A_c = \frac{1}{2}\mu kT\sum_t[B_t + D_t - \ln(B_t + 1) - \ln(D_t + 1)] \tag{3}$$

where $\mu$ is the number of covalent junctions and

$$B_t = \kappa^2(\lambda_t^2 - 1)(\lambda_t^2 + \kappa)^{-2} \tag{4}$$

$$D_t = \lambda_t^2\kappa^{-1}B_t \tag{5}$$

Here, $\kappa$ is the constraint parameter, defined as

$$\kappa = \langle(\Delta R)^2\rangle_{ph}/\langle(\Delta s)^2\rangle_0 \tag{6}$$

The numerator on the right-hand side of eq 6 is the mean square fluctuation of a junction in a phantom network. The denominator is the mean square fluctuation of a junction from the center of constraints to which it is assumed to be elastically attached. The value of $\kappa$ determines the shape of the stress–strain relation. In the case of a phantom network, no constraints operate on the junction, and $\langle(\Delta s)^2\rangle_0$ is very large (infinity) and $\kappa$ becomes zero. In the affine model limit, the fluctuations of junctions are frozen and $\langle(\Delta s)^2\rangle_0$ equates to zero, leading to an infinitely large $\kappa$. The parameter $\kappa$, which represents a measure of entanglements of chains with their surroundings in the real network, is assumed[14] to be proportional to the number of junctions in the volume occupied by a given chain; i.e.,

$$\kappa = I\langle r^2\rangle_0^{3/2}(\mu/V^\circ) \tag{7}$$

where $I$ is the constant of proportionality, $V^\circ$ is the reference volume. For tetrafunctional junctions, eq 7 may be written as[14]

$$\kappa = I(N_A d/2)^{3/2}(\langle r^2\rangle_0/M)^{3/2}(\xi/V^\circ)^{-1/2} \tag{8}$$

The important term in eq 3 is the sum $B_t + D_t$. Substituting from eqs 4 and 5 leads to the explicit form of this sum as

$$B_t + D_t = \kappa\frac{\lambda_t^2 - 1}{\lambda_t^2 + \kappa} \tag{9}$$

The logarithmic terms in eq 3 lead to rather complicated expressions when written explicitly in terms of extension

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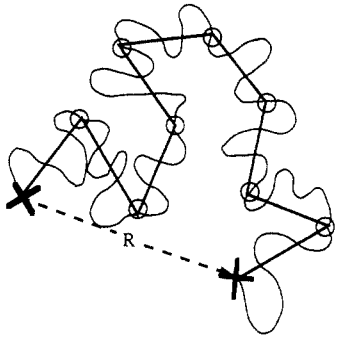


**Figure 1.** Chain contour (light curve) and primitive path (solid line) for a network chain between two covalent junctions which are placed at the end and the beginning of the chain. The dashed line shows the instantaneous chain vector **R**. The circles on the contour represent the slip-links or entanglements.

ratios. For small deformations, they are approximated as

$$-\ln(B_t + 1) - \ln(D_t + 1) = \ln\left(\frac{\lambda_t^2 + \kappa}{1 + \kappa}\right) - \ln \lambda_t^2 \quad (10)$$

Adopting the small-deformation approximation for the logarithmic terms, for the sake of simplicity, and substituting eqs 9 and 10 into eq 3 leads to the excess elastic free energy for the unconstrained junction model as

$$\Delta A_c = \frac{1}{2}\mu kT \sum_t \left[ \kappa \frac{\lambda_t^2 - 1}{\lambda_t^2 + \kappa} + \ln\left(\frac{\lambda_t^2 + \kappa}{1 + \kappa}\right) - \ln \lambda_t^2 \right] \quad (11)$$

**(ii) Contribution of Entanglements in the SL Model.** The contribution due to the topological constraints in the SL model for small deformation is given by

$$\Delta A_c = \frac{1}{2} N_s kT \sum_{i=1}^{3} \left( \frac{\lambda_i^2 - 1}{1 + \eta\lambda_i^2} + \ln \frac{1 + \eta\lambda_i^2}{1 + \eta} \right) \quad (12)$$

where $N_s$ is the number of slip-links in the system and $\eta$ is the slippage parameter which is proportional to the distance which a slip-link may slide along the chain contour. The most rigorous derivation of eq 12 has been given in the replica formulation[4] but has been alternatively derived by a simple intuitive argument.[5] The parameter $\eta$ determines the form of the stress–strain relation. Its physical meaning is obvious from the simple model given in ref 5: It is a measure for the amount of sliding of a typical entanglement between two consecutive cross-links. Consecutive cross-links mean in this context two cross-links which are topological neighbors in contrast to spatial neighbors. A more detailed consideration of the difference between topological and spatial neighbors is needed to sort out further differences in the models considered here. Such work is in progress but is beyond the scope of this paper. Here only the functional form of the free energy is important.

A rough estimate of the distance of slippage of entanglements between two topological cross-links is that one entanglement can slide between two others. Such an assumption is not unrealistic, since each slip-link is a topological barrier for another one, if both are neighbors on the same mesh. Using the standard model of the primitive path which can be viewed as the center of the tube felt by any polymer in a dense environment, shown by the broken line in Figure 1, we can define the slippage parameter in the following way: The primitive path is a random walk with a larger step length than the polymer itself; nevertheless both are random walks with the same end-to-end distance; i.e., $Nl^2 = N_{pp}\mathbf{a}^2$, where $\mathbf{a}$ is the step length of the primitive path, or equivalently the tube diameter, or the mean distance between entanglements and $N_{pp}$ is the number of entanglements between two consecutive cross-links. $N$ is the degree of polymerization, and $l$ is the Kuhn length. It is defined roughly by the mean distance of the entanglements between two topological consecutive cross-links. The actual polymer path is much larger than the primitive path. Note that the polymer is localized around the primitive path. This localization picture can be used to model the primitive path which is the center of the tube. The tube can now be conveniently modeled by a harmonic potential where the strength of the potential is the inverse of the square of the characteristic localization length. This harmonic well parameter turns out to be of the order of the radius of gyration for unconstrained or unentangled systems, whereas it is of the order of the primitive path length for entangled systems. This is consistent with the fact that the tube diameter is of the order of the step length of the primitive path.[7] Therefore the tube diameter in networks has a range from $R_g$ of the mesh down to the tube diameter $\mathbf{a}$. The first is the case if no entanglements (topological restrictions) between the mesh are present, whereas the latter corresponds to a cross-linked melt where the mesh size is larger than the entanglement distance. The effective Hamiltonian for the entangled network polymer is thus given by

$$H = \int_0^N ds \left(\frac{\partial R}{\partial s}\right)^2 + q_0^2 \int_0^N ds\, R^2(s) \quad (13)$$

where $s$ is a dimensionless contour variable and $q_0$ is the localization parameter with values ranging from the inverse of the tube diameter to the radius of gyration itself. The localization parameter has the physical meaning of the inverse square accessible length scale for the segment. This picture is oversimplified in the sense that the calculation of the effective tube diameter in networks compared to the melt at the same density and chain length is an outstanding problem and the tube diameter of the corresponding melt is used. Inclusion of such effects will not change the general result of the paper, since they will be of higher order. Here we do not aim for this calculation, but we show now the formal equivalence of the CJ and SL models.

Now the question arises as to how the effective slippage parameter can be expressed as a function of the molecular parameters, i.e. to solve the question what is the amount, measured in terms of molecular-scale quantities, which a typical entanglement is able to slide. The intuitive assumption leads to the statement that it is of the order of the mean square step length of the primitive path, i.e., the tube diameter $\mathbf{a}^2$. Therefore a measure for the slippage parameter is given by the number of Kuhn segments, $n$, between two entanglements, i.e.

$$n = (\mathbf{a}/l)^2 \quad (14)$$

If this is related to the total chain length, $N$, the slippage parameter can be expressed as $\eta = n/N$, or in more accessible quantities

$$\eta = \mathbf{a}^2/R_g^2 \quad (15)$$

At this point the relation between the CJ and the SL models becomes obvious. The slippage parameter compares the localization, i.e., the ratio of fluctuations in the constrained system to those in the unconstrained system. Therefore it is similar to the definition of $\kappa$; it is just the inverse, since $\mathbf{a}^2 \propto \langle \Delta s^2 \rangle_0$ is the fluctuation in the constrained system and $R_g^2$ is the fluctuation in the unconstrained

system. The latter point has been shown by Deam and Edwards,[15] whereas the first has been treated in refs 16 and 17.

Thus, for infinitely strong constraints the slip-link cannot slide along the contour and $\eta = 0$; i.e., every slip-link acts as a cross-link. For the phantom-like chain, the slip-link is free to slide along the contour and $\eta = \infty$ for very long chains. Thus $\eta$ varies inversely with $\kappa$, and one may write down the important relation

$$\eta = 1/\kappa \tag{16}$$

Substitution of eq 16 into eq 12 immediately leads to eq 11, which is the elastic free energy for the constrained junction model, apart from a term which vanishes at constant volume deformations.

## Conclusion

The fundamental parameter common to both the CJ and SL models of rubber elasticity is the ratio of fluctuations in the unconstrained system to those in the constrained system. In the CJ model this ratio is the $\kappa$ parameter. In the SL model this is the inverse of the slippage parameter, $\eta^{-1}$. With this identification it is now established that the dependence of the Helmholtz free energy on deformation is the same for both models as seen from a comparison of eqs 11 and 12. It is to be noted, however, that the proportionality coefficients in these expressions, i.e., $\mu$ in eq 11 and $N_s$ in eq 12, may be substantially different. This difference affects the values of the elastic free energies and the moduli obtained from them, but not their dependence on deformation.

**Acknowledgment.** B.E. gratefully acknowledges support for his stay at the Max-Planck-Institut für Polymerforschung in the summer of 1992 during which this work was initiated.

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