An application of linking probability to topological effects of polymer systems : rubber elasticity

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Abstract : We offer an application of linking probability, which is defined by the probability that two random polygons are entangled each other, to the problem of the nonlinear behavior in rubber elasticity. By taking account of topological constraint that the topological state of the network does not vary under deformation, we prove that the total entropy of the network is decomposed into two terms: the entropy of the classical theory and that due to the topological constraint. We show that the linking probability is naturally introduced in the entropy due to the topological constraint and the entropic force derived from the topological entropy behaves like the C_2 term of the Mooney-Rivlin equation.

本論文では，２本の環状ランダム鎖が絡み合う確率（絡み目確率）をゴム弾性の非線形効果の問題に用いた例を示す。ネットワークのトポロジーが変形によって変化しないというトポロジー制限を考慮に入れると，ゴムのエントロピーは古典論で導かれる項とトポロジー制限による項の２項に分解される。このトポロジー制限から導かれた２項目には絡み目確率が自然と導入されており，Moony-Rivlin 則の C_2 項と同じ様な振る舞いをする。

1 Introduction

The entanglements of polymer chains cause several non-trivial effects in many polymer systems. Although the entanglements are a matter of great importance, it is very difficult to take those into account accurately. One of elegant methods to treat the entanglements will use the topology developed in the knot theory. We expect that the topologies of closed random walks, random polygons, may help us in understanding many aspects of the entanglements. Thus, the linking and knotting probabilities for the random polygons, which are defined as probabilities that two random polygons are mutually entangled and one random polygon is entangled by itself, have been numerically estimated [1],[2]. From the behaviors of these probabilities, we can imagine how the random walks make complicated entanglements as increasing the step number N of the polygon and how the entanglements are dissolved by the excluded volume effect.

Unfortunately, the linking and knotting probabilities can not be directly introduced into most linear polymer systems even if the chains are apparently entangled. From the topological point of view, every linear chain is always equivalent to a line. Therefore, we need to connect both ends of the linear chains artificially to calculate the topological invariants. It is not, however, easy to develop such skillful manners.

In this paper, we offer an example that the linking probability is applied to a polymer system, network (rubber). For most actual rubbers, the relation between tensile force (f) and extension ratio (λ) can be expressed by the following Mooney-Rivlin (MR) equation

$$f(\lambda) = C_1\left(\lambda - \frac{1}{\lambda^2}\right) + C_2\left(1 - \frac{1}{\lambda^3}\right). \tag{1}$$

Here, the first term, C_1 term, is explained by the classical rubber theory [3]. On the other hand, the cause of the second term, C_2 term, is not trivial. One of the major ideas is that the entanglements between the polymers seem to generate some complicated effects, which lead to the C_2 term since the value of C_2 decreases as the rubber swells in the solvent. Although a lot of

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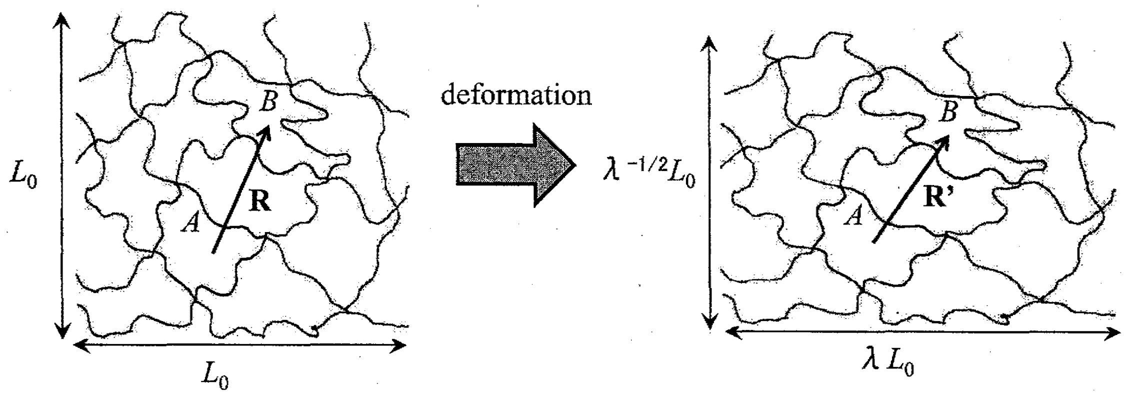

Figure 1: Illustration of topological structure of network supposed in our theory.

theories have been proposed, they are insufficient to explain all behaviors on the MR relations without supposing any fitting parameter. The most important problem is that the physical substance of the C_2 term has been ambiguously understood.

We show that the C_2 term can be definitely derived from topological constraint for a network, which is a condition that the topological structure of the network is unchanged from an initial one under the deformation (see Fig. 1). Our theory is based on the classical work of Graessley and Peason [4] in many aspects. The basic picture on the origin of the C_2 term is, however, completely different. Although they discussed the nonlinear behavior of the rubber elasticity in terms of the entanglements of the chains in the network, the results disagree with the proper behaviors of the rubber elasticity. By considering not the entanglements but the topological constraint, we demonstrate that an additional terms appears in the entropy of the rubber and it behaves like the C_2 term.

2 Topological force in rubber elasticity

For the simplicity, we shall consider the entropy of a network with a simple mesh-like structure consisting of elementary loops without any entanglement. Let us focus on a pair of loops in the network, A and B, as shown in Fig.1. The conditional probability $\Omega_{A,B}(R)$ that the two loops are disentangled and separated by a distance $R(\equiv |\mathbf{R}|)$ is given by

$$\Omega_{A,B}(R) = \int\int \Delta_{L=0}(A,B)\delta(R - |\mathbf{R}_A - \mathbf{R}_B|)\mathcal{D}(A)\mathcal{D}(B). \tag{2}$$

where $\mathbf{R}_A$ and $\mathcal{D}(A)$ denote the position of the center of mass and the path integral with the Wiener measure for the loop A, respectively. The topological invariant $\Delta_{L=0}(A,B)$ is 1 if the loop pair of A and B is topologically equivalent to the trivial link $L = 0$.

Neglecting boundary effects, we may estimate that the total entropy of the network is given by the summation of eq. (2) for every pair of the loops in the network,

$$S_{net} = \frac{1}{2}\xi K_B \int_V \rho(\mathbf{R}) \ln \Omega_{A,B}(R) d\mathbf{R} \tag{3}$$

where ξ and V are the number of loops and the volume of the network, respectively. The pair correlation function $\rho(\mathbf{R})$ is the density of the loops at a distance $\mathbf{R}$.

It is easily proved that eq. (3) is decomposed into two terms: the entropy of the classical theories and that due to the topological constraint:

$$S_{net} = S_{clas.} + S_{topo.} + const. \tag{4}$$

where $S_{clas.}$ and $S_{topo.}$ are given by

$$S_{clas.} = \frac{1}{2}\xi K_B \int_V \rho(\mathbf{R}) \ln \Gamma(R) d\mathbf{R}, \tag{5}$$

$$\Gamma(R) \equiv \frac{\int\int \delta(R - |\mathbf{R}_A - \mathbf{R}_B|)\mathcal{D}(A)\mathcal{D}(B)}{\int\int \mathcal{D}(A)\mathcal{D}(B)} \tag{6}$$

and

$$S_{topo.} = \frac{1}{2}\xi K_B \int_V \rho(\mathbf{R}) \ln P_{L=0}(R) d\mathbf{R}, \tag{7}$$

$$P_{L=0}(R) \equiv \frac{\int\int \Delta_{L=0}(A,B)\delta(R - |\mathbf{R}_A - \mathbf{R}_B|)\mathcal{D}(A)\mathcal{D}(B)}{\int\int \delta(R - |\mathbf{R}_A - \mathbf{R}_B|)\mathcal{D}(A)\mathcal{D}(B)}. \tag{8}$$

By comparing with the classical theory, we find that C_1 is given by $C_1 = \xi K_B$.

We should note that eq. (8) is equivalent to unlinking probability $P_{L=0}(R)$ that the rings A and B are disentangled at the distance R. The relation of the linking probability P_{link} and the unlinking probability $P_{L=0}$ is given by $P_{link} = 1 - P_{L=0}$.

For the present, we concentrate our attention on the term of $S_{topo.}$ derived from the topological constraint. We assume that after deformation arbitrary vector $\mathbf{R}$ in the network and corresponding $\rho(\mathbf{R})$ change into $\mathbf{R}'$ and $\rho'(\mathbf{R}')$, respectively. Supposing that the change in $\mathbf{R}$ is proportional to the macroscopic deformation of the network, so-called affine deformation, the distance R is related with R' by

$$R' = \left\{ \left(\lambda^2 - \frac{1}{\lambda}\right) \cos^2\theta + \frac{1}{\lambda} \right\}^{1/2} R \quad \equiv \alpha(\theta, \lambda) R \tag{9}$$

where θ is the angle between the directions of the extension and $\mathbf{R}$. By the conservation condition of the number of the loops, $\rho(\mathbf{R})d\mathbf{R} = \rho'(\mathbf{R}')d\mathbf{R}'$, the topological entropy after deformation by λ becomes

$$S_{topo.} = \frac{1}{2}\xi K_B \int_V \rho(\mathbf{R}) \ln\left(1 - P_{link}(\alpha R)\right) d\mathbf{R}. \tag{10}$$

Then, the topological force $f_{topo.}$ is calculated by the following formula

$$f_{topo.}(\lambda) = -T\frac{\partial S_{topo.}}{L_0 \partial \lambda} \tag{11}$$

where L_0 is the initial length of the rubber. Of course $f_{topo.}$ satisfies $f_{topo.}(\lambda = 1) = 0$.

Substituting eq. (9) and eq. (10) into eq. (11) we obtain

$$f_{topo.}(\lambda) = \frac{\xi K_B T}{L_0}\pi R_g^3 \int_0^\infty \varsigma^3 \rho(\mathbf{R}) \int_0^\pi \frac{P'_{L=0}(\alpha\varsigma)}{P_{L=0}(\alpha\varsigma)} \frac{d\alpha}{d\lambda} \sin\theta d\theta d\varsigma \tag{12}$$

where R_g is the radius of gyration for the random polygon and ς is the reduced distance $\varsigma = R/R_g$. Actually, it is convenient to divide $f_{topo.}$ by C_1 in order to omit the unknown prefactor $\xi K_B T/L_0$.

Provided that the network is homogeneous and the loops are uniformly distributed, the function of $\rho(\mathbf{R})$ will be well represented by the simplest Gaussian approximation

$$\rho(R) = \frac{\xi}{V} \cdot \left(\frac{3}{2\pi R_g^2}\right)^{3/2} \exp\left(-\frac{3}{2}\frac{R^2}{R_g^2}\right). \tag{13}$$

Note that $\rho(R)$ is normalized as $\int_V 4\pi R^2 \rho(R) dR = \xi - 1$.

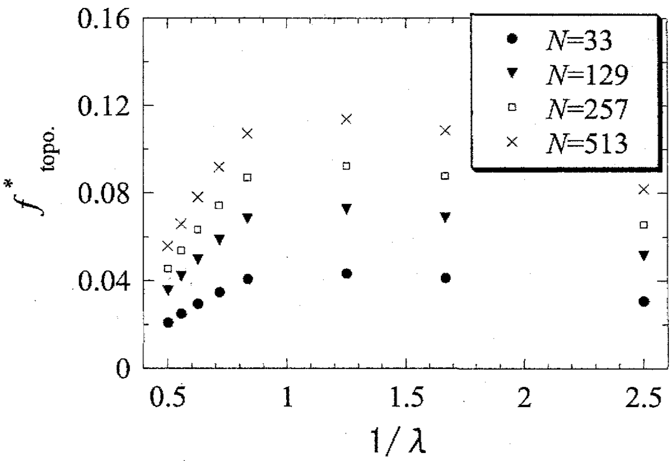

Figure 2: Mooney-Rivlin plots of reduced topological forces $f^*_{topo.}$ for N=33,129,257 and 513.

Fig. 2 shows the Mooney-Rivlin plots of the reduced topological forces $f^*_{topo.} = f_{topo.}/C_1 * (\lambda - \lambda^{-2})$ for several polygon lengths. Here we used numerical data of the linking probability given in Ref. [2]. This results agree with the experimental observations of the C_2 term that the reduced elastic force increases linearly in the region of the extension, $1/\lambda < 1$, and gradually decreases in the region of compression,$1/\lambda > 1$ [3].

3 Summary

In this paper, we have discussed the nonlinear behavior of the rubber elasticity from the topological point of view. It should be emphasized that the C_2 term of the Mooney-Rivlin equation is derived without any adjustable fitting parameter as a consequence of the topological constraint. We have already investigated the N-dependence of $C_2/C1$ and the excluded volume effect, which correspond to experiments Ref. [5] and Ref. [6]. Our results are almost consistent with the experiments although the values of the C_2/C_1 are a little smaller. From all our results, we conclude that the topological constraint of network will offer a key to solve the problem of the rubber elasticity.

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