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A theory of topological constraints in polymer networks

G. Heinrich and E. Straube[1]*

Technische Hochschule „Carl Schorlemmer" Leuna-Merseburg, Sektion Physik and Sektion Werkstoff- und Verarbeitungstechnik[1], DDR-4200 Merseburg, German Democratic Republic

Summary

This paper presents an investigation of the dependence of harmonic-like topological constraints in entangled and moderately crosslinked polymer networks on segment and crosslink density and on the deformation of the sample. The approach is an extension of a theory developed for the highly crosslinked case and for polymer melts. The results are used to discuss the influence of topological constraints on the mechanical properties of different types of rubberelastic networks.

Introduction

The model of the harmonic constraining potential is one of the physically clearest and most successfull models for the simulation of topological constraints in entangled polymer systems. It was suggested by Edwards (1) in one of his first works on bulk polymers and is widely used in the physics of polymer melts and networks.

The distribution function of a configuration $\underline{r}(s)$ of a continuous chain with the contour length L and the statistical segment length l is described by

$$p(\underline{r}(s)|\hat{\underline{r}}(s)) = N \exp\left(- \frac{3}{2l} \int_0^L (d\underline{r}(s)/ds)^2 \, ds - \sum_{j=x,y,z} w_j^2 \cdot \int_0^L (r_j(s) - \hat{r}_j(s))^2 \, ds \right) \quad (1)$$

N is the normalization factor and s the chain arc length. The chains are confined to the neighbourhood of the mean configuration, i.e. to the tube axis $\hat{\underline{r}}(s)$. The strength of the potential and therewith the mean square deviation of a segment from the tube axis,

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* To whom offprint requests should be sent

$$d_j^{\,2} = \langle (r_j(s) - \hat{r}_j(s))^2 \rangle = l^{1/2}\, w_j^{-1} \quad , \qquad (2)$$

is controlled by the parameters w_j. A number of approaches, mostly phenomenological, for the determination of the dependence of w_j on segment-, chain- or crosslink density and on the deformation of the sample exist (cf. e.g. Ref. 2). In two previous papers a statistical-mechanical approach to the calculation of the w_j was developed. The simplest case, the constraints in a highly crosslinked network, was investigated in Ref. 3. The opposite limiting case, the constraints in a melt of lineary chains, was considered in Ref. 4. Following the ideas of these approaches, the more complicated problem of the constraining potential of a moderately crosslinked network is the aim of this paper.

Theory

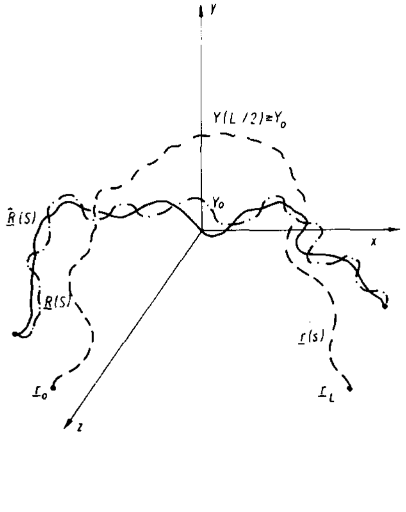
The model is illustrated in Fig. 1. We consider the increase

$$\Delta F(Y_0 | \hat{\underline{r}}_i(s), \underline{r}_{i,0}, \underline{r}_{i,L})$$

of the free energy of the i-th constraining chain with the mean configuration $\hat{\underline{r}}_i(s)$ and end-points at $\underline{r}_{i,0}$ and $\underline{r}_{i,L}$ in dependence on the displacement Y_0 of a segment of the constrained chain from the mean position. The constraining potential is then given by the contributions of all constraining chains:

$$\Delta F(Y_0) = \iiint d^3\underline{r}_{i,0}\, d^3\underline{r}_{i,L}\; D(\hat{\underline{r}}_i(s))\; p^+(\hat{\underline{r}}_i(s), \underline{r}_{i,0}, \underline{r}_{i,L}) \cdot$$

$$\cdot\, \Delta F(Y_0 | \hat{\underline{r}}_i(s), \underline{r}_{i,0}, \underline{r}_{i,L}) \qquad (3)$$



<u>Figure 1</u>

Entanglement model.

R(s) : actual configuration of the constrained chain,
$\hat{R}$(s) : mean configuration of the constrained chain,
r(s) : actual configuration of a constraining chain.

$p^+(\hat{\underline{r}}_i(s),\underline{r}_{i,0},\underline{r}_{i,L})$ is the probability density for the occurence of the corresponding entangled configuration of the chains. Moderately crosslinked networks are characterized by the fact that $\Delta F(Y_0)$ is influenced both by the constraints caused by the network junctions and by the topological constraints acting on the constraining chains. Consequently, the calculations are more complicated than in the limiting cases (3,4) but the ideas of these approaches are still applicable.

(a) The distribution functions of the actual configurations of all chains are described by Eq. (1).

(b) The distribution function of the mean configurations obeys the random walk behaviour

$$p(\hat{\underline{r}}(s)) = \hat{N} \exp\left(- \frac{3}{2l} \int_0^L ds \, (d\hat{\underline{r}}(s)/ds)^2 \right) \tag{4}$$

(c) The restrictions imposed on the configurations of the constraining chains which are caused by the constrained chain under consideration are approximately taken into account by restrictions imposed on the positions of one representative segment at the mid-point L/2 of the constraining chain, i.e.

$$p^+ \longrightarrow p^+(\hat{\underline{r}}_{i,L/2},\underline{r}_{i,0},\underline{r}_{i,L}) = \int D(\hat{\underline{r}}(s)) \; p(\hat{\underline{r}}(s)) \cdot \delta(\hat{\underline{r}}(0) - \underline{r}_{i,0}) \; \delta(\hat{\underline{r}}(L) - \underline{r}_{i,L}) \; \delta(\hat{\underline{r}}(L/2) - \hat{\underline{r}}_{i,L/2}) \tag{5}$$

(δ - Dirac's delta-function).

(d) The changes of the statistical weight ΔW and of the free energy ΔF of the i-th constraining chain with end-points at $\underline{r}_{i,0}$ and $\underline{r}_{i,L}$ and the mean configuration $\hat{r}_i(s)$ are then given by

$$\Delta W(Y_0|\hat{\underline{r}}_i(s),\underline{r}_{i,0},\underline{r}_{i,L}) = \int_{y_a}^{y_b} dy' \int D(\underline{r}_i(s)) \; p(\underline{r}_i(s)|\hat{\underline{r}}_i(s)) \cdot p(\hat{\underline{r}}_i(s)) \; \delta(\underline{r}_i(0) - \underline{r}_{i,0}) \; \delta(\underline{r}_i(L) - \underline{r}_{i,L}) \cdot \delta(y_i(L/2) - y') \; \delta(x_i'(L/2)) \; \delta(z_i'(L/2)) \tag{6}$$

with

$$\left.\begin{array}{l} y_a = Y_o \\ y_b = \infty \end{array}\right\} \qquad \qquad \left.\begin{array}{l} > 0 \end{array}\right.$$

$$\text{for } \hat{y}_i(L/2) \left\{ \begin{array}{l} \\ \\ \end{array} \right.$$

$$\left.\begin{array}{l} y_a = -\infty \\ y_b = Y_o \end{array}\right\} \qquad \qquad < 0$$

and $\Delta F(Y_o|\hat{\underline{r}}_i(s),\underline{r}_{i,0},\underline{r}_{i,L}) = -kT \ln \Delta W(Y_o|\hat{\underline{r}}_i(s),\underline{r}_{i,0},\underline{r}_{i,L})$.
Carrying out the integrations in Eq. (6) we obtain the expression (7) for the contribution ΔF to the constraining potential. The constraining potential is assumed to be caused by a pair of molecules with mirror-symmetric configurations.

$$\Delta F(Y_o|\hat{\underline{r}}_i(s),\underline{r}_{i,0},\underline{r}_{i,L}) = kT\, 4\,\pi^{-1/2} A^{3/2} K(\hat{y}_i(s),y_{i,0},y_{i,L}) \cdot \exp(-AK^2)\, Y_o^{\,2} \tag{7}$$

with

$$A = \frac{6G}{lL} \coth G \quad , \quad G \equiv \frac{1}{\sqrt{6}} \frac{lL}{d_o^{\,2}} \quad ,$$

$$K(\hat{y}_i(s),y_{i,0},y_{i,L}) = K_1 + K_2 \quad ,$$

$$K_1 = \frac{1}{2} (\cosh G)^{-1} (y_{i,0} + y_{i,L}) \quad , \tag{8}$$

$$K_2 = \frac{G}{L} (\cosh G)^{-1} \int_0^{L/2} (\hat{y}_i(u) + \hat{y}_i(L-u)) \cdot \sinh(2Gu/L)\, du$$

Using the fact that the largest contribution to the integral in the expression for K_2 comes from the vicinity of $u = L/2$, $\hat{y}_i(u)$ and $\hat{y}_i(L-u)$ are replaced by $\hat{y}_i(L/2)$. With p^+ approximated by Eq. (5), the averaging over the configurations $\hat{\underline{r}}_i(s)$ in Eq. (3) reduces then to an integration over $\hat{y}_i(L/2)$. The contribution of a pair of chains with fixed endpoints is then given by the following expression:

$$\Delta F(Y_0|\underline{r}_{i,0},\underline{r}_{i,L}) \approx kT\, 4\pi^{-1/2} A^{3/2} \frac{y_{i,0}+y_{i,L}}{2\cdot B^{1/2}\cosh G}\cdot$$

$$\cdot \exp\left(-\frac{3}{2lL}\varphi(G)\cdot(y_{i,0}+y_{i,L})^2\right)\cdot$$

$$\cdot\left[\frac{1+\Phi\left(\sqrt{\frac{3}{2lL}}\cdot\xi(G)\cdot(y_{i,0}+y_{i,L})\right)}{1+\Phi\left(\sqrt{\frac{3}{2lL}}\cdot(y_{i,0}+y_{i,L})\right)}\right]\cdot$$

$$\cdot\Bigg\{1+2\,(\cosh G-1)\cdot\xi(G)\cdot$$

$$\cdot\Big[1+\pi^{-1/2}\left(\sqrt{\frac{6}{lL}}(y_{i,0}+y_{i,L})\cdot\xi(G)\cdot\right.$$

$$\left.\cdot\left(1+\Phi\left(\sqrt{\frac{3}{2lL}}\,\xi(G)\,(y_{i,0}+y_{i,L})\right)\right)\right)^{-1}\Big]\Bigg\} \qquad (9)$$

with

$$B(G) = 1+\frac{G}{\sinh G}\frac{(\cosh G-1)^2}{\cosh G},$$

$$\xi(G) = \frac{1}{\sqrt{B(G)}}\left(1-\frac{G}{\sinh G}\cdot\frac{\cosh G-1}{\cosh G}\right), \qquad (10)$$

$$\varphi(G) = 1+\frac{G}{\cosh G\cdot\sinh G} - \xi^2(G)$$

Φ is the error function. As in References 3,4, the constraining potential in the deformed state can be obtained by introducing the displacement of the endpoints of a network chain and of the tube axis according to a microscopic deformation tensor $\underline{\underline{\lambda}}_{mic}$.

The limiting case of the unconstraint constraining chains (3) follows from Eq. (9) by setting $G = 0$. For large Flory-numbers $N_F \gg 1$, the case of strong constraints $G \gg 1$ has to be investigated. Then, the functions $\varphi(G)$ and $\xi(G)$ can be replaced by their asymptotic values 1 and 0, respectively. The ensemble averaging over the junction positions can be performed analytically setting the ratio

$$(1+\Phi(\,..\,\xi\,..))/(1+\Phi(...))$$

in Eq. (9) approximately constant. Adopting the method for the consideration of the influence of the fast relaxation process on the constraining potential introduced in Ref. 4 we obtain for the change of the free energy of the constraining chains per segment of the constraint chain ($G \gg 1$)

$$\frac{\Delta F(Y_o,(\lambda_y)_{mic})}{l} = kT\,\frac{n_s\,l}{L}\,((\lambda_y)_{mic})^{-1}\cdot G((\lambda_y)_{mic})\cdot Y_o^2$$

$$\stackrel{!}{=} \frac{1}{d_y^{\;4}}\cdot Y_o^{\;2} \tag{11}$$

n_s is the number density of statistical segments. An analytical self-consistent solution of Eq. (11) yields the generalized result

$$d_j = d_o\;(\lambda_j)^{1/2}_{mic} \quad , \qquad j = x,y,z \quad ,$$

$$d_o/l = K'\;(n_s l^3)^{-1/2} \tag{12}$$

with the numerical prefactor K' of the order one.

Discussion

The theory presented above has to be viewed as a mean--field approach to the problem of topological constraints in rubberelastic networks. This approach can be considered as most useful and best justified in the case of a large defree of coil interpenetration. In such systems strong topological constraints can be expected. The theoretical results obtained here are valid in the limiting case of dominating topological constraints in comparison to the constraints caused by the crosslinks. In this case the deformation dependence of d_j and the dependence on the chain length density are the same as in a melt (4).
Equation (12) is the basis for a theoretical treatment of the stress-strain properties of rubberlike networks. This equation is most successful in the case of networks made by crosslinking of long primary chains (2). There, the chain deformation nearly follows the macroscopic deformation, $\lambda_{mic} \simeq \lambda$. The discussion of the stress-strain properties of swollen networks (2) has suggested that with increasing swelling degree constraint release processes become important. These processes can be described by setting (2)

$$\lambda_{mic} = \lambda^b \quad , \quad b < 1 \quad .$$

It should be noted that networks prepared by endlinking of chains and treated in literature mostly within the concept of trapped entanglements (5,6), can be described by Eq. (12), too. But now the constraints have to be considered as caused by a relatively small number of entanglements which are unable to relax. Consequently, the deformation dependence of d_j does not follow Eq. (12). A simple entanglement model already proposed in Ref. 7, yielding $d_j \sim \lambda_j^{-1}$, reproduces the typical results of the concept of trapped entanglements for crosslink- and topological contributions to the stress-strain properties (2).

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