Polymer Bulletin 3, 399–406 (1980)

Polymer Bulletin

Statistical-Mechanical Theory of the Deformation Dependence of Topological Constraints in Polymer Networks

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Presented at the 7th Discussion Conference IUPAC "Polymer Networks", Karlovy Vary, CSSR, September 15-19, 1980

Summary

This paper describes a simple model of topological constraints on polymer network chains. In the frame of this model we calculate the deformation dependence of the constraining potential used in a theory of stress-strain behaviour previously.

Introduction

An extension of ideas of EDWARDS /1/ concerning topological constraints leads to a statistical-mechanical theory /2,3/ of randomly crosslinked polymer networks which yields an equation for the stress in simple tension in the form

$$\sigma = 2C_1(\lambda - \lambda^{-2}) + 2C_2^*(\lambda^{b/2-1} - \lambda^{-(b+1)}) \quad (1)$$

with

$$2C_1 = \frac{kTM}{V} \quad \text{and} \quad 2C_2^* = \frac{kTN}{V} 6^{-1/2} b \langle R^2\rangle/\rho_o^2 \quad (2)$$

The C_2 - term describes the departure from phantom network behaviour and results from effects of topological constraints, simulated by a harmonic (EDWARDS-) constraining potential /1/. M is the number of crosslinks in the volume V of the sample and N the number of primary chains in the uncrosslinked polymer from which the vulcanisate is formed. $\langle R^2\rangle = lL$ (l - statistical segment length; L - contour length) is the mean-square end-to-end distance of the primary chains, and ρ_o denotes the mean-square fluctuations of the statistical chain segment after crosslinking. k and T have their usual significance. The parameter b describes the deformation dependence of the mean fluctuations. It has been introduced /2,3/ by the relation

$$\rho_\mu = \lambda_\mu^{b/2} \rho_o \quad (\mu = x,y,z).$$

0170-0839/80/0003/0399/$01.60

In the case b = 2 the theory yields a Mooney-Rivlin equation /2/. For crosslinking points per primary chain $M/N \gtrsim 1$ one gets a ratio of the Mooney-Rivlin-parameters C_2/C_1 in the order of unity if $\rho_0^2 \simeq 1L$, i.e. mean-square fluctuations in the order of mean dimension of a single macromolecule. Such great values of ρ_0 are in disagreement with calculations made by DOI /4/ for dense polymer systems ($\rho_0^2 \ll 1L$). It was shown that the case $b < 2$ which describes a weaker deformation dependence than the affine ansatz, solves the contradictory /3/.

From a phenomenological point of view TSCHOEGL /5/ proposed a constitutive two-term elastic potential from which eq. (1) could be deduced. the first term is the neo-Hookean potential predicted by the phantom network theory of a "perfect network". The second accounts for contributions arising from "equivalent pseudo-crosslinks" modelling the topological constraints (entanglements) in real rubbers. Reasonable experimental agreement with eq. (1) has been achieved by setting b = -0.5 /5/.

The aim of this paper is to outline statistical mechanical considerations for explaining the value b = -0.5 and at last to express ρ_0 by chain parameters and polymer density.

Theory

For simulating the topological constraints of the network chains we present a simple model of an infinite chain hindered by neighbouring chains with endpoints fixed in the gel (crosslinking points). A part of the infinite chain in the mean configuration $\underset{\sim}{R}(s)$ (s - chain arc length) is approximated by a straight line which we identify with the x-axis of a co-ordinate system (Fig. 1). Further we assume that only such chains are topological active which have endpoints at $\underset{\sim}{r}_{oi}$ and $\underset{\sim}{r}_{Li}$ in one half-space $y \gtrless 0$ and any segment s_i in the xy-plane at $y_i \lesssim 0$ ("entanglement effects") or $y_i \gtrsim 0$ ("packing effects"). i denotes the chain number. The contribution of the constraining chains to the constraining potential for a segment of the considered chain is supposed to be caused by the differences of their entropy in dependence of configuration $\underset{\sim}{R}(s)$ of the constrained chain. For simplicity we characterize $\underset{\sim}{R}(s)$ by the position of the constrained segment $Y(s) = Y_o$.

For a flexible continuous Gaussian chain as a chain model the probability of finding a segment s of a chain with endpoints fixed at $\underset{\sim}{r}_o$ and $\underset{\sim}{r}_L$ in the xy-plane at $y = y$ and $-1/2 \leq x \leq 1/2$ is

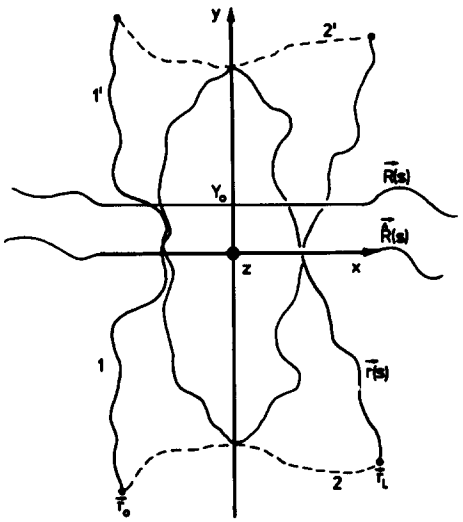

Figure 1:
A model for simulating topological constraints.

$$p(y'|\underset{\sim}{r}_o,\underset{\sim}{r}_L) = \int_{-1/2}^{1/2} dz' \int_{-1/2}^{1/2} dx' p(\underset{\sim}{r}';\underset{\sim}{r}_o;s') \; p(\underset{\sim}{r}_L,\underset{\sim}{r}';L-s'). \quad (3)$$

$$p(\underset{\sim}{r}',\underset{\sim}{r}'';s'-s'') = (3/2\pi l|s'-s''|)^{3/2} \exp(-(3/2l|s'-s''|) (\underset{\sim}{r}'-\underset{\sim}{r}'')^2) \quad (4)$$

is the distribution function of chain segment distances. For simplicity we replace the x' and z' integrations by

$$l^2 \int_{-\infty}^{+\infty}\int \ldots \; \delta(x') \, \delta(z') \, dx' \, dz'$$

and obtain the result

$$p(y'|\underset{\sim}{r}_o,\underset{\sim}{r}_L) = l^2(3/2\pi ls')^{3/2}(3/2\pi l(L-s'))^{3/2} \exp(-(3/2l(L-s')) (x_L^2+(y'-y_L)^2+z_L^2)) \exp(-(3/2ls') (x_o^2+(y'-y_o)^2+z_o^2)) \; . \quad (5)$$

For the sum of the free energy of the constraining chain with endpoints at $\underset{\sim}{r}_{oi}$, $\underset{\sim}{r}_{Li}$ and $-\underset{\sim}{r}_{oi}$, $-\underset{\sim}{r}_{Li}$ (the corresponding symmetric situation) caused by a displacement of the constrained segment from Y(s)=0 to Y(s)=Y_o we obtain

$$\Delta F_i(Y_o|\underset{\sim}{r}_{oi},\underset{\sim}{r}_{Li}) = -T\Delta S_i(Y_o|\underset{\sim}{r}_{oi},\underset{\sim}{r}_{Li}) \qquad (6)$$

with the entropy

$$\Delta S_i(Y_o|\underset{\sim}{r}_{oi},\underset{\sim}{r}_{Li}) = S_i(Y_o|\underset{\sim}{r}_{oi},\underset{\sim}{r}_{Li}) + S_i(-Y_o|\underset{\sim}{r}_{oi},\underset{\sim}{r}_{Li}) - 2\, S_i(0|\underset{\sim}{r}_{oi},\underset{\sim}{r}_{Li}) \quad . \qquad (7)$$

$S(Y_o|\underset{\sim}{r}_o,\underset{\sim}{r}_L)$ follows from the statistical weight $G(Y_o|\underset{\sim}{r}_o,\underset{\sim}{r}_L)$ of the chain with fixed position of endpoints $\underset{\sim}{r}_o$ and $\underset{\sim}{r}_L$ via

$$S(Y_o|\underset{\sim}{r}_o,\underset{\sim}{r}_L) = k \ln G(Y_o|\underset{\sim}{r}_o,\underset{\sim}{r}_L) \quad , \qquad (8)$$

and

$$G(Y_o|\underset{\sim}{r}_o,\underset{\sim}{r}_L) \sim \int_{Y_o}^{\infty} p(y'|\underset{\sim}{r}_o,\underset{\sim}{r}_L)\, dy' \qquad (9)$$

From eqn. (5) and (9) one gets

$$G(Y_o|\underset{\sim}{r}_o,\underset{\sim}{r}_L) = \text{const.}\ \exp(-(\alpha/L)((L-s')\underset{\sim}{r}_o^{\,2}+s'\underset{\sim}{r}_L^{\,2}))\ \exp(\alpha \varkappa^2)\ (1-2/\pi^{1/2}\ \mathrm{erf}(\alpha^{1/2}(Y_o-\varkappa))) \qquad (10)$$

with erf(x) the error-function, $\alpha = 3L/2ls'(L-s')$ and $\varkappa = (y_o(L-s')+y_L s')/L$.

Finally a Taylor-expansion of the error-function up to the second order yields for the free energy in long chain approximation

$$\Delta F_i(Y_o|\underset{\sim}{r}_{oi},\underset{\sim}{r}_{Li}) = kT\ 6/\pi^{1/2} l\ (3L/2ls_i'(L-s_i'))^{1/2}\ (y_{oi}/s_i' + y_{Li}/(L-s_i'))\ Y_o^{\,2} \quad . \qquad (11)$$

In eq. (11) all terms containing x_{oi}, x_{Li}, z_{oi}, z_{Li} do vanish.

The contribution of all network chains i to the constraining potential is given by

$$\Delta F(Y_o) = \sum_i \left\langle \Delta F_i(Y_o|\underset{\sim}{r}_{oi},\underset{\sim}{r}_{Li}) \right\rangle$$

$$= \int d^3 r_o \int d^3 r_L \; p^+(\underset{\sim}{r}_L|\underset{\sim}{r}_o)\; p(\underset{\sim}{r}_o)\, \Delta F(Y_o|\underset{\sim}{r}_o,\underset{\sim}{r}_L) \qquad (12)$$

$\langle \ldots \rangle$ denotes averaging over all positions $\underset{\sim}{r}_{oi}$, $\underset{\sim}{r}_{Li}$ of the i-th chain. $p(\underset{\sim}{r}_o) = \rho_p$ (polymer chain density) is the a priori probability for finding a chain starting point in the gel. $p^+(\underset{\sim}{r}_L|\underset{\sim}{r}_o)$ is the probability for finding a chain with starting and end point at $\underset{\sim}{r}_o$ and $\underset{\sim}{r}_L$ and any intermediate point $y' > 0$ (configurations 1 and 2' in Fig.1). In accordance with our model we approximate p^+ by

$$p^+(\underset{\sim}{r}_L|\underset{\sim}{r}_o) = \int_0^\infty dy'\; p(y'|\underset{\sim}{r}_L,\underset{\sim}{r}_o) \qquad (13)$$

with $p(y'|\underset{\sim}{r}_L,\underset{\sim}{r}_o)$ from eq.(5). The appropriate probability for the symmetric configurations 1' and 2 (Fig.1) can be written as

$$p^-(\underset{\sim}{r}_L|\underset{\sim}{r}_o) = \int_{-\infty}^0 dy'\; p(y'|\underset{\sim}{r}_L,\underset{\sim}{r}_o) \quad .$$

Performing the integration yields

$$p^+(\underset{\sim}{r}_L|\underset{\sim}{r}_o) = l^2/2\; (3/2\pi lL)^{5/2}\; L^2/(s'(L-s'))$$
$$\exp(-(\alpha/L)((L-s')\underset{\sim}{r}_o^{\,2}+s'\underset{\sim}{r}_L^{\,2}))\; \exp(\alpha\varkappa^2)$$
$$(1-(2/\pi^{1/2})\mathrm{erf}(-\alpha^{1/2}\varkappa)) \quad . \qquad (14)$$

This probability depends only on the permanent topological situation (i.e. is independent of external deformation /1/) which is fixed after the vulcanisation process. If long constraining network chains are assumed, the probability p^+ is nearly the same for all s' and the constraining segment can be assumed to be $s' = L/2$.

The free energy difference $\Delta F(Y_o)$ in the deformed state depends on the deformation by the displacement of the endpoints of the constraining chains. If we assume an affine displacement of the crosslinks,

$$\underset{\sim}{r}_{oi} \longrightarrow \underset{\approx}{\lambda}\, \underset{\sim}{r}_{oi} \quad , \quad \underset{\sim}{r}_{Li} \longrightarrow \underset{\approx}{\lambda}\, \underset{\sim}{r}_{Li} \quad , \qquad (15)$$

we obtain from eqn. (12) and (14) after expanding the error-function (for y_o, $yL \gtrsim (lL)^{1/2}$ the integrating function gives extremely small contributions to the integral) the free energy per constrained chain arc length

$$\Delta\tilde{F}(Y_o;\lambda) = \Delta F(Y_o;\lambda)/l = kT \frac{8^{3/2}}{3\pi^{1/2}} \frac{l^{1/2}}{L^{1/2}} \rho_p \lambda_y Y_o^2 \,. \tag{16}$$

Using the diagonal form of $\underline{\lambda}$ in (15) is in accordance with the assumption of the EDWARDS-theory /1/ that the constraining potential is independent from the direction of the constrained segment.

A generalization of eq. (16) then gives

$$\frac{\tilde{\Delta F}}{kT} \sim \rho_p \left(\lambda_x (X-\hat{X})^2 + \lambda_y (Y-\hat{Y})^2 + \lambda_z (Z-\hat{Z})^2 \right) \tag{17}$$

with $\hat{\underline{R}} = (\hat{X},\hat{Y},\hat{Z})$ the mean configuration and $\underline{R} = (X, Y, Z)$ the actual configuration of the constrained chain.

From eqn. (16) and (17) and from eq. (20) in /2/,

$$\frac{\tilde{\Delta F}(\lambda)}{kT} = \sum_{\substack{\mu= \\ x,y,z}} \frac{1}{\rho_\mu^4(\lambda\mu)} (R_\mu - \hat{R}_\mu)^2 \quad ,$$

follows

$$\rho_\mu \approx 0.9\, q^{1/4} (lL)^{1/2} \lambda_\mu^{b/2} \; ; \quad q = \frac{V/N}{(lL)^{3/2}} \tag{18}$$

with $b = -0.5$, i.e. the value of the TSCHOEGL-equation.

Discussion

The presented model must be regarded as a simple attempt to simulate chain constraining effects. Nevertheless it gives a proper result concerning the deformation dependence of the constraining entropic potential which is in agreement with experimental observations /5/. In this sense the b=-0.5 result gives a support of the network theory in /2,3/, especially for the statistical interpretation of the Mooney-Rivlin-like behaviour of the tensile stress.

Eq. (16) indicates that in good approximation the constraining potential is a harmonic-like. This confirms the idea of the tube-like confinement /6,7/ due to the topological restrictions that chains cannot pass through each other. EDWARDS and DEAM /8/ argued that the density of entanglements dominates

the tube radius ρ_o. Our model indicates that both "entanglement effects" and "packing effects" give contributions (but with different weight) to the constraining potential.

The estimation of the tube-radius is one important problem in the field of concentrated polymer solutions and several attempts have been made to calculate it in terms of a harmonic potential /1,4,9,10/. Though EDWARDS /1,10/ and DE GENNES /9/ used different approaches, they reached the same result for an uncrosslinked concentrated polymer solution, namely $\rho_o \sim \rho_p^{-1/2}$. DOI /4/ criticized this result using scaling requirements which should be satisfied in the continuous Gaussian chain model. He found $\rho_o \sim \rho_p^{-1}$ under the conditions $(1L)^{3/2} \gg \rho_p^{-1}$ and $\rho_p l^2 L \ll 1$ which should be realized at very large degrees of polymerization. We note that the result $\rho_o \sim \rho_p^{-1/4}$ (eq. (18)) gives support for BUECHE's relation $n_c \sim \rho_p^{-1}$ /11/, where n_c is the critical degree of polymerization below which the tube-model breaks down and which is defined by $l n_c^{1/2}/\rho_o = \text{const.}$ Using eq. (18) this relation yields the ρ_p^{-1} dependence.

It is interesting to note that the tube-like model can be reformulated in the frame of the primitive chain concept /12/ in which is assumed ρ_o to be equal to the average length of a primitive chain step at equilibrium. In this model the calculation of ρ_o in /13/ yields $\rho_o \sim \rho_p^{-3/4}$ using the scaling concept (DE GENNES /14/) in polymer physics and $\rho_o \sim \rho_p^{-3/5}$ /12/, respectively, using a mean-field theory. DOI and EDWARDS /12/ argued that a deformation modifies the tube only longitudinally but not transversally. The different assumption of changing the tube diameter by external deformation, proposed by MARRUCCI et.al. /15,16/, is in principle agreement with our result.

Further, we note that the presented model gives hope for explaining the relaxation behaviour of the Mooney-Rivlin parameters /17/. The "fast" relaxation of C_1 after a sudden deformation may be explained by the balancing process of tensile forces acting on the primitive subchains /12/. On the other hand, the "slow" C_2 relaxation may be expected to be determined by a segment diffusion process (may be a partial reptation diffusion) which forces the distribution of segment position around $\hat{R}$ after deformation to the new equilibrium distribution.

We note finally that the characteristic swelling behaviour of polymer networks (decreasing C_2-value

with increasing degree of equilibrium swelling) may be explained in a natural manner. There are two effects causing the swelling result. First, the increase in the ρ_0-dimensions, and second, the loosening from the condition that crosslinks are embedded in the network structure (condition of fixed endpoints) and hence a loosening from the assumption of affine displacement of junctions under strain /18,19, 20/. Considerations under this viewpoint are in progress.

References

/1/ S.F. EDWARDS, Proc. Phys. Soc. (London), 92, 9, (1967)
/2/ G. HEINRICH, E. STRAUBE, and G. HELMIS, Zeitschrift für phys. Chemie, 260, 737 (1979)
/3/ G. H EINRICH, E. STRAUBE, and G. HELMIS, Plaste und Kautschuk, 26, 561 (1979)
/4/ M. DOI, Journ. Phys., A 8, 417 and 959 (1975)
/5/ N.W. TSCHOEGL, Abstracts of Ninth Europhysics Conference on Macromolecular Physics, Jablonna, Poland, 1979
/6/ P.G. DE GENNES, Journ. Chem. Phys., 55, 572 (1971)
/7/ S.F. EDWARDS and J.W.V. GRANT, Journ. Phys., A 6, 1169 (1973)
/8/ R.T. DEAM and S.F. EDWARDS, Phil. Trans. Roy. Soc. (London), A 280, 317 (1976)
/9/ P.G. DE GENNES, Journ. Phys. Lett., 35, L133 (1974)
/10/S.F. EDWARDS, Brit. Polym. Journ., 140 (1977)
/11/F. BUECHE, Physical Properties of Polymers, N.Y.: Interscience, 1962
/12/M. DOI and S.F. EDWARDS, Journ. Chem. Soc., Faraday Transactions II, 74, 1789 and 1802 (1978)
/13/M. DAOUD, et.al., Macromolecules, 8, 804 (1975)
/14/P.G. DE GENNES, Scaling Concepts in Polymer Physics, Cornell University, Ithaka, N.Y.,1979
/15/G. MARRUCCI and B. DE CINDO, Rheol.Acta,19,68 (1980)
/16/G. MARRUCCI and J.J. HERMANS, Macromolecules, 13, 380 (1980)
/17/B. ERMAN, Abstracts of Ninth Europhysics Conf. on Macromol. Physics, Jablonna, Poland, 1979
/18/P.J. FLORY, Proc. Roy. Soc. (London), A 351 , 351 (1976)
/19/P.J. FLORY, Journ. Chem. Phys., 66, 5720 (1977)
/20/P.J. FLORY, Macromolecules,12, 119 (1979)

Received October 17, 1980
Accepted October 21, 1980

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