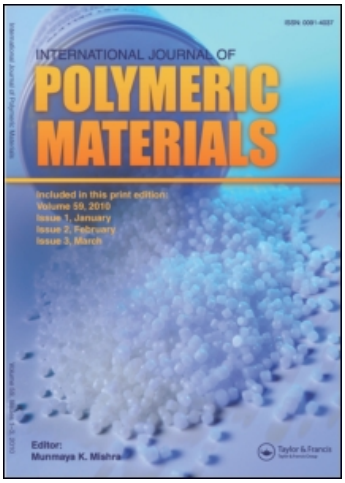

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The Theory of High Elasticity and Birefringence of Rubbers

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The Theory of High Elasticity and Birefringence of Rubbers†

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On the basis of a "channel" model an attempt has been made to account for the limitation of the number of possible chain conformations in bulk elastomer. Each chain is supposed to fluctuate near its average position—the "channel", determined by the conditions of bulk polymer formation. Then the probability of a certain chain conformation existence is reduced with the increase of its deviations from the channel axis. Chain fluctuations along the channel axis are free from any constraints because such a change of the chain conformations is not connected with the variation of its neighbours locations. In the first approximation (when the chain and the channel are divided into two parts) the calculations based on the model pointed out lead to the free energy formula deduced earlier by the author while starting from partly different assumptions. The formula fits well the experimental data for various types of deformations.[19] Particularly, the theoretical dependence of true stress, σ, on deformation has a linear form when plotted in coordinates $\sigma/2(\lambda^2 - 1/\lambda)$ versus $1/\lambda$ (λ is the extension ratio). It permits consideration of the present study as being a theoretical basis for the Monney–Rivlin formula from the molecular point of view. Calculated on the same grounds, the theoretical dependence of birefringence, Δn, on λ at uniaxial tension also has a linear form in coordinates $\Delta n/2(\lambda^2 - 1/\lambda)$ versus $1/\lambda$ in accordance with the experimental observations. However, it has a somewhat larger slope than the corresponding dependence for σ. Therefore $\Delta n/\sigma$ is found to be only slightly dependent function of λ, i.e. according to the theory presented Bruster's law should hold for rubbers only approximately.

INTRODUCTION

The classical rubber-like elasticity theory[1–3] is known to lead to considerable deviations from experiment[4,5] when describing the different types of the deformational interrelations. Many attempts based on the various physical premises have been made to improve the theory.[6–14] Without any critical discussion of these works we point out only that the weakest point in the

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classical theory of rubber elasticity lies in the consideration of the network of "phantom chains" transparent to one another and themselves. Such a situation differs considerably from that in the real bulk elastomers where the number of possible chain conformations is essentially restricted by the presence of neighbours. Therefore the recent attempts[15,16] to take into consideration the steric interactions between the network chains are of great interest. These theories could be named as theories of the real polymer networks because the model accepted there reproduces the reality of the strain of bulk elastomers much better than the classical ones. Unfortunately at the present stage the conclusions of these theories cannot be examined experimentally in detail, and some of their starting points are open to doubt.

The basic physical idea of works by Edwards[15] and Helmis,[16] taking into account the influence of surrounding chains, is the same as in the early published papers by the author.[17–19] As follows from these papers,[19] our results fit quite well the experimental data on various types of deformation and give qualitative explanations for a wide scope of experimental regularities in the equilibrium properties of rubber-like materials. However the presentation of the theory in the papers cited somehow lacked the necessary strictness. In particular, it was based on the consideration of the chain conformations arising after very rapid (instantaneous) deformation and their consequent change during the stress relaxation. Thereby it has been postulated that the process of the recovery of equilibrium distribution of chain conformations can not reach total completion in the deformed state due to steric obstructions from the neighbouring chains. Although one has no doubts about this statement, the confinement pointed out did not follow from the model accepted for calculation, which left a certain feeling of dissatisfaction.

The object of the present study is twofold. First we wish to present the theory more rigorously on the basis of the slightly modified ideas about a "channel", which were already used in the works cited.[15,16] It will allow us to ignore the non-equilibrium state as an intermediate stage and to reveal more strictly the essence of the assumptions made during the development of the theory.

Secondly, we wish to develop the theory of rubber birefringence on the basis of the same notions about the "channel". According to the classical rubber-like elasticity theory, Bruster's law is known to hold, i.e. the proportionality must be observed in strained rubber between the birefringence Δn and stress σ, based on the cross-sectional area of the deformed sample.[4] The validity of this conclusion has been frequently checked experimentally, the values of Bruster's constant $c = \Delta n/\sigma$ being always close to those calculated from the optical anisotropy of the polymeric chains.[20] But despite this, the present state of the rubber birefringence theory is not quite satisfactory. As has been already pointed out, dependences of the stress on the deformation

ε as predicted by the classical theory are not in accord with experiment. The same is true of the theoretical dependences of Δn on ε.[21,22] And only the similar nature of divergences in both cases permits the theory to give the correct interrelation between Δn and σ. That is why the development of the birefringence theory to describe correctly the dependency of Δn on ε, is a necessary task for improving the rubber elasticity theory.

PHYSICAL PREMISES OF THE THEORY

Flory[2] was the first to pay attention to steric interaction between the network chains. He has pointed out that the entanglements of the type shown in Figure 1a, act as extra effective network junctions. Since then the conception of entanglements gained popularity. Its various aspects has been reviewed by Graessley.[23] However, as pointed out in the work elsewhere,[19] the steric interaction of the entanglement type does not differ in principle from that shown in Figure 1b when the chains are crossed. In both cases the chains AB and CD mutually restrict the number of possible conformations, the extent of this restriction being dependent on the distance d between their axes. When $d = 0$ the situations shown in Figures 1a and 1b become equivalent and in the case of negative d (i.e. when the chain AB in Figure 1b is displaced upwards above the chain CD) the crossed chains become entangled. Let us pay attention to one essential detail. Due to free slipping in the contact point both types of steric interaction have no influence on the value of chain fluctuations in the direction of their end-to-end vectors; only the distribution function of their transverse dimensions is disturbed.

It is apparent that in bulk polymer the situations shown in Figure 1 are repeated many times along a certain chain. So one can imagine the location

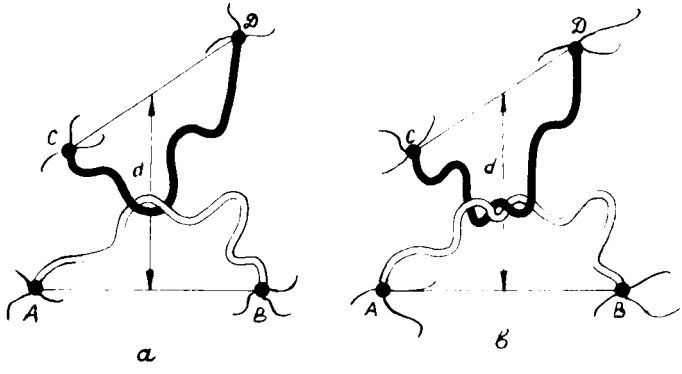

FIGURE 1 Various types of the steric chain interactions: a entanglement, b crossed chains.

of the chain in bulk such as shown schematically in Figure 2. Due to entanglements and chain crossing the chain is kept near a certain average position—a "channel". Any deviation from the channel causes the deformation of the contacting chains that generates an elastic force to return the chain to the previous position. It takes place only for deviations normal to the channel contour; the displacement of the chain along its channel as mentioned above does not meet any obstruction. It is one of the differences in the model construction accepted in the present work and in the works elsewhere.[15,16] The latter assume that the fluctuations of the intermediate chain links positions are restricted to the same extent in all directions. We believe this assumption to be insufficiently realistic.

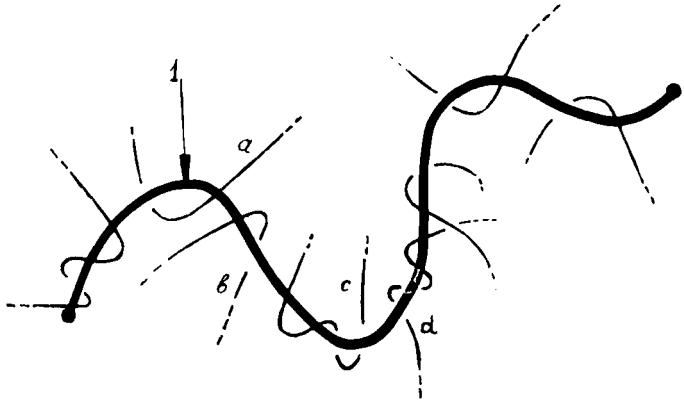

FIGURE 2 Chain in bulk elastomer (scheme): 1—the chain under consideration; a,b—entanglements; c,d—crossed chains.

The situation shown in Figure 2 can be reproduced by the model shown in Figure 3. One of the possible chain conformations is marked here by the fat black curve, and the channel by the hollow one. The chain is divided into a certain number of equal segments—submolecules which junction points

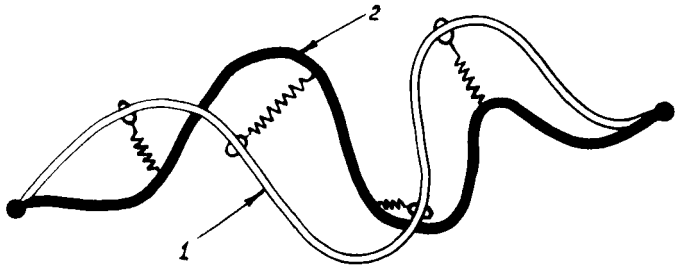

FIGURE 3 The model of a "channel" (scheme): 1—the channel, 2—the chain under consideration.

are connected to the channel by means of the springs imitating elastic response of the environment. The springs are rigidly attached to the chain and slip freely along the channel contour. To complete the model construction one needs some other quite natural assumptions:

1) In the case of the chains having the same end-to-end vectors R, the distribution function of channel conformations is identical to that for an isolated chain fixed at the same points.

2) All channel contours are deformed affinaly with gross behavior of the sample.

3) The direction of the channel at a given point of its division into equal parts is assumed to coincide with the direction of the straight line connecting two adjacent points of channel division.

Other assumptions are similar to those of conventional rubber elasticity theory. Unfortunately, essential mathematical difficulties are met when one calculates the model with arbitrary number of division points. So we confine ourselves to considering only the first approximation when the chains are divided solely into two submolecules. In this case, according to the above assumption, the chain end-to-end vector should be assumed as giving the direction of the channel.

THEORY, THE FIRST APPROXIMATION

Let the sample of cured elastomer be deformed in three mutually perpendicular directions by the extension ratios λ_1, λ_2 and λ_3. Then, in accordance with the assumptions made, the distance between the ends of a certain chain, characterized by the vector $\vec{R} = X\vec{i} + Y\vec{j} + Z\vec{k}$ for an unstrained system, will be determined now by

$$\vec{R}' = \lambda_1 X\vec{i} + \lambda_2 Y\vec{j} + \lambda_3 Z\vec{k} \tag{1}$$

and the vector $\vec{\rho}$ that determined the location of the point of channel division will be transformed into $\vec{\rho}' = \lambda_1\xi\vec{i} + \lambda_2\eta\vec{j} + \lambda_3\zeta\vec{k}$. Given the chain under discussion consists of N links each of length l, the distribution function of its conformations characterized by the location of the middle chain link (x, y, z), will be

$$\begin{aligned} W_1(x, y, z)\,dx\,dy\,dz &= \Omega \exp\{-\alpha[x^2 + y^2 + z^2 + (\lambda_1 X - x)^2 + (\lambda_2 Y - y)^2 \\ &\quad + (\lambda_3 Z - z)^2]\} \cdot \exp\left\{-\frac{K'h^2}{2kT}\right\} dx\,dy\,dz \\ &= \Omega \cdot W(x, y, z)\,dx\,dy\,dz \end{aligned} \tag{2}$$

where $\alpha = 3/Nl^2$, and Ω is a normalization factor.

The last exponent in (2) is the Boltzmann factor giving the statistical weight of chain conformation at different extent of its deviation from the channel contour. K' is the proportionality factor between elastic response of the surrounding chains at the junction of the submolecules and the deviation of the point from the channel contour—h. Note that in the first approximation of the theory the action of the surrounding chains on the whole chain under consideration is assumed to be concentrated at the junction point of the two submolecules. Since, in accordance with the ideas developed, K is of a kinetic origin it is convenient to introduce a new notation

$$K = K'/2kT \tag{3}$$

According to the model accepted h is the projection of the vector between the division point of the chain and that of the channel on the plane normal to the channel contour. Obviously, for the first approximation under discussion

$$h^2 = [(\vec{r} - \vec{\rho}')\vec{R}']^2/R'^2 \tag{4}$$

where $\vec{r} = x\vec{i} + y\vec{j} + z\vec{k}$ is a vector describing the position of the middle point of the chain.

Entropy of the chain under consideration may be represented as a sum of entropies of its two comprising submolecules:

$$\begin{aligned} S_1 &= -k\alpha[\langle r^2\rangle + \langle(\vec{R}' - \vec{r})^2\rangle] \\ &= -k\alpha \int_{-\infty}^{\infty}\int\int [r^2 + (\vec{R}' - \vec{r})^2] W_1(x, y, z)\, dx\, dy\, dz \\ &= k\alpha \frac{d}{d\alpha} \ln\left\{\int_{-\infty}^{\infty}\int\int W(x, y, z)\, dx\, dy\, dz\right\} \\ &= k\alpha \frac{d}{d\alpha} \ln J \end{aligned} \tag{5}$$

Adding the exponents in (2) one has

$$\begin{aligned} W(x, y, z) &= \exp\{-B(x, y, z, 1)\} \\ &= \exp\{-[(2\alpha + K - q\lambda_1^2 X^2)x^2 + (2\alpha + K - q\lambda_2^2 Y^2)y^2 \\ &\quad + (2\alpha + K - q\lambda_3^2 Z^2)z^2 - 2q\lambda_1\lambda_2 XYxy - 2q\lambda_1\lambda_3 XZxz \\ &\quad - 2q\lambda_2\lambda_3 YZyz - 2\lambda_1 p_x x - 2\lambda_2 p_y y - 2\lambda_3 p_z Z + \alpha R'^2 \\ &\quad - q[\vec{\rho}'\vec{R}']^2]\} \end{aligned} \tag{6}$$

where

$$\vec{p} = \alpha\vec{R}' + K\vec{\rho}' - q\vec{R}'(\vec{\rho}'\vec{R}'); \qquad q = K/R'^2$$

To calculate J the exponent in (6) should be diagonalized. It could be done

by Jacobi procedure[24] considering $B(x, y, z, 1)$ as a quadratic form of four variables, the last of which equalizes to 1. The diagonalized quadratic form will be

$$B(x', y', z', 1) = \mathscr{D}_1 x'^2 + (\mathscr{D}_2/\mathscr{D}_1)y'^2 + (\mathscr{D}_3/\mathscr{D}_2)z'^2 + (\mathscr{D}_4/\mathscr{D}_3) \tag{7}$$

where D_i are angular minors of the i order of the original quadratic form $B(x, y, z, 1)$ matrix.

Jackobian of the transformation carried out is equal to 1. Therefore:

$$J = (\pi^{3/2}/\sqrt{\mathscr{D}_3}) \cdot \exp[-(\mathscr{D}_4/\mathscr{D}_3)] \tag{8}$$

and

$$S_1 = -k\alpha\left\{\frac{1}{2}\frac{d}{d\alpha}\ln \mathscr{D}_3 + \frac{d}{d\alpha}\left(\frac{\mathscr{D}_4}{\mathscr{D}_3}\right)\right\} \tag{9}$$

Direct calculations give:

$$\mathscr{D}_3 = 2\alpha(K+2\alpha)^2 \tag{10}$$

and

$$\mathscr{D}_4 = \{\alpha R'^2 - q[\vec{\rho}'\vec{R}']^2\}\mathscr{D}_3 - (K+2\alpha)^2\alpha^2 R'^2 - 2\alpha K^2(K+2\alpha)\frac{[\vec{\rho}'\vec{R}']^2}{R'^2} \tag{11}$$

Substituting these expressions into (9) we find:

$$S_1 = -k\left[\frac{K+6\alpha}{2(K+2\alpha)} + \frac{\alpha R'^2}{2} + \frac{2\alpha K^2}{(K+2\alpha)^2}\frac{[\vec{\rho}'\vec{R}']^2}{R'^2}\right] \tag{12}$$

This is the expression for entropy of the chain when the middle point of the channel has coordinates ξ, η, ζ in an underformed state. Having no possibility to analyze here the origin of the different terms in the expression (12) we would like only to point out that the first one is due to the fluctuations of the submolecules junction point. For a free chain ($K = 0$) that is equal to $3k/2$ corresponding to three degrees of freedom. When $K \to \infty$ only one degree of freedom is left (fluctuations along the channel) and the first term turns into $k/2$. As for the elastic properties, this term is of no importance since it does not depend on the deformation, but it contributes to the final result when the equilibrium swelling and birefringence are calculated. The second term in (12) is due to the change of the distance between chain ends, and the third one is due to the change of the mean square distance between the middle point of the chain and the straight line connecting its ends, i.e. due to the change of chain "transversal dimensions".

To obtain S_2, an average entropy for the chains having end-to-end vector R in an unstrained system, the expression (12) must be averaged over all the channel conformations possible, i.e. over all accessible positions of its middle point. According to the assumptions made earlier, the proper distribution

function has the form:

$$W_2(\xi, \eta, \zeta)\, d\xi\, d\eta\, d\zeta = \left(\frac{2\alpha}{\pi}\right)^{3/2} \cdot \exp\left(\frac{\alpha R^2}{2}\right) \times \exp\{-\alpha[\rho^2 + (\vec{R} - \vec{\rho})^2]\}\, d\xi\, d\eta\, d\zeta \tag{13}$$

Hence

$$\langle \xi \rangle = \frac{X}{2}; \quad \langle \eta \rangle = \frac{Y}{2}; \quad \langle \zeta \rangle = \frac{Z}{2}$$

$$\langle \xi^2 \rangle = \frac{1}{2\alpha} + \frac{X^2}{4}; \quad \langle \eta^2 \rangle = \frac{1}{2\alpha} + \frac{Y^2}{4}; \quad \langle \zeta^2 \rangle = \frac{1}{2\alpha} + \frac{Z^2}{4} \tag{14}$$

Substituting (14) into (12) and bearing in mind that owing to independence of the coordinates the average value of the product is equal to the product of the average values of the comultipliers, we have

$$S_2 = -k\left[\frac{K + 6\alpha}{2(K + 2\alpha)} + \frac{\alpha R'^2}{2} + \left(\frac{K}{K + 2\alpha}\right)^2 \left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - \frac{\lambda_1^4 X^2 + \lambda_2^4 Y^2 + \lambda_3^4 Z^2}{\lambda_1^2 X^2 + \lambda_2^2 Y^2 + \lambda^2 Z^2}\right)\right] \tag{15}$$

To obtain S, the entropy of the strained network, we need two more averagings: over all possible orientations of vector R and over all possible values of its modulus, then multiplying the result by ν – number of network chains per unit volume. Such averagings have already been made in[19] (see formulae (8)–(12) in the work). Using the result obtained there one can write

$$S = -\frac{\nu k}{2}\frac{K + 6\alpha}{K + 2\alpha} - \frac{\nu k}{2}\frac{\langle R^2 \rangle}{\langle R_0^2 \rangle}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) - \nu k\left(\frac{K}{K + 2\alpha}\right)^2 \left\{\lambda_3^2 + \frac{\lambda_2 \lambda_3^2}{\sqrt{\lambda_1^2 - \lambda_3^2}} F(\beta, \varkappa) + \lambda_2 \sqrt{\lambda_1^2 - \lambda_3^2}\, E(\beta, \varkappa)\right\} \tag{16}$$

where $R_0^2 = Nl^2$, the mean square length of an isolated molecule consisting of N links,

$$F(\beta, \varkappa) = \int_0^{\sin\beta} \frac{dt}{\sqrt{(1 - t^2)(1 - \varkappa^2 t^2)}}; \quad E(\beta, \varkappa) = \int_0^{\sin\beta} \sqrt{\frac{1 - \varkappa^2 t^2}{1 - t^2}}\, dt \tag{17}$$

are incomplete elliptic integrals of the 1st and 2nd order, respectively, which modulus $\varkappa$ and argument β are defined by the relations:

$$\varkappa^2 = [\lambda_1^2(\lambda_2^2 - \lambda_3^2)]/[\lambda_2^2(\lambda_1^2 - \lambda_3^2)]; \quad \sin\beta = \sqrt{\lambda_1^2 - \lambda_3^2}/\lambda_1 \tag{18}$$

Asymmetry of the expression (16) relative to λ_i is connected with the assumption $\lambda_1 \geqslant \lambda_2 \geqslant \lambda_3$ made during the last averaging. And the original expression (15) has a completely symmetrical form. Supposing $\lambda_1 = \lambda_2 =$

$\lambda_3 = 1$ in (16), we find the entropy of underformed network

$$S_0 = -\frac{\nu k}{2}\frac{K+6\alpha}{K+2\alpha} - \frac{3\nu k}{2}\frac{\langle R^2\rangle}{\langle R_0^2\rangle} - 2\nu k\left(\frac{K}{K+2\alpha}\right)^2 \tag{19}$$

and the free energy increment at the deformation of the network

$$\begin{aligned}\Delta F &= -T(S-S_0)\\ &= \frac{\nu kT}{2}\frac{\langle R^2\rangle}{\langle R_0^2\rangle}(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)\\ &\quad +\nu kT\left(\frac{K}{K+2\alpha}\right)^2\left\{\lambda_3^2-2+\frac{\lambda_2\lambda_3^2}{\sqrt{\lambda_1^2-\lambda_3^2}}F(\beta,\varkappa)+\lambda_2\sqrt{\lambda_1^2-\lambda_3^2}\,E(\beta,\varkappa)\right\}\end{aligned} \tag{20}$$

The expression (20) within an accuracy of the coefficient in front of the figure brackets coincides with the result previously obtained in [17,19]. Having left for a time the comparison of consequences from the expression with experiment let us pass to consideration of birefringence in a deformed network.

We shall start from the result of Kuhn and Grun[25] according to which the polarizabilities of a single chain in the direction of its end-to-end vector and in the perpendicular one (γ_1 and γ_2, respectively within the accuracy of the first non-vanishing term in the expansion over degrees of the end-to-end distance R, are equal to:

$$\begin{aligned}\gamma_1 &\approx N\left[\frac{\alpha_1+2\alpha_2}{3}+\frac{2}{5}(\alpha_1-\alpha_2)\left(\frac{R}{Nl}\right)^2\right];\\ \gamma_2 &\approx N\left[\frac{\alpha_1+2\alpha_2}{3}-\frac{1}{5}(\alpha_1-\alpha_2)\left(\frac{R}{Nl}\right)^2\right]\end{aligned} \tag{21}$$

where α_1 and α_2 are longitudinal and lateral polarizabilities of the chain link.

Applying these relations to each submolecule and using the well-known optical formulae[26] one can write the components of the polarizability tensor of a deformed network P_{ij} as:

$$P_{ii} = \sum_k^{2\nu}[(\gamma_{1k}-\gamma_{2k})\cos^2\psi_{ik}+\gamma_{2k}] \tag{22}$$

where the summation is performed over all the submolecules per network unit volume and $\cos\psi_{ik}$ are the directional cosines of each submolecule. It is evident that,

$$\cos^2\psi_{xk} = x_k^2/r_k^2;\quad \cos^2\psi_{yk} = y_k^2/r_k^2;\quad \cos^2\psi_{zk} = z_k^2/r_k^2$$

at $1 \leqslant k \leqslant \nu$ and

$$\begin{aligned}&\cos^2\psi_{xk} = (\lambda_1 X-x)^2/(\vec{R}'-\vec{r})^2;\quad \cos^2\psi_{yk} = (\lambda_2 Y-y)^2/(\vec{R}'-\vec{r})^2;\\ &\cos^2\psi_{zk} = (\lambda_3 Z-z)^2/(\vec{R}'-\vec{r})^2 \qquad \text{at } \nu+1 \leqslant k \leqslant 2\nu\end{aligned} \tag{23}$$

Substituting (21) and (23) into (22) we have

$$P_{xx} = P_0 + \frac{2\nu}{5}(\alpha_1 - \alpha_2)\left\{3\left[\left\langle \frac{x^2}{Nl^2}\right\rangle + \left\langle \frac{(\lambda_1 X - x)^2}{Nl^2}\right\rangle\right] - \left\langle \frac{r^2}{Nl^2}\right\rangle - \left\langle \frac{(\vec{R}' - \vec{r})^2}{Nl^2}\right\rangle\right\} \tag{24}$$

and similar expressions for P_{yy} and P_{zz}. Here P_0 is referred to as polarizability of an unstrained network:

$$P_0 = \frac{\alpha_1 + 2\alpha_2}{3}\sum_{k=1}^{\nu} N_k \tag{25}$$

and the angular brackets mean the averaging over all the chain conformations at a given channel position, over all channel positions possible, over the modulus and orientations of vector $\vec{R}$. The values of $\langle r^2/Nl^2\rangle + \langle(\vec{R}' - \vec{r})^2/Nl^2\rangle$ have been already obtained earlier (see formulae (5)–(16)) and the problem reduces to calculation of mean square values of the submolecules length projections. To do this it is convenient to introduce an auxiliary parameter "a" into the formula (6) for the distribution function $W(x, y, z)\,dx\,dy\,dz$

$$W_3(x, y, z)\,dx\,dy\,dz = \exp\{-\alpha[ax^2 + y^2 + z^2 + a(\lambda_1 X - x)^2 + (\lambda_2 Y - y)^2 + (\lambda_3 Z - z)^2]\} \cdot \exp\{-Kk^2)\}\,dx\,dy\,dz \tag{26}$$

It is easy to see that

$$3\left[\left\langle \frac{x^2}{Nl^2}\right\rangle_r + \left\langle \frac{(\lambda_1 X - x)^2}{Nl^2}\right\rangle_r\right] = \alpha\int_{-\infty}^{\infty}\int\int [x^2 + (\lambda_1 X - x)^2]W_1(x, y, z)\,dx\,dy\,dz$$

$$= -\left\{\frac{d}{da}\ln\left[\int_{-\infty}^{\infty}\int\int W_3(x, y, z)\,dx\,dy\,dz\right]\right\}_{a=1}$$

$$= -\left[\frac{d}{da}\ln J'\right]_{a=1} \tag{27}$$

where "r" means the averaging over all chain conformations at the channel location given.

By adding the exponents in (26) taking into consideration the expression (4) and diagonalizing the resulting polynom $B'(x, y, z, 1)$ in the same manner as before, one has

$$B'(x', y', z', 1) = \mathscr{D}'_1 x'^2 + \frac{\mathscr{D}'_2}{\mathscr{D}'_1}y'^2 + \frac{\mathscr{D}'^3}{\mathscr{D}'_2}z'^2 + \frac{\mathscr{D}'_4}{\mathscr{D}'_3} \tag{28}$$

and

$$J' = (\pi^{3/2}/\sqrt{\mathscr{D}'_3})\exp[-(\mathscr{D}'_4/\mathscr{D}'_3)] \tag{29}$$

which after putting in (27), gives:

$$3\left[\left\langle\frac{x^2}{Nl^2}\right\rangle_r+\left\langle\frac{(\lambda_1X-x)^2}{Nl^2}\right\rangle_r\right]=\left\{\frac{1}{\mathscr{D}'_3}\left[\frac{1}{2}\left(1-\frac{\mathscr{D}'_4}{\mathscr{D}'_3}\right)\frac{d\mathscr{D}'_3}{da}+\frac{d\mathscr{D}'_4}{da}\right]\right\}_{a=1}$$
$$=\frac{1}{\mathscr{D}'_3}\left[\frac{1}{2}\left(1-\frac{\mathscr{D}'_4}{\mathscr{D}'_3}\right)\left(\frac{d\mathscr{D}'_3}{da}\right)_{a=1}+\left(\frac{d\mathscr{D}'_4}{da}\right)_{a=1}\right] \quad (30)$$

Calculating the angular minors of the modified quadratic form $B(x, y, z, 1)$ matrices:

$$\mathscr{D}'_3=2\alpha(K+2\alpha)[2\alpha a+K-(1-a)q\lambda_1^2X^2] \quad (31)$$

$$\mathscr{D}'_4=\{\alpha R'^2_2-q[\vec{\rho}'\vec{R}']^2\}\mathscr{D}'_3-(K+2\alpha)^2p_{1x}^2-(2\alpha a+K)(K+2\alpha)(p_{1y}^2+p_{1z}^2)$$
$$+q(K+2\alpha)(\lambda_2^2Y^2+\lambda_3^2Z^2)p_{1x}^2+q[(2\alpha a+K)\lambda_3^2Z^2+(K+2\alpha)\lambda_1^2X^2]p_{1y}^2$$
$$+q[(2\alpha a+K)\lambda_2^2Y^2+(K+2\alpha)\lambda_1^2X^2]p_{1z}^2-2q(K+2\alpha)\lambda_1\lambda_3XZp_{1x}p_{1z}$$
$$-2q(K+2\alpha)\lambda_1\lambda_2XYp_{1x}p_{1y}-2q(2\alpha a+K)\lambda_2\lambda_3YZp_{1y}p_{1z} \quad (32)$$

where

$$\vec{p}_1=\alpha\vec{R}'_1+K\vec{\rho}'-q\vec{R}'(\vec{\rho}'\vec{R}');\quad \vec{R}'_1=a\lambda_1X\vec{i}+\lambda_2Y\vec{j}+\lambda_3Z\vec{k};$$
$$\vec{R}'_2=\sqrt{a}\,\lambda_1X\vec{i}+\lambda_2Y\vec{j}+\lambda_3Z\vec{k} \quad (33)$$

and their derivatives

$$\left[\frac{d\mathscr{D}'_3}{da}\right]_{a=1}=2\alpha(2\alpha+K)(2\alpha+q\lambda_1^2X^2); \quad (34)$$

$$\left[\frac{d\mathscr{D}'_4}{da}\right]_{a=1}=2\alpha^2(K+\alpha)(K+2\alpha)\lambda_1^2X^2+2\alpha^3(K+2\alpha)R'^2-2\alpha q(K+2\alpha)^2[\vec{\rho}'\vec{R}']^2$$
$$-2\alpha q(K+2\alpha)\lambda_1^2X^2[\vec{\rho}'\vec{R}']^2+2\alpha qK^2\lambda_2^2\lambda_3^2(\zeta Y-\eta Z)^2$$
$$+2\alpha K^2(K+2\alpha)\lambda_1^2\xi^2+2\alpha q^2(K+2\alpha)\lambda_1^2X^2(\vec{\rho}'\vec{R}')^2$$
$$-4\alpha qK(K+2\alpha)\lambda_1^2\xi X(\vec{\rho}'\vec{R}') \quad (35)$$

after putting of (10), (11), (34) and (35) in (30) we have

$$3\left[\left\langle\frac{x^2}{Nl^2}\right\rangle_r+\left\langle\frac{(\lambda_1X-x)^2}{Nl^2}\right\rangle_r\right]=\frac{\alpha}{K+2\alpha}+\frac{q\lambda_1^2X^2}{2(K+2\alpha)}+\alpha\frac{\lambda_1^2X^2}{2}-\frac{qK^2}{(K+2\alpha)^2}[\vec{\rho}'\vec{R}']^2$$
$$+\frac{q^2K}{(K+2\alpha)^2}\lambda_1^2X^2[\vec{\rho}'\vec{R}']^2+\frac{qK^2}{(K+2\alpha)^2}$$
$$\times\lambda_2^2\lambda_3^2(\zeta Y-\eta Z)^2+\frac{K}{K+2\alpha}\lambda_1^2\xi^2$$
$$+\frac{q^2\lambda_1^2X^2}{K+2\alpha}(\vec{\rho}'\vec{R}')-\frac{2qK}{K+2\alpha}\lambda_1^2\xi X(\vec{\rho}'\vec{R}') \quad (36)$$

The next averaging based on the distribution function and taking into

consideration the relations (14) results in:

$$3\left[\left\langle\frac{x^2}{Nl^2}\right\rangle_{r,\rho}+\left\langle\frac{(\lambda_1 X-x)^2}{Nl^2}\right\rangle_{r,\rho}\right]$$

$$=\frac{\alpha}{K+2\alpha}+\frac{K}{2(K+2\alpha)}\frac{\lambda_1^2X^2}{\lambda_1^2X^2+\lambda_2^2Y^2+\lambda_3^2Z^2}+\alpha\frac{\lambda_1^2X^2}{2}+\frac{K^2}{(K+2\alpha)^2}$$

$$\times\left[\lambda_1^2+\frac{\lambda_1^2X^2(\lambda_1^4X^2+\lambda_2^4Y^2+\lambda_3^4Z^2)}{(\lambda_1^2X^2+\lambda_2^2Y^2+\lambda_3^2Z^2)^2}-2\frac{\lambda_1^4X^2}{\lambda_1^2X^2+\lambda_2^2Y^2+\lambda_3^2Z^2}\right]$$

$$=\frac{\alpha}{K+2\alpha}+\frac{K}{2(K+2\alpha)}\frac{\lambda_1^2X^2}{\lambda_1^2X^2+\lambda_2^2Y^2+\lambda_3^2Z^2}+\frac{\lambda_1}{2}\frac{\partial}{\partial\lambda_1}$$

$$\left\{\frac{\alpha R'^2}{2}+\left(\frac{K}{K+2\alpha}\right)^2\left[\lambda_1^2+\lambda_2^2+\lambda_3^2-\frac{\lambda_1^4X^2+\lambda_2^4Y^2+\lambda_3^4Z^2}{\lambda_1^2X^2+\lambda_2^2Y^2+\lambda_3^2Z^2}\right]\right\} \tag{37}$$

It is easy to see that after adding (37) to the similar expressions for the other projections we obtain the same expression as within the square brackets in formula (15).

Let us make now the averaging based on the orientations of vector $\vec{R}$. Note that the average value of the expression in figure brackets in formula (37) has been already obtained and is equal to:

$$\Phi(\lambda_1,\lambda_2,\lambda_3)=\frac{1}{2}\frac{\langle R^2\rangle}{\langle R_0^2\rangle}(\lambda_1^2+\lambda_2^2+\lambda_3^2)$$

$$+\left(\frac{K}{K+2\alpha}\right)\left[\lambda_3^2+\frac{\lambda_2\lambda_3^2}{\sqrt{\lambda_1^2-\lambda_3^2}}F(\beta,\varkappa)+\lambda_2\sqrt{\lambda_1^2-\lambda_3^2}\,E(\beta,\varkappa)\right] \tag{38}$$

Thus it leaves only the average values of the terms like $\lambda_1^2X^2/R'^2$ to be calculated. Passing to spherical coordinates and using the procedure of [20] we have:

$$\left\langle\frac{\lambda_1^2X^2}{R'^2}\right\rangle=\frac{\lambda_1^2}{\lambda_1^2-\lambda_2^2}-\frac{\lambda_1^2\lambda_2}{(\lambda_1^2-\lambda_2^2)\sqrt{\lambda_1^2-\lambda_3^2}}E(\beta,\varkappa);$$

$$\left\langle\frac{\lambda_2^2Y^2}{R'^2}\right\rangle=-\frac{\lambda_2^2}{\lambda_1^2-\lambda_2^2}+\frac{\lambda_2^3\sqrt{\lambda_1^2-\lambda_3^2}}{(\lambda_1^2-\lambda_2^2)(\lambda_2^2-\lambda_3^2)}E(\beta,\varkappa)-\frac{\lambda_2\lambda_3^2}{(\lambda_2^2-\lambda_3^2)\sqrt{\lambda_1^2-\lambda_3^2}}F(\beta,\varkappa);$$

$$\left\langle\frac{\lambda_3^2Z^2}{R'^2}\right\rangle=\frac{\lambda_2\lambda_3^2}{(\lambda_2^2-\lambda_3^2)\sqrt{\lambda_1^2-\lambda_3^2}}[F(\beta,\varkappa)-E(\beta,\varkappa)] \tag{39}$$

Bearing in mind the relations (28)

$$\frac{\partial F(\beta, æ)}{\partial \beta} = \frac{1}{\sqrt{1-æ^2 \sin^2 \beta}}; \quad \frac{\partial E(\beta, æ)}{\partial \beta} = \sqrt{1-æ^2 \sin^2 \beta};$$
$$\frac{\partial F(\beta, æ)}{\partial (æ^2)} = \frac{E(\beta, æ)}{2æ^2 æ'^2} - \frac{F(\beta, æ)}{2æ^2} - \frac{\sin \beta \cdot \cos \beta}{2æ'^2 \sqrt{1-æ^2 \sin^2 \beta}};$$
$$\frac{\partial E(\beta, æ)}{\partial (æ^2)} = \frac{E(\beta, æ) - F(\beta, æ)}{2æ^2}; \quad æ'^2 = 1-æ^2 \tag{40}$$

By differentiating $\Phi(\lambda_1, \lambda_2, \lambda_3)$ we obtain the final expressions for the main polarizabilities of a deformed network:

$$P_{xx} = P_1 + \frac{\nu}{5}(\alpha_1 - \alpha_2)\left\{\frac{K}{K+2\alpha}\left[\frac{\lambda_1^2}{\lambda_1^2-\lambda_2^2} - \frac{\lambda_1^2\lambda_2}{(\lambda_1^2-\lambda_2^2)\sqrt{\lambda_1^2-\lambda_3^2}} E(\beta, æ)\right]\right.$$
$$+\frac{\langle R^2\rangle}{\langle R_0^2\rangle}\lambda_1^2 + \left(\frac{K}{K+2\alpha}\right)^2\left[\frac{\lambda_1^2\lambda_3^2}{\lambda_1^2-\lambda_2^2} + \left(\lambda_2\sqrt{\lambda_1^2-\lambda_3^2}\right.\right.$$
$$\left.\left.\left. - \frac{\lambda_2^3\lambda_3^2}{(\lambda_1^2-\lambda_2^2)\sqrt{\lambda_1^2-\lambda_3^2}}\right) E(\beta, æ)\right]\right\};$$

$$P_{yy} = P_1 + \frac{\nu}{5}(\alpha_1 - \alpha_2)\left\{\frac{K}{K+2\alpha}\left[-\frac{\lambda_2^2}{\lambda_1^2-\lambda_2^2} + \frac{\lambda_2^3\sqrt{\lambda_1^2-\lambda_3^2}}{(\lambda_1^2-\lambda_2^2)(\lambda_2^2-\lambda_3^2)} E(\beta, æ)\right.\right.$$
$$\left.- \frac{\lambda_2\lambda_3^2}{(\lambda_2^2-\lambda_3^2)\sqrt{\lambda_1^2-\lambda_3^2}} F(\beta, æ)\right] + \frac{\langle R^2\rangle}{\langle R_0^2\rangle}\lambda_2^2 + \left(\frac{K}{K+2\alpha}\right)^2\left[-\frac{\lambda_2^2\lambda_3^2}{\lambda_1^2-\lambda_2^2}\right.$$
$$\left.\left.+ \frac{\lambda_2}{\sqrt{\lambda_1^2-\lambda_3^2}}\left(1 - \frac{\lambda_1^2}{\lambda_2^2-\lambda_3^2}\right)\left(\lambda_3^2 F(\beta, æ) - \frac{\lambda_2^2(\lambda_1^2-\lambda_3^2)}{\lambda_1^2-\lambda_2^2} E(\beta, æ)\right)\right]\right\};$$

$$P_{zz} = P_1 + \frac{\nu}{5}(\alpha_1 - \alpha_2)\left\{\frac{K}{K+2\alpha}\left[\frac{\lambda_2\lambda_3^2}{(\lambda_2^2-\lambda_3^2)\sqrt{\lambda_1^2-\lambda_3^2}}(F(\beta, æ) - E(\beta, æ))\right]\right.$$
$$+\frac{\langle R^2\rangle}{\langle R_0^2\rangle}\lambda_3^2 + \left(\frac{K}{K+2\alpha}\right)^2\left[\lambda_3^2 + \frac{\lambda_2\lambda_3^2}{\sqrt{\lambda_1^2-\lambda_3^2}}\left(1 + \frac{\lambda_1^2}{\lambda_2^2-\lambda_3^2}\right)\right.$$
$$\left.\left.\times (E(\beta, æ) - F(\beta, æ))\right]\right\} \tag{41}$$

where

$$P_1 = P_0 + \frac{2\nu}{5}(\alpha_1 - \alpha_2)\left[\frac{\alpha}{K+2\alpha} - \left\langle \frac{r^2}{Nl^2}\right\rangle - \left\langle \frac{(\vec{R}' - \vec{r})^2}{Nl^2}\right\rangle\right] \tag{42}$$

is a common term in the expressions for P_{ii}. Asymmetry P_{ii} relative to λ_i is connected with the assumption $\lambda_1 \geqslant \lambda_2 \geqslant \lambda_3$ made while calculating $\Phi(\lambda_1, \lambda_2, \lambda_3)$ and expressions (39).

Passing from the polarizabilities to the refractive indexes by means of the Lorentz–Lorenz formula

$$(n^2-1)/(n^2+2) = (4\pi/3)\cdot P \tag{43}$$

we have

$$\frac{4\pi}{3}(P_1-P_2) = \frac{n_1^2-1}{n_1^2+2} - \frac{n_2^2-1}{n_2^2+2} \approx \frac{6\bar{n}}{(\bar{n}^2+2)}\Delta n \tag{44}$$

hence

$$\Delta n = \frac{2\pi(\bar{n}^2+2)^2}{9\bar{n}}(P_1-P_2) \tag{45}$$

where $\bar{n}$ is the mean value of the refractive index, P_1 and P_2 are two of the three main polarizabilities given by Eq. (41).

COMPARISON OF THE THEORY WITH EXPERIMENT

A detailed comparison of the consequences from the expression (20) with the deformational dependences of various types has already been carried out in the work.[19] Particularly it has been found in these works that for an uniaxial tension the connection between the actual stress σ and the extension ratio λ is given by the relation:

$$\sigma = vkT\frac{\langle R^2\rangle}{\langle R_0^2\rangle}\left(\lambda^2-\frac{1}{\lambda}\right)+vkT\left(\frac{K}{K+2\alpha}\right)^2 \times\left[-\frac{1}{\lambda}+\frac{3}{2}\frac{\lambda^2}{\lambda^3-1}+\frac{\lambda^5-4\lambda^2}{2(\lambda^3-1)^{3/2}}\tan^{-1}\sqrt{\lambda^3-1}\right] \tag{46}$$

The form of the dependence in Mooney–Rivlin coordinates[5] at $C_1 = vkT/2(\langle R^2\rangle/\langle R_0^2\rangle) = 0.5$ and $C_c = vkT/2[K/(K+2\alpha)]^2 = 1$ is shown in Figure 4. As one can see from the figure, the dependence of $\sigma/2(\lambda^2-1/\lambda)$ on $1/\lambda$ has a pronounced linear part (deviation from linearity is less than 1%) lying within the limits $0.25 < 1/\lambda < 0.85$, i.e. in that region of λ variation where experimental data may be obtained with sufficient accuracy. Such a form of the dependence of stress on extension ratio is equivalent to Mooney–Rivlin formula confirmed perfectly for uniaxial extension by numerous experimental data.[5,28] As for the deviations from the linearity at $1/\lambda < 0.25$ and $1/\lambda > 0.85$, they can not be found in common experiments, in the first case, due to inaccessibility of the region $\lambda > 4.0$ to be measured (non-Gaussian effects arise), in the second case, large experimental errors at small deformations. Experimental data confirming the existence of such deviations are given in the work.[19]

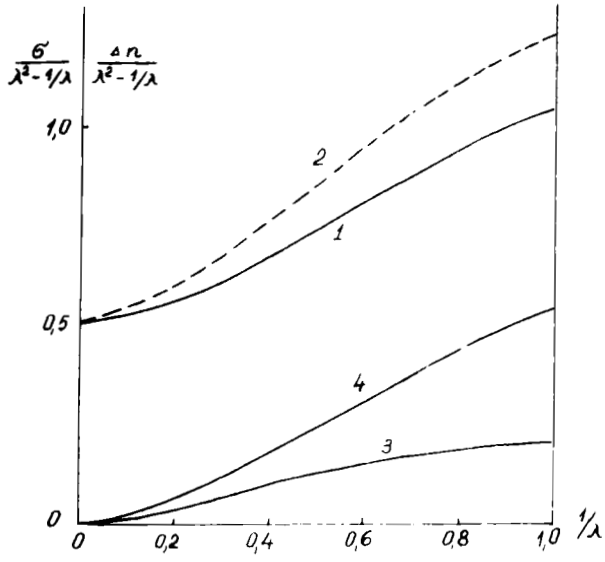

FIGURE 4 Theoretical dependencies for uniaxial extension in Mooney–Rivlin coordinates. 1—$\sigma/2\ (\lambda^2 - 1/\lambda)$ (formula (46)) at $C_1 = 0.5$, $C_c = 1.0$; 2—$\Delta n/2(\lambda^2 - 1/\lambda)$ (formula (50)) at $C_1 = 0.5$, $C_c = 1.0$, $c = 1.0$ and $K(K + 2\alpha) = 1$; 3—$\Phi_1/(\lambda^2 - 1/\lambda)$; 4—$\Phi_2/(\lambda^2 - 1/\lambda)$.

Let us calculate now the value of birefringence in rubber at uniaxial extension. Assuming $P_1 = P_{xx}$, $P_2 = P_{yy}$ in formula (35) and $\lambda_1 = \lambda$; $\lambda_2 = \lambda_3 = 1/\sqrt{\lambda}$ and bearing in mind that[30]

$$F(\beta, \varkappa) = A_0 + \frac{1}{2} A_1 \varkappa^2 + \frac{3}{8} A_2 \varkappa^4 + \cdots$$

$$E(\beta, \varkappa) = A_0 - \frac{1}{2} A_1 \varkappa^2 - \frac{1}{8} A_2 \varkappa^4 - \cdots \tag{47}$$

where

$$A_0 = \int_0^\beta du = \sin^{-1} \frac{\sqrt{\lambda^3 - 1}}{\lambda^{3/2}} = \tan^{-1} \sqrt{\lambda^3 - 1};$$

$$A_1 = \int_0^\beta \sin^2 u \, du = \frac{1}{2} \tan^{-1} \sqrt{\lambda^3 - 1} - \frac{\sqrt{\lambda^3 - 1}}{2\lambda} \tag{48}$$

after doing the uncertainty

$$\lim_{\substack{\lambda_2 \to 1/\sqrt{\lambda} \\ \lambda_3 \to 1/\sqrt{\lambda}}} \left\{ \frac{1}{\lambda_2^2 - \lambda_3^2} [F(\beta, \varkappa) - E(\beta, \varkappa)] \right\}$$

$$= \frac{\lambda^4}{2(\lambda^3 - 1)} \tan^{-1} \sqrt{\lambda^3 - 1} - \frac{\lambda}{2\sqrt{\lambda^3 - 1}} \tag{49}$$

we find

$$\Delta n = \frac{2\pi\nu(\bar{n}^2+2)^2}{45\,\bar{n}}(\alpha_1-\alpha_2)\left\{\frac{K}{K+2\alpha}\left[\frac{2\lambda^3+1}{2(\lambda^3-1)}-\frac{3}{2}\frac{\lambda^3}{(\lambda^3-1)^{3/2}}\tan^{-1}\sqrt{\lambda^3-1}\right]\right.$$
$$+\frac{\langle R^2\rangle}{\langle R_0^2\rangle}\left(\lambda^2-\frac{1}{\lambda}\right)+\left(\frac{K}{K+2\alpha}\right)^2\left[-\frac{1}{\lambda}+\frac{3}{2}\frac{\lambda^2}{\lambda^3-1}+\frac{\lambda^5-4\lambda^2}{2(\lambda^3-1)^{3/2}}\right.$$
$$\left.\left.\times\tan^{-1}\sqrt{\lambda^3-1}\right]\right\}$$
$$=\frac{2\pi\nu(\bar{n}^2+2)^2}{45\,\bar{n}}(\alpha_1-\alpha_2)\left[\frac{K}{K+2\alpha}\Phi_1+\frac{\langle R^2\rangle}{\langle R_0^2\rangle}\left(\lambda^2-\frac{1}{\lambda}\right)+\left(\frac{K}{K+2\alpha}\right)^2\Phi_2\right]. \quad (50)$$

From the comparison of the formulae (46) one can easily see that the latter contains the extra terms (the first square bracket in formula (50)) along with the expression proportional to σ. Thus it follows from the theory suggested that Bruster's law does not hold, contrary to numerous experimental data. Let us analyse how essential the contradiction is. For the sake of this let us consider the dependence of $\Delta n/2(\lambda^2-1/\lambda)$ on $1/\lambda$. In Figure 4 the dependences are shown of $\Phi_1/(\lambda^2-1/\lambda)$ and $\Phi_2/(\lambda^2-1/\lambda)$ on $1/\lambda$. They are practically linear in the whole interval of λ accessible for the measurements. Their limiting values at $\lambda \to 1$ are equal to 0.200 and 0.533, respectively. Unfortunately, we cannot compare the values of coefficients in front of square brackets in (50) since the values of K are unknown and one is not sure that the relation between the coefficients will be the same when dividing the chain into a larger number of submolecules. But assuming $K/2(K+2\alpha) = 1$ then the contribution into Δn from the extra term Φ_1 must be less than 40% of the term Φ_2 contribution.

Thus according to the theory presented, the dependences of Δn on λ must be close to a straight line in Mooney–Rivlin coordinates, but their slope should be slightly larger than that for the corresponding ones for σ. In Figure 4 the dependence of $\Delta n/2(\lambda^2-1/\lambda)$ on $1/\lambda$, calculated by the formula (50) at $C_1 = 0.5$; $C_c = 1.0$; $K/(K+2\alpha) = 1$, and $c = 2\pi\nu(\bar{n}^2+2)^2(\alpha_1-\alpha_2)/45\bar{n}kT = 1$, is shown. At such a relation between σ and Δn Bruster's law is held with sufficient accuracy. The ratio $\Delta n/\sigma$ is changed only by 10% when λ varying from 1 to 3. That is well within the limits of the experimental errors for the most of experiments.

The literature evidence[21,22] shows that the dependence of Δn on λ are really linearized in Mooney–Rivlin coordinates, i.e. analogous to the stress

$$\sigma/2(\lambda^2-1/\lambda) = A_1 + A_2/\lambda \quad (51)$$

they can be presented in the form:

$$\Delta n/2(\lambda^2-1/\lambda) = B_1 + B_2/\lambda \quad (52)$$

At the same time $A_2/A_1 \neq B_2/B_1$. The scattering of the data, however, is very

large. Thus, according to Ishikawa and Nagai[21] studying three samples of cis-polybutadiene at different temperatures the ratio B_2A_1/B_1A_2 varies from 1.04 to 2.44, and for three out of twelve their results given there it is even less than 1. In the work of Ilavsky and Prins[22] studying ten samples of Poly(2-hydroxyethyl methacrylate) with various density of network cross-links for four cases out of twenty-eight the value of $B_2A_1/B_1A_2 < 1$ were also observed. However, judging by the datum scattering these results should be regarded as experimental errors. And average values of B_2A_1/B_1A_2 are equal to 1.3 in the first work and to 1.7 in the second one that is in reasonable agreement with the theory suggested. More detailed examination of the theory would be possible only after analysing the structure of the coefficients in formula (50) and obtaining more reliable experimental data.

As mentioned above the detailed comparison of the consequences from the expression (20) for various types of deformational dependences has already been carried out in the work.[19] The model of a "channel" used here gives not only the possibility of more strict presentation of the theory based on the ideas about steric interaction of the network chains but helps to reveal the structure of the coefficient C_c (an analog of C_2 in Mooney–Rivlin equation). It gives new possibilities for further experimental checks which will be the subject of the following works.

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