MOLECULAR ORIGIN OF CONSTANTS IN THE THEORY OF RUBBER-LIKE ELASTICITY CONSIDERING NETWORK CHAINS STERIC INTERACTION

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Abstract - A theory of rubber-like elasticity is suggested, based on the "channel" model simulating the network chains steric interaction. The theory describes well the stress-strain dependences for various types of deformation. In particular, for an uniaxial tension the theoretical dependences are straightened in Mooney-Rivlin coordinates. The two elastic constants of the theory are expressed in terms of the network molecular parameters. Dependences of these constants on the network density, temperature, swelling ratio and chemical structure of a polymer are discussed.

INTRODUCTION

The problem of divergences between the classical theory of rubber-like elasticity and experimental data has been actively discussed in scientific literature for many years. Lately the increasing number of authors has been inclined to see the reasons for these divergences in the network chain steric interaction not taken into account by the classical theory. Historically Flory (Ref. 1) was the first who tried to take into consideration the steric interaction of chains. As early as in 1944 he pointed out that chain entanglements could be considered as additional effective network junctions. Since that time the entanglement concept has been widely used. Its various aspects were discussed in the review of Grassley (Ref. 2). Nevertheless, this concept does not embrace the whole problem of the chains steric interaction for, at least, two reasons. Firstly, in a block elastomer every chain is contacting the surrounding chains along its whole contour, i.e. steric interaction distribution is practically continuous. It is this reason that makes the assumption of the chain contour changes being affine under an instantaneous deformation, used in the theory of nonequilibrium properties (Ref. 3), a realistic one. As for the entanglement theory (Ref. 2), it assumes that entanglements are separated by large distances from one another. Secondly, though entanglements are limiting, similarly to junctions, the number of acceptable chains conformations this limitation is of a different nature due to a possibility of sliding in the contact points. This prevents us from identifying the entanglements with really chemical junctions.

In the recently published works (Ref. 4,5) Flory rather thoroughly discussed the nature of network chains steric interaction, but has come, in our view, to an erroneous conclusion that such an interaction could be accounted for by applying a restriction only on the junctions' fluctuations. A theory based on this, with a corresponding choice of parameters, is qualitatively simulating regularities witnessed for a cross-linked rubber under a uniaxial strain. Unfortunately, these parameters could not be directly associated with the structure of both the network and its chains.

We believe that to account for the steric interaction there is a more perspective direction of using the "channel" or "tube" model (Ref. 6,7) ensuring simulation of steric interaction along the whole contour of the chain. The physical idea on which the above works are based is very similar to that used in a number of previously published works by the author (Ref. 8-11) where a high elasticity theory suggested was satisfactorily fitting the experiment in describing strain dependencies of different types. Applying the "channel" model to the author's ideas (Ref. 12, 13) made it possible for

the theory to become more strict,although it has not changed the final inter-
relations. Unfortunately, the problem solution in the works (Ref. 12, 13) re-
presents but the first approximation. Finding higher approximations is hin-
dered by mathematical difficulties in an analytical as well as in a numeri-
cal solution. This prevents us from making more precise the strain depen-
dence of free energy component conditioned by steric interaction and, which
is the main point, from expressing the preceding coefficient through molecu-
lar parameters. In the present paper an attempt is being made to overcome
this difficulty by simplifying the model.

PHYSICAL PREMISES OF THE THEORY

It is assumed in the classical theory of rubber-like elasticity (Ref. 14)
that the chain   interaction is taking place only in the network   juncti-
ons, so the chains can adopt all the conformations possible with a certain
junctions location. A situation true for a real block elastomer could be as-
sumed to be as that shown in Fig. 1. Here the thick line denotes a frag-
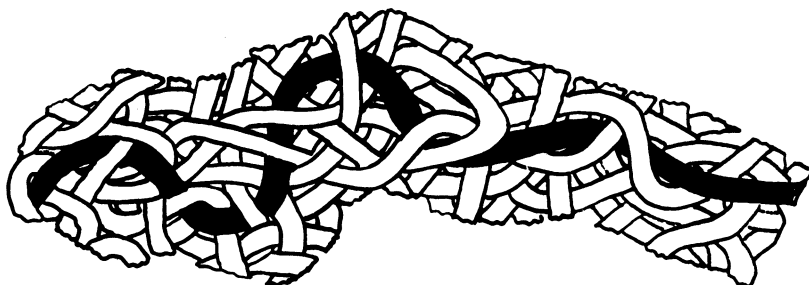

Fig. 1. Packing of macromolecules in a block elastomer.

ment of the chain under consideration. The chain is contacting its neigh-
bours   all along its contour. A change of its conformation can occur due
to: a) presence of free volume element in vicinity of chain; b) exchanging
places of its segments with the segments of neighbouring chains; c) a mutual
displacement of the chain   fragments with the fragments of neighbouring
chains in the same direction.

In the last case there arises from the neighbouring chains an elastic reac-
tion (of a kinetic nature) tending to bring back the chain under considera-
tion to its former position. In the equilibrium state analysis it is the lat-
ter type of steric interaction that matters, so the chain location in a
block elastomer can be assumed to be as is shown schematically in Fig. 2,
and the chain displacement limitations are caused not only by entanglements
(denoted by "a") but also by chains crossing the given chain ("b"). Due to
such limitations the chain fluctuates near its certain location ("channel")
whose conformation is determined by the molecules interlocation in the net-
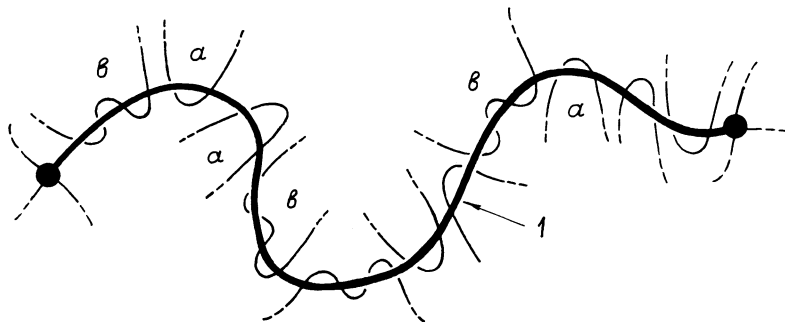work's formation moment. Obviously, the neighbours are limiting the chain

Fig. 2. The chain in a block elastomer (scheme). 1 - the chain
under consideration; a - entanglements; b - crossing chains.

fluctuations only in the direction normal to the channel contour. Fluctuations along the channel axis are free since they do not necessitate changes in the neighbours' location. That is why the chain turns out to be uniformly, on the average, elongated along its whole contour.

The situation described can be reproduced with the help of the model shown in Fig. 3. Here the thick line denotes one of the chain's possible confor-
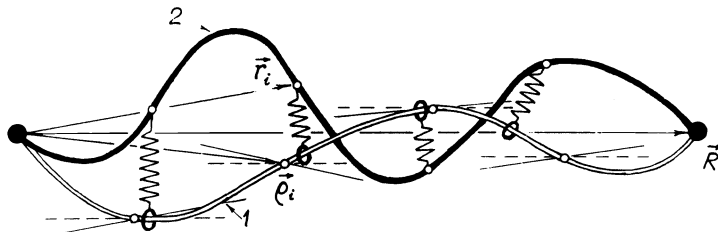

Fig. 3. The model of "channel". 1 - channel; 2 - the chain under consideration.

mations and the light line - the channel contour. The chain is divided into a certain number of equal fragments - submolecules whose junction points are connected to the channel by springs simulating the reaction of neighbouring chains. The springs are rigidly fixed to the chain and freely sliding along the channel contour. It is assumed that: a) the chains are Gaussian; b) the distribution function of channel conformations is the same as for the isolated chain fixed in the same points; c) when the material is strained the deformation of all the channel contours is affine.

For the final formulation of the model it is necessary to make two more statements. Firstly, since the channel conformation is determined by the distribution function of the channel dividing points only, a need arises to specially denote the term of "the channel axis direction in a given point". For such term we suggest the direction of a straight line connecting adjacent points dividing the chain. It is possible to show that this ensures a uniform, on the average, tension of the chain along its whole contour, which is required by the physical meaning of the problem. Such directions are shown in Fig. 3 by thin continuous lines. Secondly, as it was shown by James and Guth (Ref. 14), fluctuations of junctions in the phantom chains network do not depend on the network's deformation, so its entropy can be calculated assuming the junctions are fixed in their average locations whose displacements under deformation are affine. In the given case the situation is different. Since the junctions fluctuations are determined by fluctuations of the chains connected by these junctions, then in a real cross-linked elastomer these fluctuations must be considerably smaller than in a phantom chains network due to steric limitations imposed on the chains. Because these limitations are anisotropic (across the channel only), the limitations imposed on the junctions fluctuations should depend on the angles at which the chains are adjoining each other in the junctions and, in general case, should also be anisotropic. Under the network deformation the angles at which the chains are meeting in their junctions are changed, which in its turn causes the junction fluctuations change. The network's entropy change conditioned by the above should also be considered in the theory. The reasoning given is very close to the ideas developed by Flory in his already mentioned works (Ref. 4, 5). Although limitations imposed on the junctions are caused by the intermediate chain fragments fluctuations limitation, we believe it is erroneous to disregard the fluctuation limitations of the chains themselves and, connected with this, entropy change, as is the case with Flory.

The above reasoning creates necessary preconditions for the mathematical formulation of a problem but, as was stated already, the problem in the such form is unsolvable. Therefore, we make two simplifying suppositions, being aware

that they will change to a certain extent the final result. First, let us assume that the channel axis direction in every point of its division is the direction of a straight line connecting the chain's ends. Such directions are shown in Fig. 3 by thin dotted lines. Second, let us neglect the junctions fluctuation change under the network deformation, which makes it possible to view the junctions as fixed in their average locations. To evaluate the influence of these simplifications on the final result does not seem possible, but due to them the problem becomes solvable if the chain is divided into an arbitrary number of fragments " m + 1 ". At the moment we shall not connect " m " with any parameters of the network structure. This will be dealt with in the Discussion.

THEORY

Let us denote the chain ends connecting vector by $\vec{R} = X\vec{i} + Y\vec{j} + Z\vec{k}$, the vector connecting the chain's beginning with the "i" point of its division by $\vec{r_i} = x_i\vec{i} + y_i\vec{j} + z_i\vec{k}$, and the vector connecting the chain's beginning with the "i" point of the channel's division by $\vec{\rho_i} = \xi_i\vec{i} + \eta_i\vec{j} + \zeta_i\vec{k}$. If a sample is subjected to a deformation in respect of λ_1, λ_2, λ_3 along the three mutually perpendicular directions then, in accordance with the suppositions made in formulating the model, the vectors $\vec{R}$ and $\vec{\rho_i}$ are transformed into $\vec{R'}$ and $\vec{\rho_i'}$, respectively:

$$\vec{R'} = \lambda_1 X\vec{i} + \lambda_2 Y\vec{j} + \lambda_3 Z\vec{k}; \quad \vec{\rho_i'} = \lambda_1 \xi_i\vec{i} + \lambda_2 \eta_i\vec{j} + \lambda_3 \zeta_i\vec{k} \tag{1}$$

The problem is to find out the network's free energy, F :

$$F = \nu k T \alpha_m \left\langle r_1^2 + (\vec{r_2} - \vec{r_1})^2 + (\vec{r_3} - \vec{r_2})^2 + \ldots + (\vec{R'} - \vec{r_m})^2 \right\rangle_{r, \rho, R} \tag{2}$$

where

$$\alpha_m = 3(m+1)/2N\ell^2 \tag{3}$$

m is the number of dividing points, N is the number of the chain's statistical segments, ℓ is their length, ν is the number of chains in the unit volume, k is Boltzmann's constant and T is the absolute temperature. The subscriptes r , ρ and R near the angular brackets in (2) signify that the averaging should be carried out on all possible conformations of the chain at a given location of the channel, on all possible locations of the channel and orientations of the vector $\vec{R}$.

If the rigidity of springs in the model shown in Fig. 3 is denoted by K', then the function of the chains conformations distribution at a given location of the channel can be written as:

$$w_r(\vec{r_1}, \vec{r_2} \ldots \vec{r_m}) d\vec{r_1} d\vec{r_2} \ldots d\vec{r_m} = \Omega_r \, exp\left\{-\alpha_m\left[r_1^2 + \right.\right.$$

$$+ (\vec{r_2} - \vec{r_1})^2 + \ldots + (\vec{R'} - \vec{r_m})^2\right]\right\} exp\left\{-\frac{K'}{2kT}\left[h_1^2 + \right.\right.$$

$$\left.\left. + h_2^2 + \ldots + h_m^2 \right]\right\} d\vec{r_1} d\vec{r_2} \ldots d\vec{r_m} \tag{4}$$

The last exponent in the expression (4) is the Boltzmann's factor taking into account a decrease in the probability of chain's conformations existence as the chain deviates from the channel. Here Ω_r is the normalization factor, and $\vec{h_i}$ is the projection of the vectors $\vec{r_i} - \vec{\rho_i'}$ on the plane perpendicular to the vector $\vec{R'}$, i.e.:

$$\vec{h_i} = \left[\left[(\vec{r_i} - \vec{\rho_i'})\vec{R'}\right]\vec{R'}\right] / \vec{R'}^2 \tag{5}$$

It is easy to see that the distribution function (4) can be presented as a product of two functions - the distribution function for projections of the submolecules lengths onto the vector $\vec{R'}$:

$$W_{rR}(r_{1R}, r_{2R} \ldots r_{mR}) dr_{1R} dr_{2R} \ldots dr_{mR} =$$

$$= \Omega_{rR} exp\left\{-\alpha_m \left[r_{1R}^2 + (r_{2R} - r_{1R})^2 + \ldots + (|\vec{R}'| - r_{mR})^2\right]\right\} dr_{1R} dr_{2R} \ldots dr_{mR} \qquad (6)$$

and the distribution function for projections of the vectors $\vec{r_i}$ onto the plane normal to the vector $\vec{R}'$:

$$W_{rs}(\vec{r_{1s}}, \vec{r_{2s}} \ldots \vec{r_{ms}}) d\vec{r_{1s}} d\vec{r_{2s}} \ldots d\vec{r_{ms}} =$$

$$= \Omega_{rs} exp\left\{-\alpha_m \left[r_{1s}^2 + (\vec{r_{2s}} - \vec{r_{1s}})^2 + \ldots + (\vec{r_{ms}} - \vec{r_{m-1,s}})^2 + r_{ms}^2\right] - \right.$$

$$\left. - \frac{K'}{2kT}\left[(\vec{r_{1s}} - \vec{\varrho_{1s}'})^2 + (\vec{r_{2s}} - \vec{\varrho_{2s}'})^2 + \ldots + (\vec{r_{ms}} - \vec{\varrho_{ms}'})^2\right]\right\} d\vec{r_{1s}} d\vec{r_{2s}} \ldots d\vec{r_{ms}} \qquad (7)$$

where

$$\vec{r_{is}} = \left[[\vec{r_i} \vec{R}']\vec{R}'\right]/R'^2; \quad \vec{\varrho_{is}'} = \left[[\vec{\varrho_i'} \vec{R}']\vec{R}'\right]/R'^2; \quad \vec{h_i} = \vec{r_{is}} - \vec{\varrho_{is}};$$

$$r_{iR} = (\vec{r_i} \vec{R}')/|\vec{R}'| \qquad (8)$$

Thus the averaging on all possible conformations of the chain at a given location of the channel comes to the solution of two problems: a one-dimensional problem for the chain with freely fluctuating division points and two-dimensional problem for the chain whose division points are linked with the channel by means of springs. The graphic scheme of the second problem is shown in Fig. 4. Such a division of the distribution function, leading
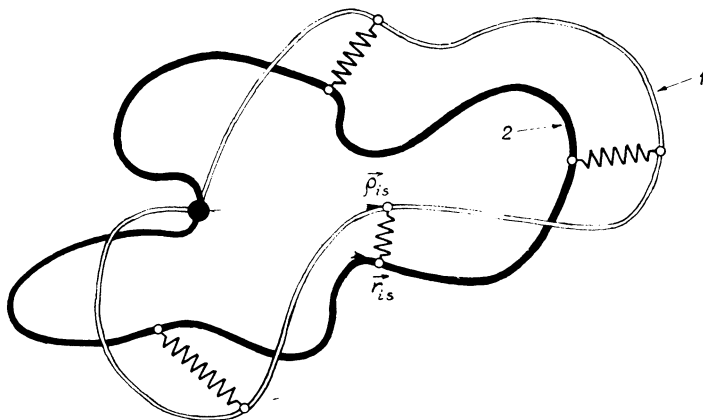

Fig. 4. The channel model projection onto the plane perpendicular to $\vec{R}'$: 1 — the channel; 2 — the chain under consideration.

to a considerable simplification of the mathematical aspect of the problem, proves to be possible only after the simplifying assumption of the channel's axis being parallel in all its points to the vector $\vec{R}'$. Otherwise the coordinates of all the submolecules become part of the W_r function, in the form of products, and the analytical averaging by the latter seems impossible. Now the expression for F can be written in the following form:

$$F = F_R + F_s = \nu kT\alpha_m \left[\left\langle r_{1R}^2 + (r_{2R} - r_{1R})^2 + \ldots + (|\vec{R}'| - r_{mR})^2\right\rangle_{r,\varrho,R} + \right.$$

$$\left. + \left\langle r_{1s}^2 + (\vec{r_{2s}} - \vec{r_{1s}})^2 + \ldots + (\vec{r_{ms}} - \vec{r_{m-1,s}})^2 + r_{ms}^2\right\rangle_{r,\varrho,R}\right] \qquad (9)$$

Averaging of the expression within the first angular brackets is not difficult. It is obvious that

$$\left\langle r_{1R}^2 + (r_{2R} - r_{1R})^2 + \ldots + (|\vec{R}'| - r_{mR})^2\right\rangle_r = -d\ln \mathcal{J}_{rR}/d\alpha_m \qquad (10)$$

where

$$J_{rR} = \underbrace{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty}}_{m} W_{rR} \, dr_{1R} \, dr_{2R} \ldots dr_{mR} \qquad (11)$$

Using the transformation

$$r_{iR} = U_i + (i/i+1)U_{i+1} + \ldots + (i/m)U_m + (i/m+1)|\vec{R}'| \qquad (12)$$

the exponent index in (6) is reduced to a diagonal form, and after integration we have

$$J_{rR} = \Omega_{rR} \sqrt{\pi^m / \alpha_m^m (m+1)} \, exp\left[-\alpha_m (R'^2/m+1)\right] \qquad (13)$$

from which

$$\left\langle r_{1R}^2 + (r_{2R} - r_{1R})^2 + \ldots + (|\vec{R}'| - r_{mR})^2 \right\rangle_r = m/2\alpha_m + (\lambda_1^2 X^2 + \lambda_2^2 Y^2 + \lambda_3^2 Z^2)/(m+1) \qquad (14)$$

Since this expression does not depend on the coordinates of the channel division points and

$$\langle X^2 \rangle = \langle Y^2 \rangle = \langle Z^2 \rangle = \langle R^2 \rangle / 3 \qquad (15)$$

then, after substituting it in (9), we have

$$F_R = m\nu kT/2 + (\nu kT/2)(\langle R^2 \rangle / Ne^2)(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) \qquad (16)$$

which differs only by a constant (that can be neglected furthermore) from the expression for the free energy, arising from the classical theory of rubber-like elasticity. Thus the classical component of free energy is connected with the deformations of chains in the "longitudinal direction".

To average the expression in the second angular brackets in (9) we shall use the same method:

$$\left\langle r_{1s}^2 + (\vec{r}_{2s} - \vec{r}_{1s})^2 + \ldots + (\vec{r}_{ms} - \vec{r}_{m-1,s})^2 + r_{ms}^2 \right\rangle = -d \ln J_{rs}/d\alpha_m \qquad (17)$$

$$J_{rs} = \underbrace{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty}}_{m} W_{rs} \, d\vec{r}_{1s} \, d\vec{r}_{2s} \ldots d\vec{r}_{ms} \qquad (18)$$

To reduce the exponent index in the distribution function W_{rs} to a diagonal form it is convenient to use the method of Jacoby (Ref. 15) in accordance with which the diagonalized square form can be expressed as:

$$B(\vec{U}_1, \vec{U}_2 \ldots \vec{U}_m) = \mathcal{D}_1 U_1^2 + (\mathcal{D}_2/\mathcal{D}_1)U_2^2 + \ldots + (\mathcal{D}_m/\mathcal{D}_{m+1})U_m^2 + (\mathcal{D}_{m+1}/\mathcal{D}_m) \qquad (19)$$

where $\mathcal{D}_i$ are the angular minors of the i order of the original square form $B(\vec{r}_{1s}, \vec{r}_{2s} \ldots \vec{r}_{ms})$. Since the Jacobian of this transformation equals to unity as in the case of the equation (12), then

$$J_{rs} = \Omega_{rs} \sqrt{\pi^m / \mathcal{D}_m} \, exp\left(-\mathcal{D}_{m+1}/\mathcal{D}_m\right) \qquad (20)$$

and

$$-d \ln J_{rs}/d\alpha_m = (d \ln \mathcal{D}_m/d\alpha_m)/2 + \left[d(\mathcal{D}_{m+1}/\mathcal{D}_m)\right]/d\alpha_m \qquad (21)$$

For $\mathcal{D}_i$ the following recurrent correlation is correct:

$$\mathcal{D}_i = (2\alpha_m + K)\mathcal{D}_{i-1} - \alpha_m^2 \mathcal{D}_{i-1} \qquad (22)$$

and it is expressed by polynomials of Chebyshev (Ref. 16) of the second kind:

$$\mathcal{D}_i = \alpha_m^i U_i(1 + K/2\alpha_m); \quad U_i(\delta) = Sinh(i+1)\delta/Sinh\,\delta \qquad (23)$$

Here a new designation was introduced:

$$K = K'/2kT \tag{24}$$

Direct calculations are easily showing that algebraic complements for the ij element of the determinant $\mathscr{D}_m$ have the form of:

$$A_{ij} = \alpha_m^{j-i} \mathscr{D}_{i-1} \mathscr{D}_{m-j} = \alpha_m^{m-1} U_{i-1}(1 + K/2\alpha_m) U_{m-j}(1 + K/2\alpha_m)$$

at $j \geqslant i$ and

$$A_{ij} = \alpha_m^{i-j} \mathscr{D}_{j-1} \mathscr{D}_{m-i} = \alpha_m^{m-1} U(1 + K/2\alpha_m) U_{m-i}(1 + K/2\alpha_m) \tag{25}$$

at $i \geqslant j$.

With the help of these expressions we can calculate $\mathscr{D}_{m+1}$ using the formula for the bordered determinant (Ref. 17):

$$\mathscr{D}_{m+1} = \mathscr{D}_m K \sum_{i=1}^{m} \varrho_{is}'^2 - K^2 \alpha_m^{m-1} \sum_{i=1}^{m} U_{i-1} U_{m-j} \varrho_{is}'^2 -$$

$$- 2K^2 \sum_{j=1}^{m} \sum_{i=1}^{j-1} U_{i-1} U_{m-j} (\vec{\varrho}_{is}' \vec{\varrho}_{js}') \tag{26}$$

Substituting expressions (23) and (26) into the formula (17) and taking into account the correlation (8) we get the following:

$$\langle r_{1s}^2 + (\vec{r}_{2s} - \vec{r}_{1s})^2 + \ldots + (\vec{r}_{ms} - \vec{r}_{m-1,s})^2 + r_{ms}^2 \rangle_r = (d\mathscr{D}_m/d\alpha_m)/2 +$$

$$+ K^2 \sum_{i=1}^{m} \left([\vec{\varrho}_i' \vec{R}']^2 / R'^2 \right) \left\{ d \left(U_{i-1} U_{m-i} / \alpha_m U_m \right) / d\alpha_m \right\} +$$

$$+ 2K^2 \sum_{j=1}^{m} \sum_{i=1}^{j-1} \left\{ \left([\vec{\varrho}_i' \vec{R}'][\vec{\varrho}_j' \vec{R}'] \right) / R'^2 \right\} \left\{ d \left(U_{i-1} U_{m-j} / \alpha_m U_m \right) / d\alpha_m \right\} \tag{27}$$

The first summand in the right hand part can be neglected henceforth, since it does not depend on λ_i. The expression (27) should be averaged by the distribution function W_ϱ determining the probability of the channel division points location:

$$W_\varrho(\vec{\varrho}_1, \vec{\varrho}_2 \ldots \vec{\varrho}_m) d\vec{\varrho}_1 d\varrho_2 \ldots d\vec{\varrho}_m =$$

$$= (m+1)^{3/2} (\alpha_m/\pi)^{3m/2} \exp\left(\alpha_m R^2/(m+1)\right) \exp\left\{ -\alpha_m \left[\varrho_1^2 + \right.\right.$$

$$\left.\left. + (\vec{\varrho}_2 - \vec{\varrho}_1)^2 + \ldots + (\vec{\varrho}_m - \vec{\varrho}_{m-1})^2 + (\vec{R} - \vec{\varrho}_m)^2 \right] \right\} d\vec{\varrho}_1 d\vec{\varrho}_2 \ldots d\vec{\varrho}_m \tag{28}$$

The change of variables

$$\vec{\varrho}_i = \vec{p}_i + (i/i+1)\vec{p}_{i+1} + (i/i+2)\vec{p}_{i+2} + \ldots + (i/m)\vec{p}_m + (i/m+1)\vec{R} \tag{29}$$

analogous to the change of (12) leads to the following form of W_ϱ:

$$W_\varrho(\vec{p}_1, \vec{p}_2, \ldots \vec{p}_m) d\vec{p}_1 d\vec{p}_2 \ldots d\vec{p}_m =$$

$$= (m+1)^{3/2}(\alpha_m/\pi)^{3m/2} \exp\left(\alpha_m R^2/m+1\right) \exp\left\{ -\alpha_m \left[2p_1^2 + \right.\right.$$

$$\left.\left. + \frac{3}{2}p_2^2 + \frac{4}{3}p_3^2 + \ldots + \frac{i+1}{i}p_i^2 + \ldots + \frac{m+1}{m}p_m^2 + \frac{1}{m+1}R^2 \right] \right\} d\vec{p}_1 d\vec{p}_2 \ldots d\vec{p}_m \tag{30}$$

Let us consider now the scalar product in the expression (27):

$$\left([\vec{\varrho}_i' \vec{R}'][\vec{\varrho}_j' \vec{R}'] \right) = \sum_{k=0}^{m-i} \sum_{\ell=0}^{m-j} \frac{ij}{(i+k)(j+\ell)} \left([\vec{p}_{i+k}' \vec{R}'][\vec{p}_{j+\ell}' \vec{R}'] \right) =$$

$$= \sum_{k=0}^{m-i} \sum_{\ell=0}^{m-j} \frac{ij}{(i+k)(j+\ell)} \left[\lambda_2^2 \lambda_3^2 (v_{i+k}Z - w_{i+k}Y)(v_{j+\ell}Z - w_{j+\ell}Y) + \right.$$

$$\left. + \lambda_1^2 \lambda_3^2 (w_{i+k}X - u_{i+k}Z)(w_{j+\ell}X - u_{j+\ell}Z) + \lambda_1^2 \lambda_2^2 (u_{i+k}Y - v_{i+k}X)(u_{j+k}Y - v_{j+k}X) \right] \quad (31)$$

Here

$$\vec{p}_i = u_i \vec{i} + v_i \vec{j} + w_i \vec{k}; \quad \vec{p}_i' = \lambda_1 u_i \vec{i} + \lambda_2 v_i \vec{j} + \lambda_3 w_i \vec{k} \quad (32)$$

When averaging by the distribution function W_ρ all the members containing multipliers of the $u_i u_j$ or the $u_i v_i$ type result in zero, and

$$\langle u_i^2 \rangle = \langle v_i^2 \rangle = \langle w_i^2 \rangle = i/2\alpha_m (i+1) \quad (33)$$

Then, after summation over k and i, we have:

$$\left\langle \left([\vec{p}_i' \vec{R}'][\vec{p}_j' \vec{R}'] \right) \right\rangle_{r,\varrho} =$$

$$= i(m-j+1)\left[(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) R'^2 - \lambda_1^4 X^2 - \lambda_2^4 Y^2 - \lambda_3^4 Z^2 \right] / 2\alpha_m (m+1) \quad (34)$$

where $j \geqslant i$. Substituting the result into the formula (27) we have the following:

$$\left\langle r_{1s}^2 + (\vec{r}_{2s} - \vec{r}_{1s})^2 + \ldots + (\vec{r}_{ms} - \vec{r}_{m-1,s})^2 + r_{ms}^2 \right\rangle_{r,\varrho} = (d\mathscr{D}_m / d\alpha_m)/2 +$$

$$+ (2C_c / \nu kT)\left[\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - (\lambda_1^4 X^2 + \lambda_2^4 Y^2 + \lambda_3^4 Z^2)/(\lambda_1^2 X^2 + \lambda_2^2 Y^2 + \lambda_3^2 Z^2) \right] \quad (35)$$

where C_c denotes the sums independent of λ_i:

$$C_c = \frac{\nu kT K^2}{4} \frac{d}{d\alpha_m} \left[\sum_{i=1}^{m} \frac{i(m-i+1)}{m+1} \frac{U_{i-1} U_{m-i}}{\alpha_m U_m} + \right.$$

$$\left. + 2 \sum_{j=1}^{m} \sum_{i=1}^{j-1} \frac{i(m-j+1)}{m+1} \frac{U_{i-1} U_{m-j}}{\alpha_m U_m} \right] \quad (36)$$

The expression within the square brackets of formula (35) is identical with the respective expressions obtained earlier (Ref. 11-13) where it was averaged by orientation of the vector $\vec{R}$. Using the result obtained in those works we can put down the following:

$$F_s = \nu kT \alpha_m \left\langle r_{1s}^2 + (\vec{r}_{2s} - \vec{r}_{1s})^2 + \ldots + (\vec{r}_{ms} - \vec{r}_{m-1,s})^2 + r_{ms}^2 \right\rangle_{r,\varrho,R} =$$

$$+ 2C_c \left\{ \lambda_3^2 + \left(\lambda_2 \lambda_3^2 / \sqrt{\lambda_1^2 - \lambda_3^2} \right) F(\beta, \mathscr{x}) + \lambda_2 \sqrt{\lambda_1^2 - \lambda_3^2} \, E(\beta, \mathscr{x}) \right\}, \quad (37)$$

where $F(\beta, \mathscr{x})$ and $E(\beta, \mathscr{x})$ are incomplete elliptic integrals of the first and the second kinds, respectively:

$$F(\beta, \mathscr{x}) = \int_0^{\sin\beta} \frac{dt}{\sqrt{(1-t^2)(1-\mathscr{x}^2 t^2)}}; \quad E(\beta, \mathscr{x}) = \int_0^{\sin\beta} \sqrt{\frac{1-\mathscr{x}^2 t^2}{1-t^2}} \, dt \quad (38)$$

which modulus $\mathscr{x}$ and argument β are determined by the correlations:

$$\mathscr{x}^2 = \left[\lambda_1^2 (\lambda_2^2 - \lambda_3^2) \right] / \left[\lambda_2^2 (\lambda_1^2 - \lambda_3^2) \right]; \quad \sin\beta = \sqrt{\lambda_1^2 - \lambda_3^2} / \lambda_1 \quad (39)$$

Asymmetry of the expression (37) with respect to λ_i is connected with the assumption $\lambda_1 \geqslant \lambda_2 \geqslant \lambda_3$ made when averaging by orientation of the vector $\vec{R}$ although the initial expression (35) is completely symmetrical. Denoting in

the expression (36) U_i by hyperbolic functions and making summation we get after differentiation by α_m the following:

$$C_c = \frac{\nu k T K^2}{16 \alpha_m} \left\{ -\frac{Cosh\,\delta}{Sinh^3\delta} \left[Cnth\,\delta - (m+1) Cnth\,(m+1)\delta \right] + \right.$$

$$\left. + \frac{1}{Sinh^2\delta} \left[-\frac{1}{Sinh^2\delta} + \frac{(m+1)^2}{Sinh^2(m+1)\delta} \right] \right\} \qquad (40)$$

where

$$\delta = Cosh^{-1}(1 + K/2\alpha_m) \qquad (41)$$

Assuming m=1 we find out that

$$C_c = (\nu kT/4)(K/K + 2\alpha_1)^2 \qquad (42)$$

which fits the result obtained earlier for the first approximation (Ref. 12, 13). Starting from m=2 the value of $Cnth(m+1)\delta$ is practically equal to unit which makes it possible to simplify considerably the formula (40):

$$C_c \approx (\nu k T K^2 / 32 \alpha_m^2\, Sinh^4\delta) \left[(m+1) Sinh\,2\delta - Cosh\,2\delta - 3 \right] \qquad (43)$$

Thus finally the free energy of the deformed network takes the following form:

$$F = F_R + F_s = C_1 (\lambda_1^2 + \lambda_2^2 + \lambda_3^2) +$$

$$+ 2C_c \left\{ \lambda_3^2 + (\lambda_2 \lambda_3^2 / \sqrt{\lambda_1^2 - \lambda_3^2}) F(\beta, \varkappa) + \lambda_2 \sqrt{\lambda_1^2 - \lambda_3^2}\, E(\beta, \varkappa) \right\} \qquad (44)$$

where

$$C_1 = (\nu kT/2)(\langle R^2 \rangle / N \ell^2) \qquad (45)$$

and C_c is determined by the expression (43).

DISCUSSION

Geometric interpretation of F versus λ

The expression for the free energy (44) is a sum of two components of which the first is connected with changes of the chain "longitudinal" dimensions and the second with those of "lateral" ones. This revives to a certain degree the ideas of Kuhn (Ref. 18) who assumed that the entropy decrease of chains under deformation is connected with the change of their "length", "width" and "thickness". And though later on Kuhn refused to take into account the two latter constituents (Ref. 19), he pointed out that steric interaction of the chains should lead to the network modulus increase as compared with the classical theory prediction. One may consider that in the present paper an attempt is being made to quantitatively express these considerations of qualitative nature.

It turns out that the deformational dependence of the free energy constituent due to changes of chain lateral dimensions is different as compared with the constituent connected with changes of the chain lengths. To understand the reason for this as well as the reason for why the increase of the division points number, assuming the channel axis is parallel to the end-to-end vector $\vec{R}'$, does not change the nature of the F_s deformational dependence it will be helpful to analyse the model from the geometric point of view. Moreover such analysis will enable us to have a notion of degree of the final result deviation caused by the assumption of the channel axis being parallel to the vector $\vec{R}'$.

For the sake of simplification let us assume that the rigidity of springs in the model shown in Fig. 3 tends to infinity. Such an assumption will not distort the geometric analysis essence. Then in accordance with the simplifying assumptions made in the present work the chain division points will slide along the family of straight lines parallel to the vector $\vec{R}'$, as it
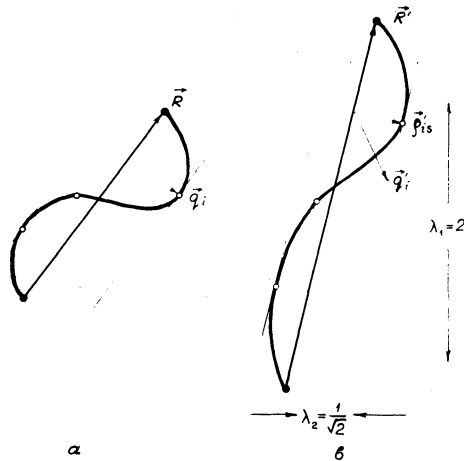
Fig. 5. The geometric scheme equivalent to the channel model
in the assumption of the channel axis being parallel to the
chain end-to-end vector. K $\rightarrow \infty$; a - the initial state;
b - the state under strain.

is shown in Fig. 5a. Location of these straight lines in respect of $\vec{R}$ is
determined by vectors $\vec{q}_i$ which modulus is a characteristic of their dis-
tance from $\vec{R}$. Values of $|\vec{q}_i|$ are determined by the distribution function
of the channel division points which, in accordance with the assumption made
in the model formulation, is supposed to be identical with the distribution
function for the isolated chain which ends are fixed in the same points.
When the sample is strained (Fig. 5b) the vectors $\vec{q}_i$ are transformed in
accordance with the same law as the vector $\vec{R}$:

$$\vec{q}_i' = \lambda_1 q_x \vec{i} + \lambda_2 q_y \vec{j} + \lambda_3 q_z \vec{k} \qquad (46)$$

but in a strained state it is not $|\vec{q}_i'|$ but $|\vec{\rho}_{is}'|$

$$\vec{\rho}_{is} = \big[[\vec{q}_i' \vec{R}']\vec{R}'\big]\big/R'^2 \qquad (47)$$

that are characterising the distance between the channel and the axis of
chain. And it is the difference in the transformation laws of $\vec{R}$ and $\vec{\rho}_{is}$
that causes a different nature of the deformational dependence of F_s as com-
pared with F_R . The law of $\vec{\rho}_{is}$ changing under strain (47) is a common one for
all the channel division points. It is this circumstance that leads to a
situation when the type of deformational dependence of F_s is preserved with
any number of the division points m. But this is correct only with the
assumption of the channel axis being parallel to the end-to-end vector.
Without this assumption when the channel axis is located at different angles
to $\vec{R}$ in various points of its division such a uniformity of $\vec{\rho}_{is}$ changing
under strain is broken.

An analysis of scheme in Fig. 5 enables us to make two more important con-
clusions. Firstly, since the type of the radial distribution function for
intermediate points of the chain, determining the distribution of $\vec{q}_i$, does
not depend on the distance between the chain's ends (Ref. 20), then the
increase of $\vec{R}$ should lead to the decrease of angles between the channel's
axis and the straight line connecting the chain's ends. Therefore F_s to a
certain degree should depend on $\langle R^2 \rangle$ in contrast to the result obtained in the
present work. Furthermore, under high strains when $|\vec{R}'|$ increases, the
channel axis tends to be parallel to $\vec{R}'$. It may be concluded from this that
refusal of simplifying assumption of the channel axis being parallel to the
end-to-end vector leads to a correction of the deformational dependence F_s
obtained in the present work, and first of all under small deformations.

Secondly, it is known that the value of additional (with respect to the classical one) constituent of stress in rubber under tension is decreasing with an increase of deformation. The reason for this is easily understood when considering Fig. 5. With an increase of deformation the angle between the vector $\vec{R}$ and the direction of elongation is decreasing, the channel is "forced" close to the straight line connecting the chain ends, and the change of $|\vec{\rho_{is}}|$ determining the value of f_s is continuously decreasing.

Analysis of the deformational dependence
A thorough comparison of consequences of the expression (44) with experimental data for various types of deformation was carried out elsewhere (Ref.11). It was shown there that the theory is in a good agreement with experiment in all cases, it being possible to describe the experimental results of Treloar (Ref. 21) for uniaxial and biaxial deformation and shear obtained with the same rubber, using the same values of C_1 and C_c. Small divergences in de- scribing the curves of two-dimensional extension and shear are seen only under small deformations. This fact acquires now especial interest in con- nection with the above made analysis. Here we shall confine ourselves to the consideration of the uniaxial deformation only. The dependences of stress under uniaxial extension f_e and compression f_c on λ , resulting from the expression (44), have the following form:

$$f_e = 2C_1\left(\lambda - \frac{1}{\lambda^2}\right) + 2C_c\left[-\frac{1}{\lambda} + \frac{3}{2}\frac{\lambda}{\lambda^3-1} + \frac{\lambda^4-4\lambda}{2(\lambda^3-1)^{3/2}}\tan^{-1}\sqrt{\lambda^3-1}\right] \quad (48)$$

$$f_c = 2C_1\left(\lambda - \frac{1}{\lambda^2}\right) + 2C_c\left[-\frac{1}{\lambda^2} + \frac{4\lambda-\lambda^4}{4(1-\lambda^3)^{3/2}}\ell n\frac{1+\sqrt{1-\lambda^3}}{1-\sqrt{1-\lambda^3}} - \frac{3}{2}\frac{\lambda}{1-\lambda^3}\right] \quad (49)$$

Calculated on their basis the dependence of $\varphi = f/2(\lambda-1/\lambda^2)$ on $1/\lambda$ at $C_1=0$ and $C_c=I$ is shown in Fig. 6. In agreement with experimental data the dependence possesses a well expressed linear part within the range of $1/\lambda$ changing from 0.2 to 0.85. Beyond this range the experimental data in the
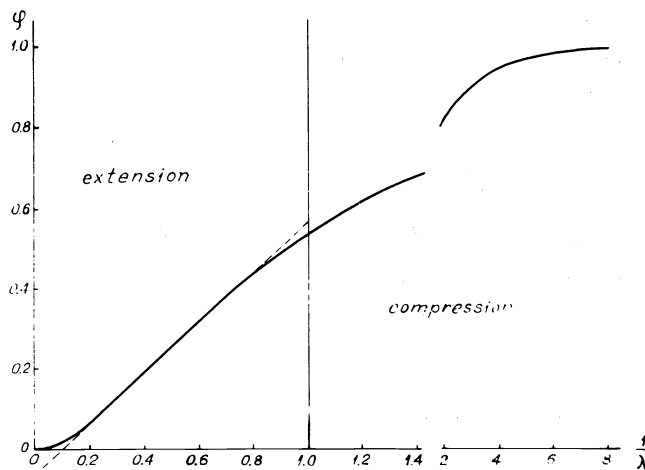

Fig. 6. Theoretical dependence of stress on extension ratio for the uniaxial deformation in the Mooney-Rivlin coordina- tes. The dotted line approximates a linear part of the depen- dence.

region of extension can not be obtained with a sufficient accuracy, but as it was pointed out elsewhere(Ref. 11) there are indirect indications of deviations from linearity beyond that range. In the region of compression the

value of φ is increasing from 0.533 at $\lambda = 1$ to 1.0 at $\lambda \to 0$. This contradicts the scarce experimental findings existing for the region. Thus, according to the data of Rivlin and Saunders (Ref. 22), the value of φ in the region of compression is practically constant. It is noteworthy that the mentioned divergence between theory and experiment reveals itself only in the presentation of data in the Mooney-Rivlin coordinates. In the ordinary coordinates, as was already mentioned, the data for various strain types are quite satisfactorily described at the same values of C_1 and C_c. In the region of extension the dependence of φ on $1/\lambda$ is practically equivalent to the dependence resulting from the empiric theory of Mooney-Rivlin (Ref. 23, 24) which has served as a basis for processing numerous experimental data. For the constant C_2 of this theory a whole number of regularities was established. It is expedient therefore to find out a connection between C_c and C_2, without forgetting that such a connection is correct only for the extension data because only in this case the theoretical dependences of Mooney-Rivlin and those obtained in the present work coincide. The linear part of dependence of φ on $1/\lambda$ in the region of extension can be described with high accuracy by the linear equation (the dotted line in Fig. 7):

$$\varphi = f_e/2(\lambda - 1/\lambda^2) = C_1 + C_c\left[-0.0612 + 0.6232/\lambda\right] \qquad (50)$$

while in accordance with Mooney-Rivlin we have

$$\varphi = C_1 + C_2/\lambda \qquad (51)$$

Hence $C_c = 1.605 C_2$. This correlation will be used when comparing the theoretical value of C_c with the experimental one.

Molecular significance of parameters K and m

The expression (43) for C_c does not allow yet to find its numerical value since it contains two unknown parameters K and m. So far it is clear, from the reasoning during the model formulation, only that K is characterising elastic properties of the medium surrounding the chain under consideration and that m should be large enough to provide limitation of fluctuations along the whole contour of the chain. It is obvious that introduction of distributed interaction of the chain with its surroundings is not desirable since it will cause difficulties in expressing K in terms of molecular parameters. In the distribution function W_{r_δ} expressed by the equation (7) K determines the fluctuation decrease of intermediate points of the chain as compared with isolated chain. Therefore we should have analysed at the molecular level such a decrease of chain fluctuations, caused by the presence of neighbours, and in accordance with that, chosen the value of K. But this represents an extremely difficult task. In the present work a more simple, though less strict, way for expressing K and m in terms of molecular parameters has been chosen. If one takes into account only the closest neighbours with which the chain is directly contacting, then it is natural to take m as the number of neighbouring chains deformed during a displacement of the chain under consideration. These can be the chains forming the entanglements or simply crossing the given chain, i.e. all the cases shown in Fig. 2. Then the parameter $K' = 2kTK$ should be ascribed with the significance of "lateral" rigidity of the neighbouring chains, i.e. of proportionality factor between the applied force and the chain fragment displacement in a radial direction. The latter can be found out from the radial distribution function for an intermediate link of the chain (Ref. 20):

$$w(r)dr = \Omega \exp\left\{-3Nr^2/2i(N-i)\ell^2\right\} dr \qquad (52)$$

From this:

$$K_i' = 3NkT/i(N-i)\ell^2; \qquad K_i = 3N/2i(N-i)\ell^2 \qquad (53)$$

and

$$K_i/\alpha_m = N^2/i(N-i)(m+1) \qquad (54)$$

Obviously K should be averaged over all the values of i since neighbouring chains can contact the given chain in any of their points. Let us assume that the contacting chains are divided into the same number of submolecules as the chain under consideration and perform averaging over the values of K in

the all division points, i.e.

$$\frac{K}{\alpha_m} = \frac{1}{m} \sum_{i=1}^{m} \frac{K_i}{\alpha_m} = \frac{m+1}{m} \sum_{i=1}^{m} \frac{1}{i\,(m+1-i)} \qquad (55)$$

The parameter m will be evaluated from a comparison with experimental data. In the work by Boyer and Miller (Ref. 25) there is given a generalised dependence of C_2/C_1 on $2C_1$ established on the basis of experimental data of many authors for vulcanizates of natural rubber. We shall assume the front factor $\langle R^2 \rangle / N\ell^2$ in the formula (45) as equal to unit and choose the value of $C_1 = 0.166$ MPa which corresponds to 100 monomeric units in the chain. In accordance with the above mentioned dependence the values $C_2/C_1 = 0.6$ or $C_c = 0.16$ MPa correspond to this value of C_1. By varying m we find out that the formula (43) gives this value at m=12. This value, to which approximately 8 monomeric units in the submolecule are corresponding, is seemingly overstated since in calculating of K/α_m only closest neighbours had been taken into account. In practice K should be larger because the reaction from a contacting chain under strain can be conditioned not only by its own rigidity but by rigidity of chains beyond this one as well.

Dependence of C_c on the network's density

It is known that C_1 and C_2 depend in different ways on the network's density: at low densities $C_2 > C_1$ and its increase is faster, but with increasing densities the increase of C_2 becomes slower and from a certain value ν, C_2 reaches a constant value. In this region $C_2 < C_1$. This regularity, at least qualitatively, follows from the theory suggested. In accordance to formulae (43) and (45) the values of C_1 and C_c are proportional to ν. But with the increase of ν the contour length of chains decreases, hence m decreases too. This leads to a slower rate of increase for C_c. Figure 7 shows the dependence of C_c on C_1, calculated by formulae (43) and (45) at $\langle R^2 \rangle / N\ell^2 = 1$. The same figure contains a generalized experimental dependence of C_c on C_1 for vulcanizates of natural rubber calculated from the data given elsewhere (Ref. 25). Both curves are located approximately in the same manner. A quantitative deviation can be connected not only with the approximate nature of the theory but also with that experimentally found values of C_1 are not pro-
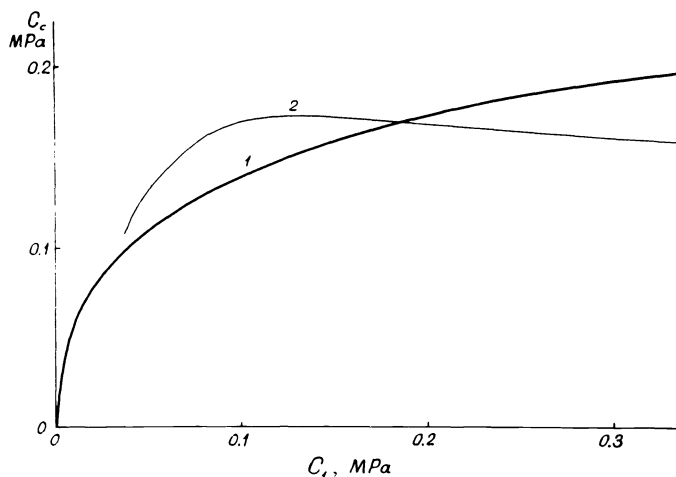

Fig. 7. Dependence of C_c on C_1: 1 — a theoretical curve in accordance with the formula (43); 2 — a generalized experimental dependence for vulcanizates of natural rubber in accordance with the work (Ref. 25).

portional to ν as it is assumed in the formula (45). Passing onto vulcani-
zates of other rubbers should lead to the change of scale along the ordina-
te axis in Fig. 7, since a change of molecular mass of a monomeric unit
should lead to a change of chain length at a given network's density and,
consequently, to the change of m.

Dependence of C_c on swelling ratio

Deviations from the classical theory of rubber-like elasticity are fastly
decreasing at rubber swelling (Ref. 26). The reason for this is easily
understandable when the formulae (43) and (45) are compared. The first one
does not contain the front factor, and already due to a decrease of chains
concentration in a swollen rubber C_c is diminishing proportionally to $\mathcal{U}_r$
(a fraction of rubber in a swollen system). For C_1 this effect is to a
considerable degree balanced by an increase of the front factor as a result
of which C_1 is changing proportionally to $\mathcal{U}_r^{1/3}$. Besides, swelling leads to
chains drifting apart and, hence, to a decrease of contacts number of each
other, i.e. to a decrease of m. It is natural to assume that due to a de-
crease of number of contacts along the chain's contour the value of m will be
diminished proportionally to $\mathcal{U}_r^{1/3}$. But the remaining contacting chains can
drift away from the chain under consideration due to introduction of solvent
molecules among them. Let us assume this effect to be also proportional to
$\mathcal{U}_r^{1/3}$, though this assumption is already not so obvious. As a result of this,
m is assumed to be proportional to $\mathcal{U}_r^{2/3}$. The dependence calculated on the
basis of these assumptions is shown in Fig. 8 (curve 1). Since in literature
on the subject (Ref. 27) the value of C_2 is calculated by the formula:

$$\varphi = f_e/2\,\mathcal{U}_r^{1/3}(\lambda - 1/\lambda^2) = C_1 + C_2/\lambda \qquad (56)$$

then, for the sake of comparison with experimental data, the value of $C_c\mathcal{U}_r^{-1/3}$
against $\mathcal{U}_r$ is ploted in Fig. 8. It drops practically linearly with a
decrease of $\mathcal{U}_r$. A linear part is extrapolated to $\mathcal{U}_r = 0.1$ on the abscissa
axis. Such type of dependence qualitatively corresponds to the data obtained
by Gumbrell, Mullins and Rivlin (Ref. 27), though the dependence plotted by
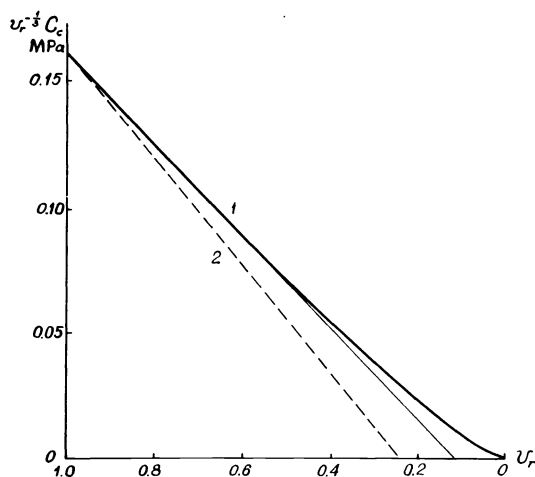them is located somewhat lower than the theoretical one (curve 2).

Fig. 8. Dependence of $C_c\mathcal{U}_r^{-1/3}$ on $\mathcal{U}_r$: 1 — the theoretical curve
calculated by the formula (43); 2 — the data of Gumbrell,
Mullins and Rivlin (Ref. 27).

Dependence of C_c on cross-sectional area of polymeric chains

Boyer and Miller, basing on the analysis of numerous experimental data, had

shown that at a given density of network (at equal C_1 values) the value of C_2 is decreasing with the increase of cross-sectional area of polymeric chains A. This fact is also naturally interpreted on the basis of the formula (43). An increase of A leads to a decrease of m for two reasons: due to a decrease of chains length (at a given ν) inversely proportional to A, and due to decrease of the number of contacts per length unit of the chain (the number of contacts being inversely proportional to $A^{1/2}$). As a result, m should be changed proportionally to $A^{-3/2}$. Dependences of C_c on A/A_{NR} (A_{NR} – a cross-sectional area of polyisoprene) are shown in Fig. 9 for C_1 =0.166 MPa (curve 1) and C_1 =0.04 MPa (curve 2). In the first case an increase of six
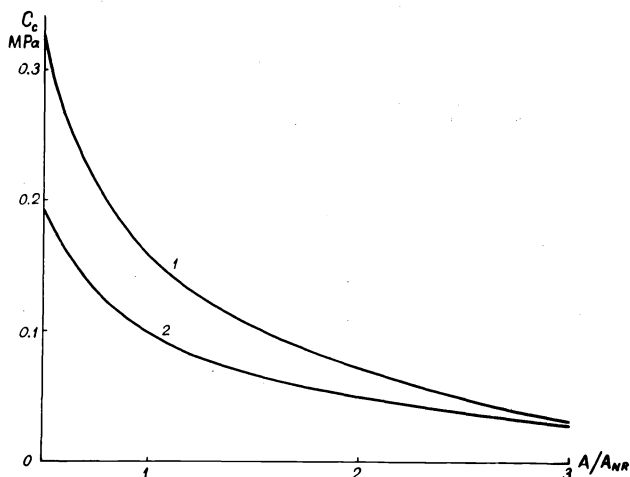

Fig. 9. Dependence of C_c on the cross-sectional area of chains A according to the formula (43): A_{NR} – the value of A for natural rubber; 1 – C =0.166 MPa; 2 – C =0.04 MPa.

times the original value of A/A_{NR} leads to a decrease of nine times of the original value of C_c, in the second case – to a decrease of six times the original value. This qualitatively corresponds to the conclusion made by Boyer and Miller, in accordance with which an increase of C_1 leads to a more pronounced dependence of C_2 on A. But quantitatively the experimental dependences are more pronounced. With A increasing six times the original value, C_2 is decreasing approximately fifteen times at C_1 =0.05 MPa and thirty five times at C_1 =0.1 MPa.

CONCLUSION

The discussion does not cover all the possibilities of comparing the theory with experiment. Thus, from comparison of the formulae (43) and (45) it is obvious that C_1 and C_c should have different types of temperature dependence since the latter does not possess the front factor. Really, the literature data (Ref. 28–30) witness for this difference. Furthermore, basing on the simplified model accepted in the present work it is possible to develop a theory of birefringence in rubbers similarly to the way which had been used elsewhere (Ref. 12, 13), and to analyse the dependence of C_1 and C_c on conditions of the network's formation (cross-linking in the extended state and cross-linking in a swollen state with a subsequent extraction of solvent). But the comparison made here and elsewhere (Ref. 11) will be enough already for declaring that in all cases the theory leads to a satisfactory agreement with experiment. This enables us to believe that the physical premises lying in the theory's basis are correct and the model chosen is satisfactory in conveying their essense. Speaking about quantitative deviations found,

mainly, in comparing dependences of C_c with experiment, it is still diffi-
cult to say to what extent they are preconditioned by simplifications
introduced in the model and to what extent they are connected with a
simplified treatment of parameters K and m. The author sets clarification
of the above question as his task for the nearest future.

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