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Contraction effects in ideal networks of flexible chains

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The mean-square distances between various points of regular Gaussian networks are calculated using a new electrical analog and solving exactly a set of difference equations both in two and in three variables through an appropriate Fourier lattice transformation. The results show that the mean-square radius of gyration of the network is of the same order of magnitude as that of a single chain for networks having a three-dimensional connectivity, while it increases logarithmically with the total number of chains for networks having a two-dimensional connectivity.

The cooperative contraction arising in an unconstrained network of long, noninteracting flexible chains is likely to appear as unexpectedly large at least in some cases. A particularly impressive effect has never been stressed, although implicit in the results obtained by James for the regular cubic network,[1] namely that the mean-square distance (msd) between junctions infinitely far apart in the topological sense, is about the same as the msd between adjacent junctions. This conclusion emphasizes the inherent limitations of the ideal network as a model for real rubber, at least if appropriate forces are not hypothesized to account for the excluded volume effects.[1] Otherwise, the network would collapse essentially to a single point.

In this paper we report a new theoretical approach which allows evaluation of the msd between any pair of junctions of an ideal regular network whose connectivity is represented by a graph infinitely extended either in two or in three dimensions (two-dimensional or three-dimensional topology). The noninteracting chains are assumed to comprise the same large number of spherically jointed links. Results will be reported for both adjacent junctions and junctions far apart, for the three cases of the square planar, the cubic and the tetrahedral network. The contraction effect for pairs infinitely far apart turns out to be essentially similar in both the tetrahedral and the cubic cases, so that it seems to be related to the topological dimensionality, rather than to the functionality of the network junctions. Conversely, the contraction factor for the single chain relative to its free state is shown to depend from the functionality only. In the planar case the msd between two junctions tends to increase indefinitely with their topological distance, although with a slow logarithmic dependence.

Most of the present results are new. The present approach will be developed in two theoretical steps. First, an electrical analogy will be proposed as a useful tool to calculate the msd between any pair of junctions in a network of ideal Gaussian chains. Second, a new mathematical approach will be described, to obtain results in a closed analytical form for a regular, infinite network. It is based on a suitable Fourier transformation, allowing reduction of a quasicyclic set of difference equations containing two or more integer variables to a set containing a lower number of variables. In the last section, the numerical results will be discussed.

THE ELECTRICAL ANALOG OF AN IDEAL NETWORK OF GAUSSIAN CHAINS

Let a chain consist of a large number n of spherically jointed links with a zero intrinsic volume and a length l. If the end-to-end elongation vector with orthogonal components (x, y, z) is small compared to the full chain extension, its probability distribution is given by the Gaussian law,

$$W_n(x, y, z) = (2\pi nl^2/3)^{-3/2} \exp[-\tfrac{3}{2}(x^2 + y^2 + z^2)/nl^2] \,. \quad (1)$$

Let us consider two such chains comprising n_1 and n_2 links, respectively, and examine two separate cases (Fig. 1): The first one corresponds to having the two chains in series, the second in parallel. For either case we may easily derive the probability distribution relative to the vector between points 1 and 2 (see Fig. 1) with components (x, y, z)

$$W_I(x, y, z) = (\text{const}) \int_{x'} \int_{y'} \int_{z'} W_{n_1}(x', y', z') \times W_{n_2}(x - x', y - y', z - z')\, dx'\, dy'\, dz' \quad (2)$$

$$W_{II}(x, y, z) = (\text{const}')\, W_{n_1}(x, y, z)\, W_{n_2}(x, y, z)$$

Performing the operations and renormalizing, it turns out that either distribution reduces to a Gaussian law [Eq. (1)], with the following equivalent numbers of links [cf. Eq. (1)]:

$$n_I = n_1 + n_2 \qquad \text{(in series)} \,,$$
$$\frac{1}{n_{II}} = \frac{1}{n_1} + \frac{1}{n_2} \qquad \text{(in parallel)} \,. \quad (3)$$

Equation (3) may also be written in terms of mean-square distances:

$$\langle r^2 \rangle_{0I} = \langle r^2 \rangle_{01} + \langle r^2 \rangle_{02}$$
$$1/\langle r^2 \rangle_{0II} = 1/\langle r^2 \rangle_{01} + 1/\langle r^2 \rangle_{02} \,. \quad (4)$$

This result suggests an electrical analogy inasmuch as it reproduces the law of combination of two resistances either in series or in parallel. Since the connection between any two junctions of any network may be obtained through a proper building up of elements associated either in series or in parallel, we may generalize the above result: In the absence of external forces, the mean-square distance between any two junctions of an ideal network of Gaussian chains is equal to the equivalent electrical resistance between the two points, if each chain is attributed a resistance R equal to its free

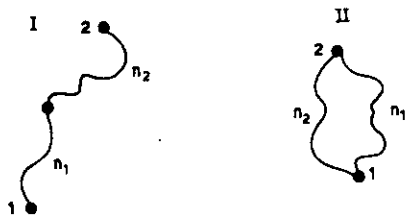

FIG. 1. Arrangement of two chains in series (I) and in parallel (II).

mean-square length $\langle r^2\rangle_0$.

A mechanical analog has been obtained by James in terms of springs by replacing "electrical resistance" with "reciprocal of the force constant." The electrical point of view may be preferred both because it does not require vectorial quantities and because the mathematical approach to the electrical networks may be more familiar. However, an important mechanical implication must always be remembered: Namely that if $\mathcal{R}$ is the equivalent resistance between any two junctions, an average unitary displacement between them is obtained by applying opposite forces equal to $3kT/\mathcal{R}$ along the direction under consideration. Effects of different forces are superposable.

We want to stress that all the above implies that the distribution function of the distance between any two network points is always Gaussian.[1]

ILLUSTRATION OF THE MATHEMATICAL METHOD AND APPLICATION TO THE SQUARE NETWORK

As a first example we shall consider an infinite polymer network having a square planar topology (see Fig. 2). For this case and throughout the paper we assume that all chains have the same number of spherically jointed links. This implies that all resistors in the electrical analog have the same resistance.

Let us associate each vertex with two integer variables (l, m) giving its position in the network, and let (j, k) and (r, s) be two general vertices of the network. The mean-square end-to-end distance of the corresponding junctions can be evaluated in terms of the equivalent resistance between the two points. Denoting by $v(l, m)$ the electrical potential of the general vertex (l, m), we apply a current source I to the vertex (j, k) and a current source $-I$ to the vertex (r, s). The equivalent resistance can thus be written as

$$\mathcal{R}(j, k; r, s) = [v(j, k) - v(r, s)]/I \,. \tag{5}$$

The Kirchhoff equation for the network gives, in terms of Kronecker delta functions:

$$4v(l, m) - v(l+1, m) - v(l-1, m) - v(l, m+1) - v(l, m-1)$$
$$= IR[\delta(l-j)\,\delta(m-k) - \delta(l-r)\,\delta(m-s)] \,, \tag{6}$$

where l and m are integer variables ranging from $-\infty$ to $+\infty$.

In order to solve Eq. (6) we shall make use of the operational properties of the Fourier lattice transform.

Given an arbitrary function of integer arguments $f(l_1, l_2, l_3)$ satisfying a periodic condition on the variable l_1, i.e., $f(l_1+N, l_2, l_3) = f(l_1, l_2, l_3)$, we define its Fourier lattice transform with respect to l_1 as

$$F(q_1, l_2, l_3) = \sum_{l_1} f(l_1, l_2, l_3)\, e^{iq_1 l_1} \quad (l_1 = 1, 2, \ldots, N) \,.$$

The antitransformation theorem states that

$$f(l_1, l_2, l_3) = N^{-1} \sum_{q_1} F(q_1, l_2, l_3)\, e^{-iq_1 l_1}$$

$$q_1 = 2\pi/N, \ldots, n(2\pi/N), \ldots, N(2\pi/N) \,.$$

The usefulness of the lattice transformation depends on its operational properties:

$$f(l_1, \ldots) \rightarrow F(q_1, \ldots)$$

$$f(l_1 - p, \ldots) \rightarrow F(q_1, \ldots) e^{-ipq_1}$$

which may be applied to Eq. (6) to get its transform with respect to l:

$$2(2 - \cos q)\, V(q, m) - V(q, m+1) - V(q, m-1)$$
$$= IR[e^{ijq}\delta(m-k) - e^{irq}\delta(m-s)] \,. \tag{7}$$

In order to get a transformable equation we must introduce a periodic boundary condition over l. This can be done by wrapping the square network into an infinite cylinder whose circumference contains N edges. Results for the infinite network can be obtained by letting N go to infinity. Equation (7) is an ordinary difference equation whose solution bounded for $m \rightarrow \pm\infty$ can be easily found. We shall solve the problem for two particular cases:

(1) equivalent resistance of the single chain;

(2) equivalent resistance between vertices lying far apart on the same row.

For the first case we may put $j=0$, $k=0$, $r=0$, $s=-1$ in Eq. (7), getting as a solution for the infinite network:

$$V(q, m) = IR\,\frac{[(2-\cos q) + \sqrt{(2-\cos q)^2 - 1}]^{-m}}{3 - \cos q + \sqrt{(2-\cos q)^2 - 1}} \quad \text{for } m \geq 0$$

$$= -IR\,\frac{[(2-\cos q) + \sqrt{(2-\cos q)^2 - 1}]^{m+1}}{3 - \cos q + \sqrt{(2-\cos q)^2 - 1}}$$

$$\text{for } m \leq -1 \,. \tag{8}$$

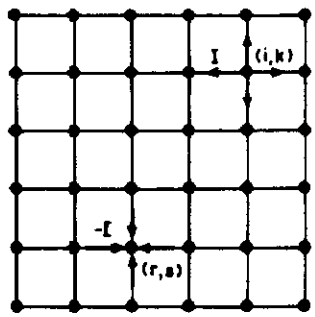

FIG. 2. Current-source arrangement for calculating the equivalent resistance between vertices (i, k) and (r, s) in the square network.

From Eq. (5) we get

$$\mathcal{R}(0,0;0,-1)=[v(0,0)-v(0,-1)]/I\ . \tag{9}$$

Antitransforming Eq. (8) and making use of Eq. (9), we obtain for the equivalent resistance of the single chain

$$\mathcal{R}_s=R/\pi\int_0^{2\pi}\frac{dq}{3-\cos q+\sqrt{(2-\cos q)^2-1}}$$

This integral is elementary, and its value is

$$\mathcal{R}_s=R/2\ . \tag{10}$$

This result was already obtained by Eichinger for the general tetrafunctional network on the basis of some conjectures.[2]

Proceeding now to the second case to be analyzed, we put into Eq. (7) $j=L$, $k=0$, $r=-L$, and $s=0$, and obtain

$$V(q,m)=IR\frac{i\sin Lq}{\sqrt{(2-\cos q)^2-1}}\times\left[(2-\cos q)+\sqrt{(2-\cos q)^2-1}\right]^{-|m|} \tag{11}$$

Making use of Eq. (5) and converting into an integral the antitransformation sum, we get for the infinite network:

$$\mathcal{R}(L,0;-L,0)=\frac{2}{\pi}R\int_0^{\pi}\frac{\sin^2 Lq\,dq}{\sqrt{(2-\cos q)^2-1}}\ . \tag{12}$$

The evaluation of the integral appearing in Eq. (12) gives for very large L (see Appendix A)

$$\mathcal{R}(L,0;-L,0)=CR+(R/\pi)\ln 2L, \tag{13}$$

where C is a numerical constant of the order of unity.

We conclude that the mean-square distance between far separated junctions in a network having a square topology diverges logarithmically. Since long range properties are presumed to depend only on topological dimensionality[3] and not on the particular kind of connectivity, we assume that Eq. (13) may be extrapolated to all regular networks having a two-dimensional topology.

NETWORKS HAVING A THREE-DIMENSIONAL TOPOLOGY

Cubic network

Considering at first the cubic network, we remark that the msd between two general junctions (j,k,t) and (r,s,z) can be calculated putting, as usual, two current sources of opposite sign $\pm I$ on the corresponding vertices of the electrical analog.

The equivalent resistance between the two junctions can be written according to an extended form of Eq. (5):

$$\mathcal{R}(j,k,t;r,s,z)=[v(j,k,t)-v(r,s,z)]/I\ . \tag{14}$$

For the cubic network we write the corresponding Kirchhoff equation

$$\begin{aligned}&6v(l_1,l_2,l_3)-v(l_1+1,l_2,l_3)-v(l_1-1,l_2,l_3)\\&-v(l_1,l_2-1,l_3)-v(l_1,l_2-1,l_3)-v(l_1,l_2,l_3+1)\\&-v(l_1,l_2,l_3-1)\\&=IR[\delta(l_1-j)\delta(l_2-k)\delta(l_3-t)-\delta(l_1-r)\delta(l_2-s)\delta(l_3-z)]\ .\end{aligned} \tag{15}$$

For three-dimensional networks a convenient Green function $g(l_1,l_2,l_3)$ may be introduced, which is bounded to vanish at infinity.

We define g as the bounded solution of the equation

$$\begin{aligned}&6g(l_1,l_2,l_3)-g(l_1+1,l_2,l_3)-g(l_1-1,l_2,l_3)\\&-g(l_1,l_2+1,l_3)-g(l_1,l_2-1,l_3)-g(l_1,l_2,l_3+1)\\&-g(l_1,l_2,l_3-1)=IR\delta(l_1)\delta(l_2)\delta(l_3)\ .\end{aligned} \tag{16}$$

Applying a triple lattice transform, the solution of Eq. (16) can readily be found:

$$g(l_1,l_2,l_3)=\frac{IR}{16\pi^3}\iiint_C\frac{e^{-i(q_1l_1+q_2l_2+q_3l_3)}}{3-\cos q_1-\cos q_2-\cos q_3}\,dq_1\,dq_2\,dq_3 \tag{17}$$

In terms of g we may express the general solution of Eq. (15)

$$v(l_1,l_2,l_3)=g(l_1-j,l_2-k,l_3-t)-g(l_1-r,l_2-s,l_3-z)\ . \tag{18}$$

To compute the equivalent resistance of the single chain we may choose $j=0$, $k=0$, $t=0$, $r=1$, $s=0$, and $z=0$. Substituting Eq. (18) into Eq. (14) and making use of Eq. (17) we easily find

$$\mathcal{R}(0,0,0;1,0,0)=R/3\ . \tag{19}$$

The msd between junctions far apart can be calculated if we put $j=0$, $k=0$, $t=0$, $r=M_1$, $s=M_2$, and $z=M_3$ where M_1, M_2, and M_3 are large integers.

Applying Eq. (18) we let M_1, M_2, M_3 go to infinity, and observe that the following limiting result holds: $\lim g(M_1,M_2,M_3)=0$, as $M_{1,2,3}\to\pm\infty$. Therefore we get

$$\mathcal{R}_\infty=2g(0,0,0)/I\ . \tag{20}$$

Equation (20) holds for all kinds of three-dimensional networks and will be used again in this paper. For the cubic network we obtain

$$\mathcal{R}_\infty=\beta R\ , \tag{21}$$

where β is given by the following integral

$$\beta=\frac{1}{\pi^3}\iiint_0^{\pi}\frac{dq_1\,dq_2\,dq_3}{3-\cos q_1-\cos q_2-\cos q_3}\ .$$

This integral has been evaluated by Watson.[4,5] It can be written in terms of elliptic integrals of the first kind, i.e.,

$$\beta=2^{3/2}p_2'p_3'K(p_2)K(p_3)/\pi^2\ ,$$

where

$$p_2=(\sqrt{3}-\sqrt{2})(2-\sqrt{3})$$

$$p_3=(\sqrt{3}+\sqrt{2})(2-\sqrt{3})$$

$$p_2'=\sqrt{1-p_2^2}$$

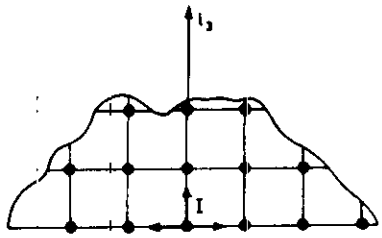

FIG. 3. Cross-sectional view of the cubic network in the vicinity of the boundary.

$$p_3' = \sqrt{1 - p_3^2}\ .$$

Numerically $\beta = 0.505462\ldots$

Equation (19) has been obtained by James[1] too, who also gave 0.5 as an approximate value for the fluctuation of the distance between junctions remote from one another in the network.

In the general case the integral appearing in Eq. (17) cannot be calculated analytically. Nevertheless we obtain quite easily in some specific case

$$g(\pm 1, 0, 0) = g(0, \pm 1, 0) = g(0, 0, \pm 1) = IR(\tfrac{1}{2}\beta - \tfrac{1}{3}) \quad (22)$$

Let us now investigate the influence of border effects. We shall calculate the msd between junctions lying far apart on the boundary of a very large cubic network. In Fig. (3) a cross section of the network is represented, in the vicinity of the free boundary $l_3 = 0$. Denoting by $g_b(l_1, l_2, l_3)$ the Green function of the problem defined by Eq. (16) and the boundary condition

$$\begin{aligned} &5g_b(l_1, l_2, 0) - g_b(l_1+1, l_2, 0) - g_b(l_1-1, l_2, 0) \\ &\quad - g_b(l_1, l_2+1, 0) - g_b(l_1, l_2-1, 0) - g_b(l_1, l_2, 1) \\ &\quad = IR\delta(l_1)\delta(l_2)\ , \end{aligned} \quad (23)$$

we obtain the msd between remote boundary junctions from Eq. (20)

$$\mathcal{R}_{b\infty} = 2g_b(0, 0, 0)/I\ . \quad (24)$$

The problem for $g_b(l_1, l_2, l_3)$ is defined over the half space $l_3 \geq 0$, but can be artificially extended over the whole space without violating the boundary condition (23), if we add a fictitious current source I located at point $(0, 0, -1)$. Thus we obtain $g_b(0, 0, 0) = g(0, 0, 0) + g(0, 0, +1) = IR(\beta - \frac{1}{6})$. From Eq. (24), we get at last

$$\mathcal{R}_{b\infty} = R(2\beta - \tfrac{1}{3}) = 0.677591\ldots R. \quad (25)$$

It is easy to show that the mean-square distance between one junction at the interior and one lying on the boundary tends to the limit $\frac{1}{2}(\mathcal{R}_\infty + \mathcal{R}_{b\infty})$ for a high topological distance.

The diamond network

All vertices belonging to the diamond network lie on the lattice points of a cubic lattice having its constant equal to $a/\sqrt{3}$, where a is the length of the tetrahedral edge. From a geometrical point of view the vertices of the tetrahedral network may be conveniently placed in two classes A and B (see Fig. 4). Each vertex belonging to one class is surrounded by four vertices belonging to the other. Values of the potential referring to vertices belonging to either class A or B will be denoted by u and v, respectively. In order to calculate the Green functions g_u and g_v of the problem we put a positive current source I on vertex $(0, 0, 0) \in A$. The Kirchhoff equation for the general vertex splits into a system of two distinct equations, one for each class of equivalence:

$$\begin{aligned} &4g_v(l_1, l_2, l_3) - g_u(l_1-1, l_2-1, l_3-1) \\ &\quad - g_u(l_1-1, l_2+1, l_3+1) - g_u(l_1+1, l_2-1, l_3+1) \\ &\quad - g_u(l_1+1, l_2+1, l_3-1) = 0 \\ &4g_u(l_1, l_2, l_3) - g_v(l_1+1, l_2+1, l_3+1) \\ &\quad - g_v(l_1+1, l_2-1, l_3-1) - g_v(l_1-1, l_2+1, l_3-1) \\ &\quad - g_v(l_1-1, l_2-1, l_3+1) = IR\delta(l_1)\delta(l_2)\delta(l_3)\ . \end{aligned} \quad (26)$$

Denoting by G_u and G_v the triple lattice transforms of the Green functions, we obtain from Eq. (26)

$$\begin{aligned} U(\mathbf{q}) &= (3 - \cos 2q_1 \cos 2q_2 - \cos 2q_2 \cos 2q_3 \\ &\quad - \cos 2q_1 \cos 2q_3)^{-1} IR \\ V(\mathbf{q}) &= U/4[e^{i(q_1+q_2+q_3)} + e^{i(q_1-q_2-q_3)} + e^{i(q_2-q_1-q_3)} \\ &\quad + e^{i(q_3-q_1-q_2)}]\ . \end{aligned} \quad (27)$$

From Eq. (27) we may calculate the msd between adjacent junctions for the diamond network, obtaining as a result $\frac{1}{2}R$, as for the case of the square network. It is interesting to calculate the msd between junctions lying far apart. From Eq. (20) we get: $\mathcal{R}_\infty = 2g_u(0, 0, 0)/I$, where $2g_u(0, 0, 0)/I$, denoted by ηR, is given by

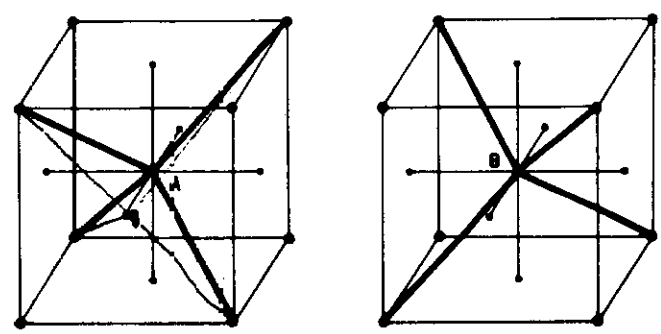

FIG. 4. Two geometrically nonequivalent vertices in the diamond network.

$$\tfrac{1}{2}\eta = \frac{1}{(8\pi)^3}\int_0^{2\pi}\!\!\int\!\!\int \frac{dq_1\,dq_2\,dq_3}{3-\cos 2q_1\cos 2q_2-\cos 2q_1\cos 2q_3-\cos 2q_2\cos 2q_3} \tag{28}$$

After a change of variable we obtain

$$\tfrac{1}{2}\eta = \frac{1}{\pi^3}\int_0^{\pi}\!\!\int\!\!\int \frac{d\phi_1\,d\phi_2\,d\phi_3}{3-\cos\phi_1\cos\phi_2-\cos\phi_1\cos\phi_3-\cos\phi_2\cos\phi_3}$$

This integral has also been evaluated by Watson,[5] who gets

$$\tfrac{1}{2}\eta = 3[\Gamma(1/3)]^6/2^{14/3}\pi^4$$

Numerically

$$\mathcal{R}_\infty = R\eta = 0.896441\cdots R\ . \tag{29}$$

A GENERAL RESULT FOR THE SINGLE CHAIN COMPRESSION FACTOR IN ANY REGULAR NETWORK

In Fig. 5 two adjacent vertices P_1 and P_2 of a regular n functional network are represented. In order to calculate the equivalent resistance between the two vertices, (i.e., the msd of the corresponding chain), we put a positive current source I on vertex P_1 and a negative one $-I$ on vertex P_2. The equivalent resistance between P_1 and P_2 is given by $[v(P_1)-v(P_2)]/I$. By making use of the superposition rule we consider separately the application of the two sources. Application of the single current source I to vertex P_1 gives rise, for symmetry reasons, to a current I/n flowing from P_1 to P_2. The induced potential difference is $\Delta v^I = RI/n$. Analogously, the single current source $-I$ located at the point P_2 induces a potential difference $\Delta v^{II} = RI/n$. Summing the two contributions we evaluate the single chain equivalent resistance

$$\mathcal{R}_s = (2/n)R\ . \tag{30}$$

THE RADIUS OF GYRATION OF AN INFINITE REGULAR NETWORK HAVING A THREE-DIMENSIONAL CONNECTIVITY

The radius of gyration of a system of N equal mass points is given by the Lagrange formula

$$\langle s^2\rangle = N^{-2}\sum_{i<j}\langle r_{ij}^2\rangle\ , \tag{31}$$

where $\langle r_{ij}^2\rangle$ denotes the msd between points i and j of the system.

For $N \gg 1$ Eq. (31) may be written in the more suitable form

$$\langle s^2\rangle = \tfrac{1}{2}\overline{\langle r_{ij}^2\rangle}\ , \tag{32}$$

averaging over i and j. Identifying the material points with the freely jointed links of any ideal network, the above equation may be written in terms of equivalent resistances as follows:

$$\langle s^2\rangle = \tfrac{1}{2}\overline{\mathcal{R}_{ij}}\ . \tag{33}$$

In an infinite network, the overwhelming majority of pairs (i, j) refers to units which are very far apart. Therefore the average indicated in Eq. (33) may be performed on a convenient subsystem consisting of two far separated chains C_1 and C_2, where unit i belongs to C_1 and unit j to C_2. Let P_1 and Q_1 be the junctions connected by chain C_1. Analogous meaning is given to P_2 and Q_2 (Fig. 6).

Let then α_1 (α_2) represent the fraction of the links contained within the chain, connecting vertex $P_1(P_2)$ with the ith (jth) unit. Equation (33) can be recast in the form

$$\langle s^2\rangle = \tfrac{1}{2}\overline{\mathcal{R}(\alpha_1,\alpha_2)}\ ;\quad 0\le\alpha_1\le 1\ ,\quad 0\le\alpha_2\le 1\ .$$

We define by $g(\alpha)$ the value of the electrical potential induced at the source point by a current source I inserted into the chain at a distance α from one vertex. Since units i and j lie far apart, source I located at i does not induce any significant electrical potential at point j, and vice versa, so that we obtain:

$$\overline{\mathcal{R}(\alpha_1,\alpha_2)} = \overline{[g(\alpha_1)+g(\alpha_2)]}/I = 2\overline{g(\alpha)}/I\ . \tag{34}$$

Thus we get: $\langle s^2\rangle = \overline{g(\alpha)}/I$.

For a regular n-functional network we get (see Appendix B)

$$g(\alpha) = g(0) + IR\alpha(1-\alpha)(1-2/n)\ . \tag{35}$$

We observe that $g(0)$ is nothing but $\frac{1}{2}I\mathcal{R}_\infty$. Averaging Eq. (35) over α we get

$$\langle s^2\rangle = \tfrac{1}{2}\mathcal{R}_\infty + \tfrac{1}{6}[1-(2/n)]R\ . \tag{36}$$

It may be interesting to point out that the term depending on $(1-2/n)$ in the above equation is due to the larger fluctuations of the points located in the interior of the chains compared to those of the junctions. For the cubic network ($n=6$) we get $\langle s^2\rangle_C = 0.36384\cdots\langle r^2\rangle_0$. The analogous result for the diamond network ($n=4$) is

$$\langle s^2\rangle_D = 0.53155\cdots\langle r^2\rangle_0\ .$$

CONCLUDING COMMENTS

Perhaps the most general conclusion to be drawn from the above results is that the mean-square diameter of a free network with a large number N of identical chains, which depends linearly on N if their connectivity is topologically monodimensional,[6] increases with $\ln(N)$ if it is two-dimensional, and is independent of N for a three-dimensional network. Although our results have been obtained for regular networks only, considering that different types of network symmetries have been investigated, we may reasonably extrapolate the above

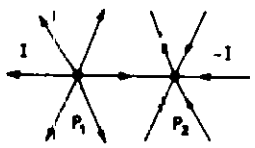

FIG. 5. Current-source arrangement for calculating the single chain equivalent resistance in a general n-functional network having a regular connectivity.

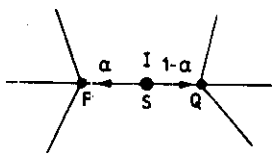

FIG. 6. Current source I located at point S inside the chain at a fractional distance α from junction P.

conclusion to irregular networks as well, provided their structure is statistically homogeneous throughout. The assumption made by Eichinger, that the mean-square radius of gyration of *any* network with tetrafunctional crosslinks is much larger than that of a single chain,[2] is therefore incorrect, and also his hypothesis that it increases with $\ln(N)$ is valid only for networks with two-dimensional connectivity. On the contrary, we show that the density of a three-dimensional free network increases linearly with the number of chains contained therein, without approaching any thermodynamic limit. A physically acceptable model of a real amorphous network may be based on a Gaussian network only under the condition that the excluded volume forces are either taken into account explicitly or tentatively simulated. An example of the latter possibility is the assumption made by James[1] and James and Guth[7] that some of the crosslinks are constrained to lie on the surface of a parallelepiped. These authors have shown that the mean-square fluctuations of the distances between the crosslinks from their average values do not depend on the dimensions of the parallelepiped. We want to point out, in this connection, that the constraints corresponding to any point of the network being fixed may be easily accounted for in our electrical analogy by simply connecting to the earth the corresponding points of the electrical network. It is thus evident that the equivalent resistance between any two points, i.e., the mean-square fluctuation of their distance, tends to decrease the more, the closer they are to the fixed points.

As a final comment, let us point out that the proof, given in Eq. (30), that the mean-square distance between adjacent crosslinks of any regular n-functional network is $2/n$ times the value for the free chain, is remarkably simple. We believe this to be a particularly meaningful example of the usefulness of the electrical analog, inasmuch as it lends itself to quite symmetrical pictures in terms of potentials and currents, avoiding recourse to vectorial quantities, such as forces and displacement vectors.

APPENDIX A

The evaluation of the integral

$$J = 2/\pi \int_0^{\pi} \frac{\sin^2 Lq\, dq}{\sqrt{(2-\cos q)^2 - 1}}$$

for very large L may be performed observing that the denominator is singular for $q = 0$. In the vicinity of $q = 0$, we have $[(2-\cos q)^2 - 1]^{-1/2} \simeq q^{-1}$. We may rewrite J as $J_1 + J_2$, where

$$J_1 = 2/\pi \int_0^{\pi} \sin^2 Lq \{[(2-\cos q)^2 - 1]^{-1/2} - q^{-1}\}\, dq$$

$$J_2 = 2/\pi \int_0^{\pi} \sin^2 Lq/q\, dq\ .$$

The integrand of J_1 is a regular function of the argument q in the interval $0 \ldots \pi$, and therefore, substituting $\sin^2 Lq$ with its average value $\frac{1}{2}$, we obtain in the limit for $L \to \infty$

$$\lim_{L\to\infty} J_1 = 1/\pi \int_0^{\pi} \{[(2-\cos q)^2 - 1]^{-1/2} - 1/q\}\, dq = B\ ,$$

which is a numerical constant of the order of unity. After an elementary change of variable, J_2 becomes

$$J_2 = 1/\pi \int_0^{2\pi L} (1-\cos x)/x\, dx\ .$$

From the definition of the cosine integral we get

$$J_2 = \gamma/\pi + \ln(2\pi L)/\pi - Ci(2\pi L)/\pi\ ,$$

where γ is the Euler–Mascheroni constant.

In the limit for very high L we obtain

$$J_2 = (1/\pi)(\gamma + \ln\pi) + \ln(2L)/\pi$$

and, putting $C = B - (1/\pi)(\gamma + \ln\pi)$,

$$\lim_{L\to\infty} J = C + (1/\pi)\ln(2L)\ ,$$

which gives exactly Eq. (13).

APPENDIX B

Let P and Q be two adjacent n-functional junctions (see Fig. 6). A current source I located in S at a distance α from P will induce a potential $v(P)$ in P. Because of the reciprocity theorem this potential is equal to the potential localized in S when we place the current source in P.

Therefore we obtain

$$v(P) = g(0) - \alpha RI/n\ .$$

Denoting by I_1 and I_2 the currents flowing, respectively, in PS and QS, we get for the potential at the source point S:

$$g(\alpha) = g(0) - \alpha RI/n - \alpha RI_1 \quad \text{(starting from } P)\ ,$$

$$g(1-\alpha) = g(0) - (1-\alpha)RI/n + (1-\alpha)RI_2 \quad \text{(starting from } Q)\ .$$

Since $g(\alpha)$ must be equal to $g(1-\alpha)$, making use of the relationship $I_1 + I_2 = I$, we get at last

$$g(\alpha) = g(0) + IRc\,(1-\alpha)(1-2/n)\ ,$$

which is Eq. (35).

[1] H. M. James, J. Chem. Phys. 15, 651 (1947).
[2] B. E. Eichinger, Macromolecules 5, 496 (1972).
[3] C. Domb, in *Stochastic Processes in Chemical Physics*, edited by K. E. Shuler (Interscience, New York, 1969).
[4] M. N. Barber, B. W. Ninham, *Random and Restricted Walks*, (Gordon and Breach New York, 1970).
[5] G. N. Watson, Q. J. Math. Oxford Ser. (1) 10, 266 (1939).
[6] P. J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience, New York 1969), Chap. 1.
[7] H. M. James and E. Guth, J. Chem. Phys. 15, 669 (1947).

An approach to rubber elasticity with internal constraints

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The effect of configurational hindrances in unswollen rubberlike networks is taken into account by assuming the existence of a proper correlation between the macroscopic deformation and the rms fluctuations of the network junctions along the various directions of space. Following James and Guth's approach, some junctions have been fixed at the surface of a proper parallelepiped in order to avoid collapse of the network, and the above correlation is expressed through the introduction of appropriate δ functions into the configurational partition function. Results identical with those previously arrived at by Flory–Hoeve–Ciferri are obtained by assuming that the rms fluctuation components transform as the macroscopic stretch ratios. This assumption cannot hold under high deformations because it implies that the junction fluctuations increase without limit with the deformation. Therefore an intermediate model is proposed where (i) the average ms fluctuations of the junctions are independent of strain, as in James–Guth theory, and (ii) *the ratios* between the rms (mean square) fluctuations are equal to those between the corresponding stretch ratios as in Flory–Hoeve–Ciferri theory. The intermediate model can explain, at least to some extent, the so-called Mooney effect. It is also shown that the relation $-[\partial \ln(\sigma/T)/\partial T]_{L,V} = d\ln\langle r^2\rangle_0/dT$ is valid for James–Guth theory only.

INTRODUCTION

The theory of rubber elasticity developed by Kuhn,[1] James and Guth,[2,3] Wall,[4] Flory and Rehner,[5] and others[6] is based upon the network model of Gaussian chains devoid of intrinsic volume and incapable of any sort of entanglements (the so-called "phantom" network). Although this model proved to be extremely useful in view both of its simplicity and of its sufficient adherence to reality for many purposes, James and Guth[2] pointed out that it suffers from a serious inadequacy, namely the network is bound to collapse to an infinite density if a proper set of forces is not simulated to account for the excluded volume effects. As an example, for networks with a three-dimensional connectivity and characterized by a regularly repeating topological structure ("regular" networks), James[2] and the present authors[7] have shown that the mean-square distance between *any* two network junctions is of the same order of magnitude as the mean-square length of the single chain connecting two neighboring junctions, if no external forces are applied. There can be no doubt that an analogous conclusion should apply to irregular networks as well, if their connectivity is three-dimensional and the parameters describing their topological structure have the same average values throughout.[7] In order to avoid the collapse of the network, James and Guth postulate that a proper number of junctions are constrained to lie at the surface of a parallelepiped.[2] James and Guth's treatment leads to the conclusion that (i) the fluctuations of the junctions in space are unaffected by the state of strain, i.e., by the dimensions of the parallelepiped, and (ii) changing any edge length of the parallelepiped by a given factor leads to a corresponding change of the average coordinates of all the junctions along the same edge (affine transformation).

The two above conclusions, correct as they are from the mathematical standpoint, do involve some problems when competition for space among the chains is considered. It is the purpose of this paper to reconsider the statistical theory of rubber elasticity with the aim of taking into some account this aspect. We want to stress that in the following we will deal exclusively with unswollen networks, where the steric constraints mutually exerted among the chains are strongest, due to the absence of the diluent. As for highly swollen networks, it is well known that both the James–Guth[2] and the Kuhn–Wall–Flory–Rehner[1,4,5] approaches are in satisfactory agreement with experiment. They both lead to the same stress–strain relation, which in simple elongation reads $f = \text{const} \times (\lambda - \lambda^{-2})$, λ being the axial stretch ratio.[3]

Perhaps the most significant attempt to account for the deviation of the observed stress at moderate elongations from the ideal behavior (which we will refer to henceforth as the Mooney effect,[8] see Fig. 1) in terms of the packing forces is due to DiMarzio.[9] He shows that the packing entropy derived from a simple cubic lattice model of the network leads to an additional stress term which is able to reproduce qualitatively the shape

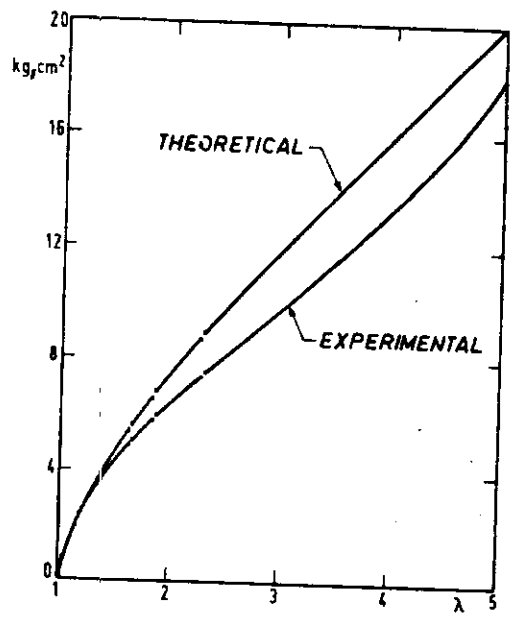

FIG. 1. Typical plots of stress vs elongation for a rubberlike sample.

of the experimental stress–strain curves where the Mooney effect shows up, although the absolute value of the correction is generally smaller than required. But the basic failure of DiMarzio's theory appears to lie in the *sign* of the correction itself; in fact the overall calculated stress is always smaller than in the absence of the Mooney effect, contrary to experimental data which show that the disappearance of this effect in progressively swollen samples is accompanied by a *decrease* in the stress intensity.[10]

We have considered a different approach to account for the intermolecular interactions. Let us anticipate only that, although the explicit mathematical treatment of this effect raises formidable difficulties, as pointed out by Freed,[11] we will take it into an approximate account by replacing the complete set of topological constraints with limitations on the degrees of freedom of the network junctions, as it will be shown in the following discussion.

GENERAL FORMULATION

The configurational partition function for a crosslinked network[11] is

$$Z(T, V_0, \Lambda) = \int d\Gamma \exp[-\beta H(\Gamma)]\delta[\mathbf{c} - \mathbf{c}(\Gamma)]\Delta[\mathbf{T}(\Gamma)] \ . \quad (1)$$

The integration is to be performed over all points Γ of the configurational phase space. The network is characterized by a deformation tensor Λ, V_0 being the volume in the undeformed reference state. $H(\Gamma)$ is the configurational energy, and $\beta = 1/kT$. The delta function in Eq. (1) accounts for the *specified connectivity* C of the network. The capital delta accounts for all remaining topological constraints T such as those forbidding the mutual crossing of two entangled chains. If, as it is often the case, the configurational energy is only expressed in terms of the interactions between atoms close to each other along the macromolecular sequence (first-neighbor interactions), the excluded volume effects should also be regarded as topological constraints. The capital delta function is bound to vanish outside a convenient subset of the phase space.

The existing theories of rubber elasticity are mainly concerned with the deformation dependent part of the free energy and, in view of this, rather drastic approximations are generally made.

In the theory developed by Wall, Flory, and Rehner (henceforth WFR) connectivity requirements are not explicitely introduced into the configurational partition function, while the actual volume and shape of the sample are considered in an indirect way. The procedure of James and Guth (henceforth JG) of accounting for the volume and shape requirements by linking the coordinates of a convenient set of surface junctions with the macroscopic deformation, satisfactory as it is from a heuristic viewpoint, raises obvious physical objections. However, we want to point out that the same essential results may also be obtained by imposing a suitable condition on the bulk density of the material.[12] In the sequel we will retain JG's original assumption because it leads to the significant results in a consistent and straightforward way.

Let us assume that in the undeformed isotropic state the network is adequately described by JG theory. In other words, the junctions fluctuate with Gaussian isotropic distributions around their average positions, under the constraint that some of them are fixed in space. Consider a pair of junctions which may be chosen close one to the other for convenience. We know from JG theory that the probability distribution of their connecting vector around its average value is also Gaussian isotropic. Given two arbitrarily chosen junctions, say 1 and 2, the probability distribution of the vector $\mathbf{r}_{12}$ calculated at $\mathbf{r}_{12} = 0$ is to be regarded as the density of probability of mutual contact. Now, *should JG theory hold in any deformed state as well*, the distribution function of $\mathbf{r}_{12}$ around its average would not change with respect to the isotropic state, although the average vector itself would be affinely transformed, with the consequence that in general the probability of finding junction 2 in any given small volume around junction 1 would be changed. In other words, the probability of having any two junctions overlapped would either increase or decrease compared with the undeformed state, depending on whether their connecting vector is oriented along the direction of elongation or at right angles to it. Obviously enough, any such change in overlapping probability between two junctions would entail a change in the probability of mutual contact for the chains adjoining them. In unswollen networks at small deformations, which presumably do not imply a substantial rearrangement of the entanglement topology, any modification of the interaction probabilities should be unlikely in practice, hindered as it is by the concerted action of entanglements and packing forces. On the basis of these considerations, let us state here the following assumption: *In any slightly deformed state of the network, the fluctuations of the junctions will change in such a way as to keep the probability of mutual overlap as close as possible to that existing in the undeformed state.*

Postponing further discussion of this point, let us remark that there exists a simple and unique way of restricting the junction fluctuations so that the overlap probability is exactly invariant with the deformation. It consists of deforming the fluctuation spheres into ellipsoids whose axes (i.e., the rms displacements from the average positions) are given by the product of the original radius of the sphere times the principal stretch ratios. There is no better way of keeping the intermolecular interactions invariant with the deformation, at least if we limit the configurational restrictions to the junctions. On the other hand, although this limitation may appear to some extent arbitrary, it seems to be justified because the junctions are the points of our system most likely involved in topological hindrances.

We are now confronted with the problem of imposing suitable restrictions to the fluctuations of the junctions, depending on the macroscopic state of deformation. To this end, *we assume the existence of a functional relationship between the deformation tensor and a suitably defined fluctuation tensor*

$$\langle \mathbf{H} \rangle = \left\langle \sum_\alpha (\mathbf{r}_\alpha - \langle \mathbf{r}_\alpha \rangle)(\mathbf{r}_\alpha - \langle \mathbf{r}_\alpha \rangle) \right\rangle \ , \quad (2)$$

where $\mathbf{r}_\alpha$ is the vector defining the position of the αth network junction, and the sum is extended over all of them. This assumption, which is *phenomenological* in nature, tends to restrict the statistical ensemble in such a way that the additional configurational hindrances induced by the deformation are minimized. If the reference axes are made to coincide with the principal axes of the deformation, the above condition may be written as

$$\langle H_i \rangle = F(\lambda_i, I_1, I_2, I_3) H^{(0)} \qquad (i = 1, 2, 3) \tag{3}$$

where λ_i is the general principal elongation ratio, $I_{1,2,3}$ are the deformation invariants,[8] $H^{(0)}$ gives the (isotropic) diagonal components of the averaged fluctuation tensor in the undeformed state, and $F(\lambda_i, I_1, I_2, I_3)$ is a *given* function whose actual form will be discussed in the following. In the thermodynamic limit the brackets can be dropped from Eq. (3) and we get an *approximate equivalent* for the factor $\Delta[T(\Gamma)]$ appearing in Eq. (1):

$$\Delta'[T(\Gamma)] \sim \prod_{i=1}^{3} \delta[H_i - F(\lambda_i, I_1, I_2, I_3) H^{(0)}] \,. \tag{4}$$

A physically equivalent representation of $\Delta'[T(\Gamma)]$ can be obtained by relating the sum of the mean square projections of the chain end-to-end distances to the macroscopic deformation:

$$\Delta'[T(\Gamma)] \sim \prod_{i=1}^{3} \delta[K_i - G(\lambda_i, I_1, I_2, I_3) K^{(0)}] \,, \tag{5}$$

where the tensor $\mathbf{K}$ is given by

$$\mathbf{K} = \frac{3}{4\nu l^2} \sum_{\alpha,\beta} \epsilon_{\alpha\beta} (\mathbf{r}_\alpha - \mathbf{r}_\beta)(\mathbf{r}_\alpha - \mathbf{r}_\beta) \,, \tag{6}$$

and $K^{(0)}$ gives the diagonal components of $\mathbf{K}$ in the undeformed state. The sum in Eq. (6) is extended over all instantaneous positions of the network junctions; $\epsilon_{\alpha\beta}$ is unity if junctions α and β are connected, zero otherwise. In the factor $3/4\nu l^2$, that has been introduced for convenience, ν is the number of equivalent segments per chain, *which is assumed to be the same for all chains*, and l is the length of the statistical segment.

The equivalence of the weighting factors [Eqs. (4) and (5)] requires that a one-to-one correspondence must be set between functions F and G. This is indeed the case, as it will be shown. Equation (5) can be written in terms of the instantaneous values of the junction coordinates without introducing the average values which are *a priori* unknown. For this reason we shall make reference to this second form of the weighting factor $\Delta'[T(\Gamma)]$.

THE MODIFIED JG PARTITION FUNCTION

By the very definition of $\mathbf{K}$ and $K^{(0)}$, we must have

$$K^{(0)} = N\bar{r}^2 / 2\nu l^2 \tag{7}$$

where N is the total number of chains and $\bar{r}^2$ is given by

$$\bar{r}^2 = \frac{1}{2N} \left\langle \sum_{\alpha,\beta} (\mathbf{r}_\alpha - \mathbf{r}_\beta)^2 \epsilon_{\alpha\beta} \right\rangle_{\text{undef. state}} \,.$$

Furthermore we must have in the undeformed state:

$$G(1, 3, 3, 1) = 1 \,. \tag{8}$$

Introducing the functionality f of the junctions, which we assume to be *constant throughout the sample*, and the total number of junctions n, we recast Eq. (7) in the form

$$K^{(0)} = n\bar{r}^2 f / 4\nu l^2 \,. \tag{9}$$

Denoting by $x_{\alpha i}$ the ith coordinate of the general junction α, (i.e., $x_{\alpha 1}$, $x_{\alpha 2}$, $x_{\alpha 3}$, for x_α, y_α, z_α), we incorporate the weighting factor (5) into the JG partition function

$$\begin{aligned} Z &= \prod_{i=1}^{3} Z_i \\ &= \prod_{i=1}^{3} \int \prod_{s=1}^{n-m} dx_{si} \exp\left[-\frac{3}{4\nu l^2} \sum_{\alpha,\beta} \epsilon_{\alpha\beta} (x_{\alpha i} - x_{\beta i})^2 \right] \\ &\quad \times \delta\left[\frac{3}{4\nu l^2} \sum_{\alpha,\beta} \epsilon_{\alpha\beta} (x_{\alpha i} - x_{\beta i})^2 - G(\lambda_i) \frac{n\bar{r}^2}{4l^2\nu} \right] . \end{aligned} \tag{10}$$

(For brevity, we omit I_1, I_2 and I_3 from the arguments of G.) Assuming that m surface junctions are kept fixed, the integration is to be performed over the position of the remaining $n-m$ free junctions.

In the absence of deformation we have $\lambda_i = 1$, $G(\lambda_i) = 1$ and the δ factor in Eq. (10) becomes ineffective in the thermodynamic limit. Under these conditions the partition function (10) effectively coincides with the original JG formulation.

We define for further reference a statistical quantity related with the undeformed state of the network

$$\bar{r}_m^2 = \frac{1}{2N} \sum_{\alpha,\beta} \epsilon_{\alpha\beta} \langle (\mathbf{r}_\alpha - \mathbf{r}_\beta)_{\text{undef. state}} \rangle^2 \,. \tag{11}$$

As it is well known, $\bar{r}_m^2$, which determines the rigidity of the material, is the *front factor* of the JG elastic constitutive equation, whereas the previously defined quantity $\bar{r}^2$ [Eq. (7)] plays the analogous role in the Flory–Hoeve–Ciferri (FHC) development[13] of the original WFR theory. For a network having a regular functionality f and a homogeneous length of the chains, $\bar{r}_m^2$ and $\bar{r}^2$ can be related through a straightforward calculation from JG partition function (see Appendix A)

$$\bar{r}_m^2 = \bar{r}^2 - (2/f)\nu l^2 \,. \tag{12}$$

Equation (12) proves that the rigidity of the sample as predicted by FHC theory is generally greater than that given by JG theory. Denoting by x_α the general Cartesian coordinate ($x = x_{1,2,3}$) of the junction α, and by λ the elongation ratio along the same axis, we calculate the corresponding contribution to the factorized partition function [see Eq. (10)]

$$\begin{aligned} Z_x &= \int \prod_{s=1}^{n-m} dx_s \exp\left[-\frac{3}{4\nu l^2} \sum_{\alpha,\beta} \epsilon_{\alpha\beta} (x_\alpha - x_\beta)^2 \right] \\ &\quad \times \delta\left[\frac{3}{4\nu l^2} \sum_{\alpha,\beta} \epsilon_{\alpha\beta} (x_\alpha - x_\beta)^2 - G(\lambda) \frac{n\bar{r}^2 f}{4\nu l^2} \right] . \end{aligned} \tag{13}$$

By making use of the Fourier representation for the delta function

$$\begin{aligned} &\delta\left[\frac{3}{4\nu l^2} \sum_{\alpha,\beta} \epsilon_{\alpha\beta} (x_\alpha - x_\beta)^2 - G(\lambda) \frac{n\bar{r}^2 f}{4\nu l^2} \right] \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \exp\left\{ \frac{3i\omega}{4\nu l^2} \left[\sum_{\alpha,\beta} \epsilon_{\alpha\beta} (x_\alpha - x_\beta)^2 - G(\lambda) \frac{n\bar{r}^2 f}{3} \right] \right\} \end{aligned} \tag{14}$$

and substituting into Eq. (13) we obtain

$$Z_x = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \exp\left[-\frac{i\omega}{4\nu l^2}G(\lambda)nf\bar{r}^2\right] \times \int\prod_{s=1}^{n-m} dx_s \exp\left[-\frac{3}{4\nu l^2}(1-i\omega)\sum_{\alpha,\beta}\epsilon_{\alpha\beta}(x_\alpha - x_\beta)^2\right] . \tag{15}$$

Upon the change of variable $q_\alpha = (1-i\omega)^{1/2}x_\alpha$ Eq. (15) is transformed into

$$Z_x = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \exp\left[-\frac{i\omega}{4\nu l^2}G(\lambda)nf\bar{r}^2\right](1-i\omega)^{-(n-m)/2} \times \int\prod_{s=1}^{n-m} dq_s \exp\left[-\frac{3}{4\nu l^2}\sum_{\alpha,\beta}\epsilon_{\alpha\beta}(q_\alpha - q_\beta)^2\right] . \tag{16}$$

Henceforth, the q variables will be denoted by a small latin subscript if they belong to free junctions, by a capital latin subscript if they refer to fixed junctions, and by a greek subscript in the general case. According to the assumptions of JG theory, the fixed junctions are affinely displaced by the deformation.

Denoting by $x_I^{(0)}$ the initial position of the Ith fixed junction, in general we obtain

$$q_I = (1-i\omega)^{1/2}x_I = (1-i\omega)^{1/2}x_I^{(0)}\lambda . \tag{17}$$

Making the simplifying assumption that no two fixed junctions are connected by a chain, we obtain from Eq. (16)

$$Z_x = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega \exp\left[-\frac{i\omega}{4\nu l^2}G(\lambda)n\bar{r}^2 f\right](1-i\omega)^{-(n-m)/2} \times \int\prod_{s=1}^{n-m} dq_s \exp\left[-\frac{3}{4\nu l^2}\sum_{ik}\epsilon_{ik}(q_i - q_k)^2 - \frac{3}{2l^2\nu}\sum_{iL}\epsilon_{iL}(q_i - q_L)^2\right] . \tag{18}$$

Introducing the matrix $C_{ik} = f\delta_{ik} - \epsilon_{ik}$, we write the second integral appearing in Eq. (18) as

$$I = \exp\left(-\frac{3}{2l^2\nu}\sum_{iL}\epsilon_{iL}q_L^2\right)\int\prod_{s=1}^{n-m} dq_s \times \exp\left\{\frac{3}{2\nu l^2}\left[-\sum_{ik}C_{ik}q_iq_k + 2\sum_i q_i h_i\right]\right\} , \tag{19}$$

where

$$h_i = \sum_L \epsilon_{iL}q_L . \tag{20}$$

Defining the quantities $\bar{q}_\alpha$ as

$$\bar{q}_\alpha \begin{cases} q_I & \text{if } \alpha \equiv I \\ \sum_k (C^{-1})_{ik}h_k & \text{if } \alpha \equiv i \end{cases} \tag{21}$$

and changing to new integration variables

$$p_i = q_i - \bar{q}_i ,$$

we diagonalize the quadratic form

$$I = \exp\left[-\frac{3}{4\nu l^2}\sum_{\alpha,\beta}\epsilon_{\alpha\beta}(\bar{q}_\alpha - \bar{q}_\beta)^2\right] \times \int\prod_{s=1}^{n-m} dp_s \exp\left(-\frac{3}{2\nu l^2}\sum_{ik}C_{ik}p_ip_k\right) . \tag{22}$$

Performing the integration we obtain

$$I = \left(\frac{2l^2\nu\pi}{3}\right)^{(n-m)/2}(\mathrm{Det}C)^{-1/2}\exp\left[-\frac{3}{4\nu l^2}\sum_{\alpha,\beta}\epsilon_{\alpha\beta}(\bar{q}_\alpha - \bar{q}_\beta)^2\right] . \tag{23}$$

Defining the quantities $\bar{x}_\alpha = (1-i\omega)^{-1/2}\bar{q}_\alpha$, we see that $\bar{x}_\alpha$ gives the average position of the corresponding junction. This is obviously true, from the very definitions of q_α and $\bar{q}_\alpha$, if α is a fixed junction. If not, we observe at first from Eqs. (21), (20), and (17) that $\bar{x}_\alpha$ does not depend on ω; in fact we have for $\alpha \equiv i$

$$\bar{x}_i = \lambda\sum_{kL}(C^{-1})_{ik}\epsilon_{kL}x_L^{(0)} = \lambda\bar{x}_i^{(0)} . \tag{24}$$

Then, introducing the variable $x_i - \bar{x}_i$ and transforming to $q_i - \bar{q}_i \equiv p_i$, we may calculate $\langle x_i - \bar{x}_i\rangle$ averaging over the partition integral, the result being zero. Furthermore Eq. (24) shows that the average positions of the junctions are displaced affinely by the deformation. Since JG partition function and the new modified partition function are equivalent in absence of deformation, we conclude that the introduction of *the weighting factor* (5) *does not affect the average positions of the network junctions*. Substituting Eq. (24) into Eq. (23), and making use of the defining equation (11), we get

$$I = \left(\frac{2l^2\nu\pi}{3}\right)^{(n-m)/2}(\mathrm{Det}C)^{-1/2}\exp\left[-\frac{n\bar{r}_m^2 f\lambda^2}{4\nu l^2}(1-i\omega)\right] . \tag{25}$$

Equation (25) can be substituted into the partition function (18)

$$Z_x = \frac{1}{2\pi}\left(\frac{2l^2\nu\pi}{3}\right)^{(n-m)/2}(\mathrm{Det}C)^{-1/2}\exp\left(-\frac{n\bar{r}_m^2 f\lambda^2}{4\nu l^2}\right)J(\lambda) , \tag{26}$$

where $J(\lambda)$ is given by

$$J(\lambda) = \int_{-\infty}^{\infty} d\omega \exp\left\{-i\omega nf\left[\frac{G(\lambda)\bar{r}^2 - \lambda^2\bar{r}_m^2}{4\nu l^2}\right]\right\}(1-i\omega)^{-(n-m)/2} . \tag{27}$$

To simplify calculations we assume that $n-m$ is an even number. With this restriction, obviously inessential or large n and m, $J(\lambda)$ can be calculated through a straightforward application of Cauchy's integral formula

$$J(\lambda) = \frac{2\pi}{[(n-m)/2-1]!}\left\{\left[\frac{G(\lambda)\bar{r}^2 - \lambda^2\bar{r}_m^2}{4\nu l^2}\right]nf\right\}^{(n-m)/2-1} \times \exp\left\{-\frac{nf}{4\nu l^2}[G(\lambda)\bar{r}^2 - \lambda^2\bar{r}_m^2]\right\} . \tag{28}$$

Substituting Eq. (28) into Eq. (26) and making use of Eq. (12), we obtain

$$Z_x = \frac{(2l^2\nu\pi/3)^{(n-m)/2}}{[(n-m)/2-1]!}(\mathrm{Det}C)^{-1/2} \times \left\{\frac{nf}{4}\left[(G(\lambda)-\lambda^2)\frac{\bar{r}^2}{\nu l^2} + \frac{2}{f}\lambda^2\right]\right\}^{(n-m)/2-1}\exp\left[-\frac{nf}{4}G(\lambda)\frac{\bar{r}^2}{\nu l^2}\right] . \tag{29}$$

From Eq. (29) we get the expression for the free energy in the thermodynamic limit ($m \ll n$; $m, n-m \to \infty$)

$$A(\lambda) = -kT\ln\left(\prod_{\lambda=\lambda_1,\lambda_2,\lambda_3} Z_x\right) = -\frac{nkT}{2}\sum_{i=1}^{3}\ln\left\{[G(\lambda_i)-\lambda_i^2]\frac{\bar{r}^2}{\langle r^2\rangle_0} + \frac{2}{f}\lambda_i^2\right\}$$

$$+\frac{nfkT}{4}\frac{\bar{r}^2}{\langle r^2\rangle_0}\sum_{i=1}^{3}G(\lambda_i)\,, \qquad (30)$$

where the usual notation $\langle r^2\rangle_0$ for the unperturbed mean square chain displacement νl^2 has been introduced. The fluctuations of the junctions are generally affected by the deformation. Denoting by x_t the general coordinate $(x_t - x_{t1,2,3})$ of the tth junction, and by λ the corresponding elongation ratio, we may calculate $\langle(x_t - \bar{x}_t|^2\rangle$ through the partition integral, obtaining as a result

$$\langle(x_t-\bar{x}_t)^2\rangle = \frac{\nu l^3}{3}C_{tt}^{-1}\left\{\frac{f}{2}[G(\lambda)-\lambda^2]\frac{\bar{r}^2}{\langle r^2\rangle_0}+\lambda^2\right\}. \qquad (31)$$

In the condition of rest $[\lambda = 1, G(1) = 1]$ we have

$$\langle(x_t-\bar{x}_t)^2\rangle^{(0)} = \frac{\nu l^2}{3}C_{tt}^{-1}\,. \qquad (32)$$

From Eqs. (31) and (32) we get

$$\langle(x_t-\bar{x}_t)^2\rangle = \left\{\frac{f}{2}[G(\lambda)-\lambda^2]\frac{\bar{r}^2}{\langle r^2\rangle_0}+\lambda^2\right\}\langle(x_t-\bar{x}_t)^2\rangle^{(0)}\,. \qquad (33)$$

The first of the two factors on the right-hand side of Eq. (33) coincides, apart from the multiplicative constant $f/2$, with the argument of the logarithmic terms in the free energy (30). Thus we conclude quite generally that, *whenever a nonvanishing coupling exists between the macroscopic deformation and the junction fluctuations, a logarithmic term appears in the free energy.* Summing Eq. (33) over all junctions of the network, we obtain

$$\left\langle\sum_t(x_t-\bar{x}_t)^2\right\rangle = \left\{\frac{f}{2}[G(\lambda)-\lambda^2]\frac{\bar{r}^2}{\langle r^2\rangle_0}-\lambda^2\right\}\left\langle\sum_t(x_t-\bar{x}_t)^2\right\rangle^{(0)} \qquad (34)$$

or, in terms of previously defined quantities [see Eqs. (3) and (4)],

$$F(\lambda) = \left\{\frac{f}{2}[G(\lambda)-\lambda^2]\frac{\bar{r}^2}{\langle r^2\rangle_0}+\lambda^2\right\}. \qquad (35)$$

Equation (35) gives the functional relationship connecting $F(\lambda)$ and $G(\lambda)$, thus establishing the formal equivalence between the two weighting factors (4) and (5).

THE FORM OF THE COUPLING FUNCTIONS $G(\lambda_i,\lambda_1,\lambda_2,\lambda_3)$ AND $F(\lambda_i,\lambda_1,\lambda_2,\lambda_3)$

From the defining Eqs. (3), (4), (5), and (6) we must have

$$G(\lambda_i),\ F(\lambda_i)\geq 0$$
$$G(1) = F(1) = 1\,.$$

Minimizing the free energy (30) with respect to $G(\lambda_i)$, which corresponds to neglecting internal constraints, we obtain

$$G(\lambda_i) = \lambda_i^2 - (\lambda_i^2-1)\frac{2}{f}\frac{\langle r^2\rangle_0}{\bar{r}^2}\,, \qquad (36)$$

$$F(\lambda_i) = 1\,, \qquad (37)$$

$$A(\lambda) = \frac{nfkT}{4}\left[\frac{\bar{r}^2}{\langle r^2\rangle_0}-\frac{2}{f}\right]\sum_{i=1}^{3}\lambda_i^2+\text{const.}\,,$$

or, from Eq. (12),

$$A(\lambda) = \frac{nfkT}{4}\frac{\bar{r}_m^2}{\langle r^2\rangle_0}\sum_{i=1}^{3}\lambda_i^2+\text{const.}\,. \qquad (38)$$

Equation (37) shows that, in the absence of internal constraints, the fluctuations of the junctions are not affected by the deformation, while Eq. (38) gives an expression for the free energy of deformation that is identical with the result of James and Guth, as it was to be expected.

The reasons for assuming the existence of a strong coupling between the directional fluctuations of the junctions and the macroscopic deformation field have been previously discussed. We have already seen in the introductory sections that the invariance of the interaction probability between any two chain sections of the network requires—as a necessary although not strictly sufficient condition—that an affine average displacement of the junctions be accompanied by an affine distortion of their fluctuations in space. With this hypothesis, and assuming that the principal deformation axes coincide with the Cartesian axes, let us now see how the *overall* mean-square fluctuations of the junctions change upon deformation [see Eqs. (2) and (3)]; we obtain

$$\sum_\alpha\sum_{i=1}^{3}\langle(x_{\alpha i}-\bar{x}_{\alpha i})^2\rangle = H^{(0)}\sum_{i=1}^{3}\lambda_i^2\,. \qquad (39)$$

Confining our attention for a while to constant-volume deformations, it is important to remark that $(\lambda_1^2+\lambda_2^2+\lambda_3^2)$ is stationary for $\lambda_1=\lambda_2=\lambda_3=1$, which means that the overall fluctuation keeps constant for small strains around the isotropic state, as it appears reasonable. On the other hand, for large deformations $\sum\lambda_i^2$ becomes larger and larger, with the paradoxical consequence that the motions associated with some of the degrees of freedom allowed to our system would increase without limit after application of physical constraints. To put it another way, at large deformations the topological constraints not only should affect the fluctuations of the junctions, they should be *almost entirely responsible for them*. We shall see later how to overcome this absurdity. Confining now our attention to small deformations, we will accept the hypothesis of affine distortion of the fluctuations, which leads to [see also Eq. (35)]

$$F(\lambda_i) = G(\lambda_i) = \lambda_i^2\,. \qquad (40)$$

Substituting Eq. (40) into the elastic free energy (30), we obtain, apart from an inconsequential additive constant:

$$A(\lambda_i) = \frac{nfkT}{4}\frac{\bar{r}^2}{\langle r^2\rangle_0}\sum_{i=1}^{3}\lambda_i^2 - nkT\ln(\lambda_1\lambda_2\lambda_3)\,. \qquad (41)$$

Considering that $\langle r^2\rangle_0$ is the mean-square end-to-end distance of the unperturbed chain, we observe that Eq. (41) coincides with the Flory–Hoeve–Ciferri[13] elastic equation. This appears to be a rather surprising result since we have started from JG statistical approach.

Let us now take into consideration the hypothesis of large deformation, specifically assuming that one of the λ_i's goes to infinity. In order to avoid the paradox of infinitely large fluctuations, we shall impose that $F(\lambda_i)$ tends to some finite limit. From Eq. (35) we get as a consequence

$$G(\lambda_i) \sim \lambda_i^2 \left(1 - \frac{2}{f} \frac{\nu l^2}{\bar{r}^2}\right) \tag{42}$$

for $\lambda_i \gg 1$, whereas for $\lambda_i \simeq 1$ we must have

$$G(\lambda_i) \sim \lambda_i^2 . \tag{43}$$

Obviously enough, the problem of finding a regular function $G(\lambda_i, I_1, I_2, I_3)$ satisfying the asymptotic conditions (42) and (43) does not admit a unique solution. However it may be deduced from Eqs. (42) and (43) that any possible solution must approach the FHC result at small deformations and JG behavior asymptotically at high deformations. The simplest way to generate a continuously differentiable function $G(\lambda_i, I_1, I_2, I_3)$ satisfying the asymptotic conditions (42) and (43), is to replace Eq. (40) by the *weaker* condition

$$G(\lambda_i) = g(I_1, I_2, I_3)\lambda_i^2 , \tag{44}$$

where $g(I_1, I_2, I_3)$ is to be determined by a minimization of the free energy. In fact the condition $G(1) = 1$ guarantees that $g \sim 1$ at small deformations, so as to satisfy Eq. (43), while the minimization requirement ensures that Eq. (42) is approached at high deformations. Using Eq. (44), as a result of the minimization process, we obtain

$$G(\lambda_i, I_1) = \lambda_i^2 - \frac{2}{f} \frac{\nu l^2}{\bar{r}^2} \lambda_i^2 \left(1 - \frac{3}{I_1}\right) , \tag{45}$$

or

$$F(\lambda_i, I_1) = 3\lambda_i^2 / I_1 . \tag{46}$$

From a physical point of view, the solution represented by Eq. (45) or (46) has some attractive features, as we shall see. It gives

$$\sum_i F(\lambda_i, I_1) = 3 . \tag{47}$$

Equation (47), which is also obtained by JG theory (that is, neglecting configurational hindrances) means that the m.s. junction fluctuations, averaged over all directions, are never increased when taking topological constraints into account. This conclusion is consistent with the intuitive idea that additional constraints should not increase the overall fluctuations of a physical system. To this extent Eq. (47) is a *necessary correction* to the strong affinity result which is obtained from Eq. (39)

$$\sum_i F(\lambda_i) = I_1 \ (\geq 3 \text{ at constant volume}) . \tag{48}$$

Substituting Eq. (45) into the general formula (30) giving the free energy of deformation, we obtain, apart from an inconsequential additive constant

$$A(\lambda) = -\frac{nkT}{2} \sum_{i=1}^{3} \ln\left(\frac{\lambda_i^2}{I_1}\right) + \frac{nfkT}{4} \frac{\bar{r}_m^2}{\langle r^2 \rangle_0} \sum_{i=1}^{3} \lambda_i^2 . \tag{49}$$

For constant volume deformations a simpler formula is obtained

$$A(\lambda) = \frac{3nkT}{2} \ln(I_1) + \frac{nfkT}{4} \frac{\bar{r}_m^2}{\langle r^2 \rangle_0} I_1 . \tag{50}$$

The force per unit undeformed cross section, referring to a uniaxial tension test, is easily obtained from Eq. (50)

$$\sigma(\lambda) = \frac{nfkT}{2} \left[\frac{\bar{r}_m^2}{\langle r^2 \rangle_0} + \frac{2}{f} \frac{3\lambda}{\lambda^3 + 2}\right] \left(\lambda - \frac{1}{\lambda^2}\right) . \tag{51}$$

If λ is arourd unity, from Eqs. (51) and (12) we have

$$\sigma(\lambda) \sim \frac{nfkT}{2} \left[\frac{\bar{r}_m^2}{\langle r^2 \rangle_0} + \frac{2}{f}\right] \left(\lambda - \frac{1}{\lambda^2}\right) = \frac{nfkT}{2} \frac{\bar{r}^2}{\langle r^2 \rangle_0} \left(\lambda - \frac{1}{\lambda^2}\right) \tag{52}$$

which corresponds to the FHC equation, whereas for $\lambda \gg 1$ James behavior is asymptotically approached

$$\sigma(\lambda) \sim \frac{nfkT}{2} \frac{\bar{r}_m^2}{\langle r^2 \rangle_0} \left(\lambda - \frac{1}{\lambda^2}\right) . \tag{53}$$

These results are consistent with the general conclusions previously drawn. Anticipating further discussion, we may say that the gradual transition, occurring at intermediate deformations, between the stiffer Flory-like elasticity (52) and the softer James–Guth behavior (53) is perhaps responsible for the so-called Mooney effect observed on dry rubbers. We wish to remark that Eqs. (49) and (50) give a physical interpretation of this effect without making recourse to the second deformation invariant I_2, which appears in the original Mooney–Rivlin empirical equation

$$A(\lambda) = C_1(I_1 - 3) + C_2(I_2 - 3) . \tag{54}$$

Our result seems to support recent criticism[14] on the physical justification for Eq. (54). It should be borne in mind that in highly swollen polymers the retractile force is usually seen to obey rather closely the $(\lambda - 1/\lambda^2)$ law within a relatively large range of λ values. Obviously enough, this may easily be interpreted according to JG theory; the effect of the packing forces being virtually absent, the network system is not bound to maintain a constant overlap probability between the various chain sections even at small deformations, with the consequence that no restriction on the junction fluctuations is required.

EXPERIMENTAL IMPLICATIONS OF THE THEORY

Figure 2 shows the plots of the tensile stress vs λ in unidirectional deformation according to the theory of James and Guth [JG, see Eq. (53)], to the Flory–Hoeve–Ciferry theory [FHC, see Eq. (52)], and to our intermediate model [IM, see Eq. (51)]. Although the first two curves differ for a scale factor only, they have been reported in order to stress that the intermediate model behaves according to FHC theory at moderate departures from $\lambda = 1$, while tending asymptotically to JG curve for large strains. We have adopted for the ratio $\bar{r}_m^2/\langle r^2 \rangle_0$ the orientative value 1/2 on the following grounds. For a regular tetrahedral network of identical amorphous polymethylene chains, e.g., all the average distances between neighboring junctions have the same value of about $5.2 \times 10^{-8} \mathfrak{N}^{1/3}$ cm ($\mathfrak{N}$ = number of $-CH_2-$ units per chain), obtained upon imposing the actual density value (~ 0.86 g/cm^3). Since the $\langle r^2 \rangle_0$ unperturbed mean-square distance is about $(16.6 \times 10^{-16} \mathfrak{N})$ cm^2 at room temperature,[15] the $\bar{r}_m^2/\langle r^2 \rangle_0$ ratio ranges between 0.35 and 0.20 for $\mathfrak{N}$ in the range 100–500 (corresponding to a range 15–75 in terms of the number of statistical segments). Considering that any deviation from a regular topology necessarily entails a broadening of the distribution of

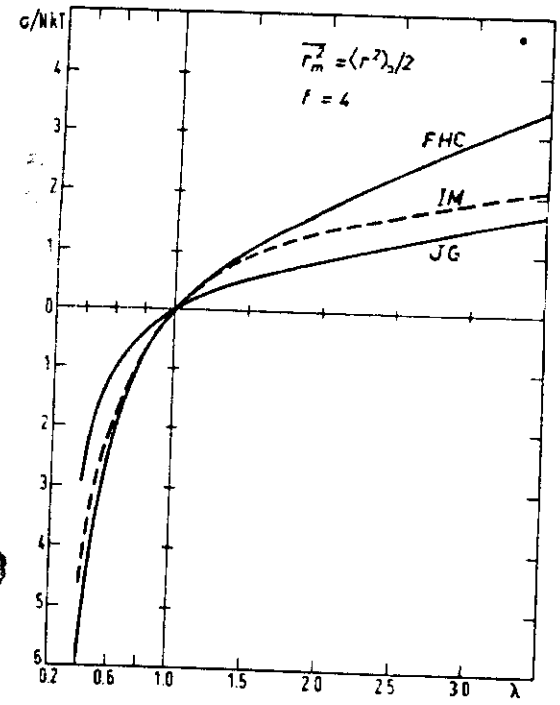

FIG. 2. Elongational stress in uniaxial tension vs the stretch ratio λ for a tetrafunctional rubber network, as predicted by Flory–Hoeve–Ciferri (FHC) theory, by James–Guth (JG) theory, and by the intermediate model (IM); see text ($N = nf/2$ is the number of chains per unit volume of the network).

the average chain vector lengths, with a consequent increase of $\overline{r}_m^2$, we have chosen a larger value for the above ratio, although keeping it lower than unity seemed reasonable. It is apparent from Fig. 2 that in simple elongation the Mooney effect is fairly well interpreted by the intermediate model. In the compression region some deviation from the $(\lambda - 1/\lambda^2)$ law is observed (see the FHC/curve for comparison), contrary to most experimental data, although the discrepancy is much less dramatic than yielded by the C_2/λ Mooney term. This is also seen from Fig. 3(a) where the deviations from the above law may be better appreciated in both cases. Figure 3(b) shows the corresponding plot obtained from experiments by Rivlin and Saunders.[16] The experimental curve, similarly to our IM curve, appears to be stationary around $\lambda = 1$ and then to decrease in the compression region at small deformations, although its eventual increase contrasts with IM predictions.

The following formula is usually assumed to relate the temperature coefficient of the unperturbed mean-square end-to-end chain distance with the retractile force

$$-[\partial \ln(\sigma/T)/\partial T]_{L,V} = d \ln\langle r^2\rangle_0/dT \,, \qquad (55)$$

where the derivative is to be evaluated at both constant length L and constant volume V of the sample. From Eqs. (52) and (53) it may be seen that Eq. (55) holds for JG theory only (in the limit of highly swollen samples), since $\overline{r}_m^2$ is invariant with temperature if we neglect the dilation coefficient of the material. Otherwise the right-hand member of the above equation must be corrected by a factor equal to

$$\left(1 + \frac{2}{f}\frac{\langle r^2\rangle_0}{\overline{r}_m^2} q\right)^{-1} ,$$

where q is either unity or $3\lambda/(2+\lambda^3)$, depending on whether FHC theory or our intermediate model is adopted. While the above factor must be always smaller than unity with the parameters chosen in Figs. 2 and 3 it should be 0.5 in both cases for $\lambda \sim 1$, increasing to 0.67 if $\overline{r}_m^2 = \langle r^2\rangle_0$. On the basis of thermodynamics considerations Krigbaum and Roe[17] also pointed out that the existence of the Mooney effect should entail some inaccuracy in Eq. (55).

It is beyond the scope of the present paper to discuss other problems related with the nonideal behavior of unswollen rubbers, especially those related with large relaxation times and with other temperature dependent effects.[10]

CONCLUDING CONSIDERATIONS

The basic assumption whereupon the present paper is developed is the following: the action of the forces mutually exerted between chain segments of an unswollen polymer network is approximately accounted for, from the statistical-mechanical viewpoint, by properly restricting the fluctuations of the junctions. The above forces arise both from packing requirements and from topological constraints; they prevent the network from collapsing to an infinitely high density,[7] and at the same time make it difficult to modify the pattern of the inter-

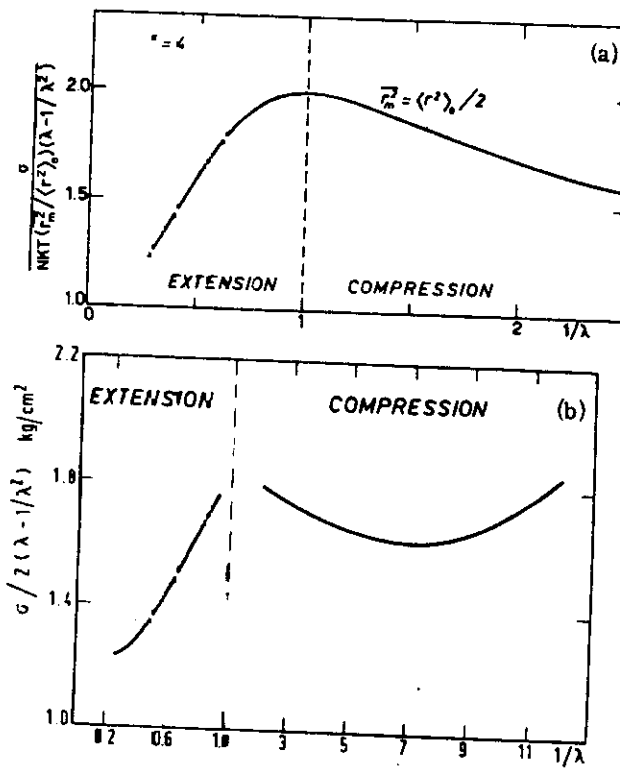

FIG. 3. (a) The ratio of the elongational stress as predicted by the IM model and JG theory plotted against $1/\lambda$ for one significant value of the rigidity factor $\overline{r}_m^2$ ($N = nf/2$ is the number of chains per unit volume of the network). (b) The ratio of the experimental elongational stress to $2(\lambda - 1/\lambda^2)$ plotted against $1/\lambda$. The experimental results are due to Rivlin and Saunders.[16]

chain contacts upon deformation. In order to take a full account of these effects, it would be necessary to develop a statistical concept of the entanglement | presumably along the lines recently indicated by Ziabicki[9,10] for the isotropic state, and to predict on a structural basis the statistical coupling between entanglements and macroscopic deformation. The methods devised by Freed[11] should be very useful in this connection.

Within the limits of our approach, which may be considered as phenomenological in nature, the requirement that the interaction probability between any two parts of the network be invariant with deformation may be satisfied if *both* the average coordinates of the junctions *and* their rms fluctuation tensor are transformed with the affinity law. By imposing the last restriction to the JG partition function we obtain an expression of the free energy [see Eq. (41)] completely identical with that derived by Flory and co-workers.[13] This conclusion is remarkable and to some extent surprising, inasmuch as, unlike Flory, (i) we explicitly account for the chain connectivity of the network, (ii) we impose the fixed volume condition through the James–Guth procedure of constraining the position of the surface junctions, thus obtaining nonzero values for the components of the chain end-to-end average vectors, and (iii) we do not introduce any entropy effect associated with the random distribution of the junctions. However, a basic common feature of both our treatment and Flory's is that the whole probability distribution of the end-to-end chain vectors—and not merely their average values, as in JG theory—is affinely transformed.

Although for an unswollen polymer the above restriction to the junction fluctuations appears to be very reasonable at small strains, it is physically untenable at large deformations because it would lead to exceedingly large fluctuations. Allowing for the fluctuations being of a finite range in the high deformation limit, we come to the conclusion that any realistic model should behave (a) like Flory's at $\lambda \sim 1$ and (b) like James and Guth's at $\lambda \gg 1$. We have considered in some detail what we believe to be the simplest of these models, denoting it as "intermediate model" (IM), because of its following reasonable features: (i) as in Flory's theory the ratios between the rms junction fluctuations along the various directions (although not their actual values) are in agreement with the affinity law; (ii) as in JG theory the overall values of the m.s. fluctuations are invariant with respect to the applied deformation. Although in the compression region the predicted discrepancy from the $(\lambda - \lambda^{-2})$ law is too pronounced as compared to most experimental data, in simple elongation the so-called Mooney effect is fairly well explained. It should be stressed that any model meeting requirements (a) and (b) should be able to interpret the Mooney effect at least to some extent, inasmuch as the slope of the force at large λ's must be smaller than required by the $(\lambda - \lambda^{-2})$ law, if the initial slope is used as a reference for normalization (see Fig. 2).

As a final comment, we want to stress that if the front factor of the tensile stress, i.e., the factor multiplying $(\lambda - \lambda^{-2})$ in Eqs. (52) and (53), is put into the form $Nk\bar{T}\bar{\rho}^2/\langle r^2\rangle_0$ (N = number of chains), then $\bar{\rho}^2$ is temperature independent for JG theory only. As a consequence, the validity of Eq. (55) is limited to this case.

APPENDIX—THE CONNECTION BETWEEN $\bar{r}^2$ AND $\bar{r}_m^2$

By the very definition of $\bar{r}^2$ we obtain

$$\bar{r}^2 = \frac{2}{nf}\left\langle \frac{1}{2}\sum_{\alpha,\beta}\epsilon_{\alpha\beta}(\mathbf{r}_\alpha - \mathbf{r}_\beta)^2 \right\rangle . \tag{A1}$$

Explicitating Eq. (A1) by means of the partition integral, we obtain

$$\bar{r}^2 = \frac{1}{nfZ}\int \prod_{i=1}^{r-m} d\mathbf{r}_i \sum_{\alpha,\beta}\epsilon_{\alpha\beta}(\mathbf{r}_\alpha - \mathbf{r}_\beta)^2 \times \exp\left[-\frac{3}{4\nu l^2}\sum_{\alpha,\beta}\epsilon_{\alpha\beta}(\mathbf{r}_\alpha - \mathbf{r}_\beta)^2\right] . \tag{A2}$$

Introducing the quantity $s = 3/4\nu l^2$, we write Eq. (A2) in the more suitable form

$$\bar{r}^2 = -\frac{1}{nf}\frac{d}{ds}\ln Z . \tag{A3}$$

An evaluation of the JG partition function gives in the thermodynamic limit:

$$Z \propto s^{-3n/2}\exp(-s\bar{r}_m^2 nf) . \tag{A4}$$

Upon substitution into Eq. (A3) we get

$$\bar{r}^2 = \frac{3}{2f}\frac{1}{s} + \bar{r}_m^2$$

or, from the definition of s,

$$\bar{r}^2 = \frac{2}{f}\nu l^2 + \bar{r}_m^2 \tag{A5}$$

that corresponds to Eq. (12) of the paper.

[1] W. Kuhn, Kolloid-Z. 76, 258 (1936); 87, 3 (1939).
[2] H. M. James, J. Chem. Phys. 15, 651 (1947).
[3] H. M. James and E. Guth, J. Chem. Phys. 15, 669 (1947).
[4] F. T. Wall, J. Chem. Phys. 10, 132, 485 (1942); 11, 527 (1943).
[5] P. J. Flory and J. Rehner, Jr., J. Chem. Phys. 11, 512 (1943).
[6] F. T. Wall and P. J. Flory, J. Chem. Phys. 19, 1435 (1951); J. J. Hermans, Trans. Faraday Soc. 43, 591 (1947).
[7] G. Ronca and G. Allegra, J. Chem. Phys. 63, 4104 (1975).
[8] L. R. G. Treloar, *The Physics of Rubber Elasticity* (Oxford, University, London, 1958), Chap. VIII.
[9] E. A. Di Marzio, J. Chem. Phys. 36, 1563 (1962).
[10] K. J. Smith, Jr., A. Green, and A. Ciferri, Kolloid-Z. 194, 49 (1964).
[11] K. F. Freed, J. Chem. Phys. 55, 5588 (1971).
[12] G. Ronca (unpublished results).
[13] P. J. Flory, C. A. Hoeve, and A. Ciferri, J. Polym. Sci. 34, 337 (1959).
[14] A. Ziabicki in E. J. Hinch and A. Ziabicki, "The Mechanics of Fluid Suspensions and Polymer Solutions: a Report on Euromech 49," J. Fluid Mech. 66, Pt. 1, 1 (1974).
[15] P. J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience New York, 1969).
[16] R. S. Rivlin and P. R. Saunders, Philos. Trans. A 243, 251 (1951).
[17] W. R. Krigbaum and R. J. Roe, Rubber Chem. Technol. 38, 1039 (1965); R. J. Roe, Trans. Faraday Soc. 62, 312 (1966).
[18] A. Ziabicki, Kolloid-Z. (to be published).

The Angular Distribution of Crystallinity in a Stretched Rubberlike Polymer

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SUMMARY:

The distribution of crystallinity around the axis of elongation in a rubberlike polymer stretched above its normal melting temperature is calculated. Although most of the basic assumptions are identical with those adopted by Flory in 1947, the model of rubber elasticity proposed by Ronca and Allegra in 1975 is explicitly adopted, and the assumption of parallelism among the crystallites is avoided. According to some experimental observations, only the extended chain crystallization mechanism is taken into consideration. The incipient crystallization temperature and the equilibrium retractile force are also obtained. The X-ray intensity distribution for the general reflection on a stretched fiber diagram is formally derived as a function of crystallite orientation. Agreement with several experimental data obtained by Cesari, Perego, Zazzetta and Gargani from crosslinked *cis*-1,4-polybutadiene may be regarded as satisfactory, considering the simplifying assumptions. According to the theoretical predictions, the crystallites formed at incipient crystallization are quite narrowly aligned around the direction of elongation. Unlike Flory's theory, the present formalism leads to no discontinuity in the derivative of the retractile force vs. the stretch ratio at the incipient crystallization point, in agreement with observation.

Introduction

Recent experimental studies on stress-induced crystallization in crosslinked polymers[1–5] suggest the existence of two distinct mechanisms of crystal formation, the first of which shows a faster kinetics and probably leads to extended-chain crystallite formation, being followed by a slower mechanism producing the usual folded-chain crystallites. Gaylord[6,7] proposed a theory of stress-induced crystallization in crosslinked networks where chain folding is explicitly taken into consideration; stress changes, crystal orientation and birefringence effects as well as the initial rate and the incipient temperature of crystallization are theoretically interpreted. Although the end-to-end vector of a crystallized chain section is assumed to be oriented along the direction of stretch, following Flory's classical theory of extended chain crystallization[8], the end-to-end orientation with respect to the stretch axis of the general chain connecting two different crosslinks is not explicitly considered, so that average results are obtained. Smith considered another interesting model[9] which is basically characterized by the assumption that the direction taken by the chain through a crystallite is determined by the first few segments entrapped within the crystallite itself. Consequently, although each chain is still assumed to traverse a crystallite only once, it may do that in either sense of direction, although with two different probabilities.

Stimulated by the experimental results obtained by Cesari, Perego et al.[4,5] on crosslinked samples of *cis*-1,4-polybutadiene, we have undertaken a theoretical study on stress-induced crystallization above the normal melting point, where essentially extended chain crystallites should form[1,4], with the main purpose of obtaining the probability distribution of the crystallizing chains at different angles with the axis of stretch. This type of information may be obtained by diffraction experiments[4,5]. Although our statistical approach is different from that proposed by Flory[8], most of the basic assumptions are the same; in particular, the system is considered to be at thermodynamic equilibrium and the entropy of nucleation is ignored. The major feature characterizing the present approach is that a chain segment is assumed here to crystallize parallel to the end-to-end chain vector, unlike Flory's hypothesis that all the crystallites are aligned in the stretch direction[8]; however, in agreement with Flory, we assume that any chain may traverse a crystallite with a single pass and only along the direction of higher probability. Another difference from Flory's approach[8,10] is that we impose different constraints to the junction fluctuations in order to account for packing effects[10,11]. Namely, by simply imposing the root-mean-square fluctuations along (x, y, z) to be proportional to $(\lambda_x, \lambda_y, \lambda_z)$, their values are rescaled so that the overall mean square (m.s.) fluctuation of each junction always keeps the same value as in the absence of strain. As Ronca and Allegra have shown[11], this type of constraint is able to reproduce rather satisfactorily the experimental data both in extension and in compression; from a conceptual viewpoint, the rescaling operation forbids any unrealistic increase of the fluctuations with increasing applied stress. As we shall see, in the present context the fluctuation constraint only affects the shape of the stress vs. strain curve, with no effect on the angular crystallinity distribution.

It should be stressed that the present model was chosen mainly for reasons of simplicity; in fact, it appears to be related with a very limited amount of ad-hoc hypotheses and of adjustable parameters. However, although our calculations lead to a satisfactory qualitative interpretation of the experimental data, the quantitative agreement is rather approximate, due to the very simplicity of the model.

General Part

Theoretical approach

As said above, the following theory is only applicable above T_m^0, i.e. the normal melting point of the unstressed sample. Our assumptions are the following:

1) The sample is at thermodynamic equilibrium[8]. This means that for any stretch ratio λ, crystallites may only form by parallel association of chains which happen to be physically contiguous. Chains that are contiguous for a given value of λ may tend to move apart if the strain changes. The corresponding crystallites must progressively melt and reform, at least partially; otherwise they would act as additional network junctions, or entanglements, thus preventing the absolute free energy minimum to be reached. Under these ideal assumptions it is reasonable to neglect the (negative) entropy related with crystal nucleation[8].

2) For any stretch ratio the uncrystallized chain sections are sufficiently far from full elongation as to conform to the Gaussian behavior.
3) The average positions of the junctions are always dictated by the law of affine deformation. As anticipated, according to the Ronca-Allegra treatment the junction fluctuations along the principal axes are $(\lambda_x \cdot k,\ \lambda_y \cdot k,\ \lambda_z \cdot k)$, k being adjusted so that $k^2(\lambda_x^2 + \lambda_y^2 + \lambda_z^2) = \text{const.}$[11].
4) Chain sequences connecting two given junctions (heretofore denoted as "chains" for brevity; any junction connects three chains at least) must contain a large number of monomeric units, i.e. at least of the order of 50 to 100. They are all assumed to be of equal length.
5) Each chain may partially crystallize, in which case the crystallized section is oriented parallel to the straight line through the average positions of the two junctions connected by the chain. Although it will be essentially immaterial for the following treatment whether a chain is involved in more than one crystallite or not, each crystallite is supposed to be only traversed along the direction which leads from the starting junction to the other. This last assumption is based on the same argument that suggests chain folding to be unlikely above T_m^0. In any event, the occurrence of opposite traverse of the crystallites should be rare[8].
6) All the chains having the same average end-to-end orientation with respect to the stretch direction crystallize to the same fractional extent, no matter what is the average distance between their end points. Actually, for small degrees of crystallinity (see next point) this assumption is equivalent to considering an average degree of crystallization (see Eqs. (5) and (6)) for the parallel chains.
7) The theory is strictly applicable under conditions of incipient crystallization[8], i.e. for an overall degree of crystallinity not exceeding about 10%.

The general expression of the elastic network free energy $A(\lambda)$ given in ref.[11] (Eqs. (49) and (50), intermediate model) may be reformulated in the following equivalent form

$$A(\lambda) = \frac{3k_B T}{Nl^2} \sum_k (\overline{\Delta x_k^2} + \overline{\Delta y_k^2} + \overline{\Delta z_k^2}) + \frac{3}{2} \frac{\nu}{f} k_B T \ln \left(\frac{\lambda_x^2 + \lambda_y^2 + \lambda_z^2}{3} \right) - k_B T \ln Z_0 \quad (1)$$

where (see Fig. 1) k_B is the Boltzmann constant, T the absolute temperature; N the uniform number of statistical segments per chain (a statistical segment comprises the shortest sequence of skeletal bonds which is essentially uncorrelated with the next segment in terms of space orientation; for *cis*-1,4-polybutadiene it seems to correspond to about 2 monomeric units[12,13]); l is the root-mean-square length of each segment; $\overline{\Delta x_k}$, $\overline{\Delta y_k}$, $\overline{\Delta z_k}$ are the average end-to-end displacements of the k-th chain along the three principal axes and the sum is extended to the ν chains of the network; f is the functionality degree of the junctions, assumed as uniform, $(\lambda_x, \lambda_y, \lambda_z)$ are the principal components of the strain tensor λ, Z_0 is the partition function of the ideal "phantom" network in the absence both of strain and of any physical constraint other than the existing topological interconnections among the junctions.

It should be clearly remindec here that any network with n-dimensional connectivity ($n > 1$) is bound to collapse to an infinite density if appropriate constraints are

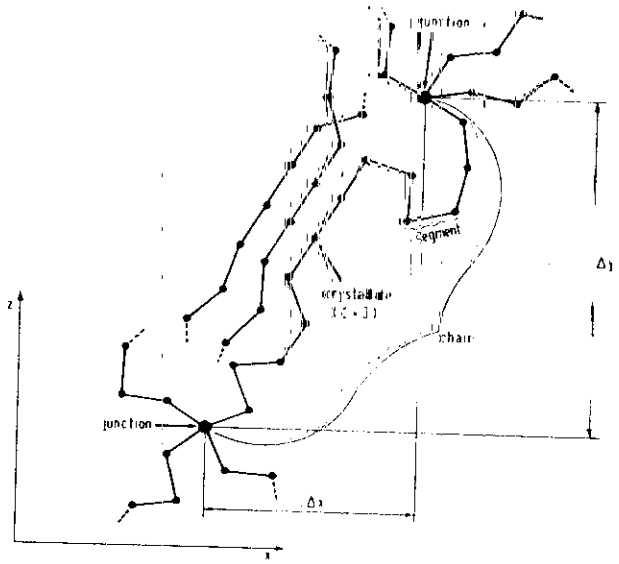

Fig. 1. Schematic drawing of a network chain comprising $N = 14$ statistical segments, $\zeta = 3$ of which are crystallized

not postulated[14,15]; consequently, Z_0 is a purely hypothetical partition function. A particularly simple way of preserving both the real average density and the actual external shape of the sample is to assume that a proper number of junctions are constrained to lie at the surface of a parallelepiped whose shape is dictated by the state of strain[14]. Consequently, $\langle\overline{\Delta x_k^2}\rangle$, $\langle\overline{\Delta y_k^2}\rangle$, $\langle\overline{\Delta z_k^2}\rangle$ never vanish even for the unstrained system.

If the general k-th chain contains ζ_k crystallized segments, its free energy changes because of i) the disappearance of the corresponding amorphous portion, ii) the appearance of the crystalline fraction and iii) the change of the average end-to-end vector *characterizing the remaining amorphous portions of the chains* from $\bar{r}_k = (\overline{\Delta x_k^2} + \overline{\Delta y_k^2} + \overline{\Delta z_k^2})^{1/2}$ to $\bar{r}_k - \zeta_k l$ (because of assumptions 3) and 5)). As for the junction fluctuations, we will assume them to be constrained as in the case of the completely amorphous network[1]. Although the term depending on $\ln[(\lambda_x^2 + \lambda_y + \lambda_z^2)/3]$, appearing in Eq. (1), is strictly valid only for amorphous chains all having the same length, we will take it to hold for partly crystallized chains as well. The lack of any dependence from chain length in the above term appears to support this approximation. Besides, we shall assume henceforth uniaxial extension at constant volume, so that $\lambda_z = \lambda$, $\lambda_x = \lambda_y = \lambda^{-1/2}$. Consequently the network free-energy becomes, for small ζ_k/N (cf. assumption 7)):

$$A_c(\lambda,\zeta) = \frac{3}{2}\frac{\nu k_B T}{f}\ln\left(\frac{\lambda^2 + 2/\lambda}{3}\right) - k_B T[\ln Z_0 - \sum \zeta_k(\partial \ln Z/\partial\zeta)_0] + g_c \sum \zeta_k + \frac{1}{2}\sum \frac{3k_B T(\bar{r}_k - \zeta_k l)^2}{2(N-\zeta_k)l^2} \tag{2}$$

where g_c is the free energy of a statistical segment within a crystallite, while the subscript zero refers to the unconstrained network. The general term $+k_B T\zeta_k(\partial \ln Z/\partial\zeta)_0$ corresponds to the disappearance of $\zeta_k(\ll N)$ statistical segments from the amorphous part of the k-th chain, while $\zeta_k g_c$ is the free energy

contribution of the same segments in the crystalline state. We will replace $-k_B T(\partial \ln Z/\partial \zeta)_0$ with g_a, i.e., the effective free energy per statistical segment in the amorphous state of incipient crystallization. After further substituting $g_a - g_c$ with $(h_f - Ts_f)$, where h_f and s_f are the enthalpy and entropy of fusion of one statistical segment, respectively, and the terms not containing ζ_k with the symbol $A_0(\lambda)$, we have from Eq. (2) (dropping the index k for simplicity):

$$A_c(\lambda, \zeta) = A_0(\lambda) - \sum \zeta(h_f - Ts_f) + \sum \frac{3k_B T(\bar{r} - \zeta l)^2}{2(N - \zeta) l^2} \tag{3}$$

It may be useful to write explicitly the above free-energy as a sum of contributions each belonging to one of the chains comprised in the network

$$A_c(\lambda, \zeta) = \sum \mathscr{A}_\zeta$$
$$\mathscr{A}_\zeta = \mathscr{A}_0(\lambda) - \zeta(h_f - Ts_f) + \frac{3k_B T}{2(N - \zeta) l^2} (\bar{r} - \zeta l)^2 \tag{4}$$

where $\mathscr{A}_0(\lambda) = A_0(\lambda)/\mathscr{N}$. According to assumption 6), all the chains having the same direction cosines for the vector $\bar{r}$ are characterized by the same crystallization degree ζ. Their crystallized segments must obviously pack among themselves within the same crystals, in view of their parallel orientation. The sub-ensemble comprising all these parallel-oriented chains will be assumed to attain its own crystallization equilibrium independently of all the other chains. There are two simplifying hypotheses under these assumptions, i.e. 1) any chain may find enough contiguous chains having (about) the same end-to-end vector, to pack with; 2) adjacent crystallites do not disturb each other. Accordingly, the parameter ζ will be derived by imposing that the sum of all the $\mathscr{A}_\zeta$'s belonging to the sub-ensemble (or, equivalently, their average value $\langle \mathscr{A}_\zeta \rangle$) is at a minimum. Let us evaluate $\langle \mathscr{A}_\zeta \rangle$ with the substitutions $w = \zeta/N$, $\gamma = \bar{r}/N$:

$$\langle \mathscr{A}_\zeta \rangle = \mathscr{A}_0(\lambda) - Nw(h_f - Ts_f) + \frac{3}{2} Nk_B T(\langle \gamma^2 \rangle - 2\langle \gamma \rangle w + w^2)/(1 - w) \tag{5}$$

After imposing the stationary condition $\partial \langle \mathscr{A}_\zeta \rangle / \partial \zeta = N^{-1} \partial \langle \mathscr{A}_\zeta \rangle / \partial w = 0$, we get

$$w = 1 - \{(1 - 2\langle \gamma \rangle + \langle \gamma^2 \rangle) 3k_B T/s_f [3k_B T/s_f - 2(T - T_m^*)]\}^{1/2} \quad \text{(only if } w \geq 0) \tag{6}$$

where $T_m^* = h_f/s_f$ is to be regarded as the melting temperature of an ideally unconstrained, undeformed network.

Although this state is essentially unrealistic, as long as the crosslinks correspond to uncrystallizable regions T_m^* should be somewhat lower than the melting temperature of the uncrosslinked polymer[8]; however, the parallel configurational entropy decrease induced by the crosslinks may exert an opposite effect. Only for infinitely long chains T_m^* must be expected to be identical with the normal melting point.

If $(\overline{\Delta x}, \overline{\Delta y}, \overline{\Delta z})$ are the cartesian components of the general average end-to-end chain vector, and $(\lambda_x, \lambda_y, \lambda_z)$ are the principal stretch ratios, the affinity assumption leads to

$$\bar{\Delta x} = \lambda_0 \cdot \bar{\Delta x}_0 = \Delta x_0/\lambda^{1/2}; \quad \bar{\Delta y} = \lambda_y \cdot \Delta y_0 = \Delta y_0/\lambda^{1/2}; \quad \bar{\Delta z} = \lambda_z \cdot \Delta z_0 = \lambda \cdot \Delta z_0 \tag{7}$$

where the zero subscript refers to the undeformed state. Furthermore we shall adopt spherical polar co-ordinates for the average end-to-end vector, distinguishing between the undeformed and deformed states. Let φ and ϕ be the angles formed by $\bar{r}_0$ and $\bar{r}$ with the z-axis, respectively, while χ is the common value of their azimuthal angles. We have

$$\begin{aligned}
&\bar{\Delta x} = \bar{r}\sin\phi\cdot\cos\chi = \bar{\Delta x}_0/\lambda^{1/2} = \bar{r}_0\sin\varphi\cos\chi/\lambda^{1/2}\\
&\bar{\Delta y} = \bar{r}\sin\phi\cdot\sin\chi = \bar{\Delta y}_0/\lambda^{1/2} = \bar{r}_0\sin\varphi\sin\chi/\lambda^{1/2}\\
&\bar{\Delta z} = \bar{r}\cos\phi = \bar{\Delta z}_0\cdot\lambda = \bar{r}_0\cos\varphi\cdot\lambda\\
&\cos\phi = \cos\varphi/(\cos^2\varphi + \lambda^3\sin^2\varphi)^{1/2}; \quad \cos\varphi = \cos\phi/(\cos^2\phi + \lambda^3\sin^2\phi)^{1/2}
\end{aligned} \tag{8}$$

where, remembering that $\bar{r}/(Nl) = \bar{\gamma}$

$$\langle\gamma\rangle = \langle\gamma_0\rangle(\lambda^2\cos^2\varphi + \sin^2\varphi/\lambda)^{1/2}; \quad \langle\gamma^2\rangle = \langle\gamma_0^2\rangle(\lambda^2\cos^2\varphi + \sin^2\varphi/\lambda) \tag{9}$$

In deriving Eqs. (8), it must be remembered that the averages are performed at constant φ. Here we will assume for simplicity that the probability distribution of $\bar{r}_0$ is gaussian and that its mean-square value is Nl^2, i.e. the same value as for the free unperturbed chain. Consequently

$$\langle\gamma_0^2\rangle = \langle\bar{r}_0^2\rangle/(N^2l^2) = 1/N; \quad \langle\gamma_0\rangle = \langle\bar{r}_0\rangle/(Nl) = \left(\frac{8}{3\pi N}\right)^{1/2} \tag{10}$$

Substituting from Eqs. (9) and (10), Eq. (6) gives the chain fractional crystallinity as a function of the external variables T and λ as well as of the angle φ defining the average orientation of the chain:

$$\begin{aligned}
w(\varphi) = 1 - \left\{\left[1 - 2\left(\frac{8}{3\pi N}\right)^{1/2}(\lambda^2\cos^2\varphi + \sin^2\varphi/\lambda)^{1/2} + \frac{1}{N}(\lambda^2\cos^2\varphi + \sin^2\varphi/\lambda)\right]\right.\\
\left.\times\frac{3k_BT}{s_f}\Big/\left(\frac{3k_BT}{s_f} - 2(T - T_m^*)\right)\right\}^{1/2}
\end{aligned} \tag{6'}$$

For a given stretch ratio λ, there is a temperature, say $T_{m\lambda}$, at which the crystallites oriented parallel to the z axis (i.e. with $\varphi = 0$) melt, or start to form (incipient crystallization). $T_{m\lambda}$ is obtained by Eq. (6'), putting $w(0) = 0$ (cf. with the corresponding Eq. (19) in ref.[9]):

$$T_{m\lambda} = T_m^*\Big/\left[1 - \frac{2}{3}\frac{k_B}{s_f}\left(2\lambda\left(\frac{8}{3\pi N}\right)^{1/2} - \lambda^2/N\right)\right] \tag{11}$$

At lower temperatures, there is a limiting angle φ_{lim} within the undeformed sample (corresponding to ϕ_{lim} for the actual sample) above which no crystallized material may exist:

$$\cos\varphi_{\lim} = \left\{\left[N\left[\left(\frac{8}{3\pi}\right)^{1/2} + \left(\frac{8}{3\pi} - \frac{2s_f(T + T_m^*)}{3k_B T}\right)^{1/2}\right]^2 - \lambda^{-1}\right] / (\lambda^2 - \lambda^{-1})\right\}^{1/2} \quad (12)$$

$$\cos\varphi_{\lim} = \lambda\cos\varphi_{\lim}/[(\lambda^2 - \lambda^{-1})\cos^2\varphi_{\lim} + \lambda^{-1}]^{1/2}$$

The first equation of Eqs. (12) is obtainable after putting $w(\varphi_{\lim}) = 0$ into Eq. (6'), while the second one derives from Eqs. (8). The positivity requirement of the quantities within square roots gives

$$T \leqslant T_{\lim} = T_m^* \Big/ \left(1 - \frac{8}{3\pi}\frac{k_B}{s_f}\right) \quad (13)$$

i.e. an upper limit is set to the temperature of crystallization, independently of the stress. An analogous requirement is also found within Flory's theory (cf. Eq. (18) of ref.[8], e.g.).

The overall fractional crystallinity of the sample may easily be obtained from Eq. (6') as

$$\alpha_w(T, \lambda) = 2\int_0^{\varphi_{\lim}} w(\varphi)\, p(\varphi)\, d\varphi \quad (14)$$

where $p(\varphi)\,d\varphi$ is the probability of finding a chain within the angle φ and $\varphi + d\varphi$ in the undeformed sample and the factor 2 in the right-hand side is due to the fact that both the (equivalent) angular intervals (0 to $\varphi_{\lim}$) and ($(\pi - \varphi_{\lim})$ to π) must be taken into consideration. Due to the statistically isotropic structure of the undeformed network we have

$$p(\varphi)\,d\varphi = \frac{1}{4\pi}\cdot 2\pi\sin\varphi\,d\varphi = \frac{1}{2}\sin\varphi\,d\varphi \quad (15)$$

Let us now obtain the probability density $W_0(\phi)$ of finding a fractional crystallinity $\frac{1}{2} W_0(\phi)\cdot\sin\phi\,d\phi$ between ϕ and $\phi + d\phi$, in the elongated sample. Obviously enough, the fractional crystallinity must be the same no matter whether the coordinates φ or ϕ are adopted, so that

$$\frac{1}{2} w(\varphi)\sin\varphi\,d\varphi = \frac{1}{2} W_0(\phi)\sin\phi\,d\phi \quad (16)$$

Differentiating the last of Eqs. (8), we get

$$W_0(\phi) = w(\phi)\,\lambda^3(\cos^2\phi + \lambda^3\sin^2\phi)^{-3/2} \quad (17)$$

where $w(\phi)$ stands for the expression given in Eq. (6'), $\cos\varphi$ and $\sin\varphi$ being substituted in terms of $\cos\phi$ and $\sin\phi$ (see Eqs. (8)).

The equilibrium retractile force of the partially crystallized sample with undeformed length L_0 is

$$f_\lambda = \frac{1}{L_0}\left(\frac{\partial A_c}{\partial \lambda}\right)_T \tag{18}$$

The free energy $A_c(\lambda, \xi)$ will be conveniently expressed in terms of the following integral, replacing the sum given in Eq. (4),

$$A_c = \int_0^\pi \langle \mathscr{A}_\zeta \rangle \cdot \frac{1}{2} \sin\varphi \, d\varphi \tag{19}$$

where $\langle \mathscr{A}_\zeta \rangle$ (see Eqs. (5) and (6')) is to be regarded as an explicit function of T, λ and of the crystallinity fraction $w(= \xi/N)$. Eq. (18) transforms to

$$f_\lambda = \frac{1}{2}\frac{1}{L_0}\int_0^\pi \left[\left(\frac{\partial \langle \mathscr{A}_\zeta \rangle}{\partial \lambda}\right)_{T,w} + \left(\frac{\partial \langle \mathscr{A}_\zeta \rangle}{\partial w}\right)_{T,\lambda} \cdot \left(\frac{\partial w}{\partial \lambda}\right)_T\right] \sin\varphi \, d\varphi \tag{20}$$

$$= \frac{1}{2}\frac{1}{L_0}\int_0^\pi \left(\frac{\partial \langle \mathscr{A}_\zeta \rangle}{\partial \lambda}\right)_{T,w} \sin\varphi \, d\varphi$$

because $(\partial \langle \mathscr{A}_\zeta \rangle / \partial w)_{T,\lambda} = 0$ corresponds to our assumption of equilibrium crystallization. Remembering Eqs. (5), (9), (10) and (6'), we obtain from Eq. (20)

$$f_\lambda = \frac{\mathscr{N} k_B T}{L_0}(\lambda - \lambda^{-2})\left(1 + \frac{12}{f}\frac{3\bar{n}}{\lambda^3 + 2}\right) - \frac{3}{2}\frac{\mathscr{N} k_B T}{L_0}\int_0^{\varphi_{\lim}} \frac{w(\varphi)}{1 - w(\varphi)}$$

$$\times \frac{d}{d\lambda}\left[-(\lambda^2 \cos^2\varphi + \lambda^{-1}\sin^2\varphi) + 2\left(\frac{8\mathscr{N}}{3\pi}\right)^{1/2} \times (\lambda^2 \cos^2\varphi + \lambda^{-1}\sin^2\varphi)^{1/2}\right] \sin\varphi \, d\varphi \tag{21}$$

where $w(\varphi)$ is given by Eq. (6'). The present theory is based on the assumption that the stretch ratio is not so large as to lead to chain extensions approaching full elongation, so that the above integrand is always positive. As a consequence the corresponding contribution to the retractile force is always negative, as expected; it vanishes for $w(\varphi) \equiv 0$, i.e. when the rubber is completely amorphous, in which case the Ronca-Allegra expression is recovered (Eq. (51), ref.[11]).

It is worth pointing out that the derivative with respect to λ of the crystallization-dependent contribution to f_λ is zero for incipient crystallization, which means that f_λ is a smooth function of λ everywhere. This conclusion may be easily obtained from Eq. (21), remembering that *both* $\varphi_{\lim}$ and $w(\varphi)$ vanish under these conditions. Unlike the present case, Flory's more simplified treatment leads to a discontinuity in the first derivative of the force vs. the fractional elongation. Although this discontinuity must be regarded as a direct consequence of the model assumptions, with no particular thermodynamic meaning, we want to remark that the impossibility to define the amorphous and crystalline regions as separate phases — as Flory clearly points out[8]

— makes the existence of any real transition unlikely. On the other hand, it is a clear experimental X-ray evidence favouring the present approach that in the course of incipient crystallization the existing crystallites are indeed quite rigorously aligned along the direction of stretch, unlike those which may form at lower temperature and/or at higher extension.

Relationship between $W_0(\phi)$ and the intensity distribution along the arcs of the X-ray reflections

In order to compare the crystal probability distribution $W_\phi(\phi)$ with the X-ray intensities on stretched fiber diagrams, we need a suitable relationship between $W_0(\phi)$ and $W_\alpha(\beta)$, i.e., the probability distribution for the general reflection making an angle α with the c axis of the crystals, as a function of the angle β with the axis of stretch (coinciding with the fiber axis). Obviously enough, except for a proportionality constant $W_\alpha(\beta)$ corresponds to the intensity distribution of the reflection under consideration for different β's. Referring to Fig. 2, the orientation in reciprocal space

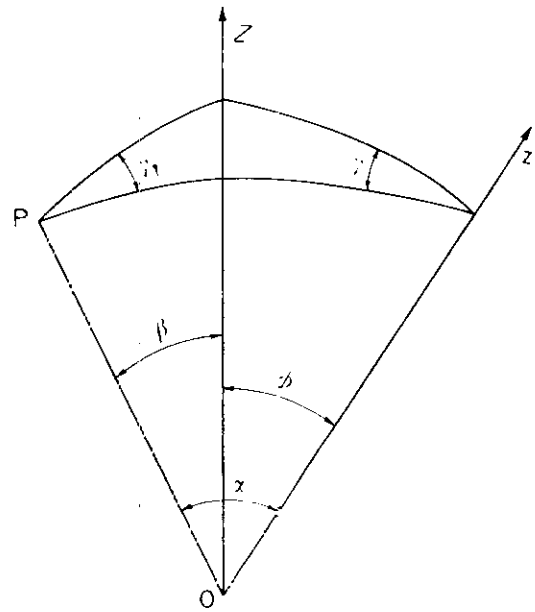

Fig. 2. Geometrical relationship among ϕ (i.e., the angle between the z axis of the general crystallite and the direction of stretch Z), β (angle between the particular reflection P belonging to the same crystallite and the Z axis) and the dihedral angles γ and γ_1

of the reflection is indicated by the unit vector $\overrightarrow{OP}$ while the c axis of the general crystal corresponds with z. In turn, the orientation of $\overrightarrow{OP}$ with respect to the axis of stretch Z is further specified by the dihedral angle γ between the plane containing Z and z and that containing z and $\overrightarrow{OP}$; for a given α, once the angle ϕ between Z and z and the dihedral angle γ are both specified, the angle β between Z and $\overrightarrow{OP}$ is uniquely determined by the well known relationship

$$\cos\gamma = \frac{\cos\beta - \cos\phi\cos\alpha}{\sin\phi\sin\alpha} \tag{22}$$

Henceforth, α will be treated as a fixed parameter, since it only depends on the particular reflection chosen. In the particular case $\alpha = 0$ (e.g., for a 00l reflection,

the c axis being orthogonal to a and b) it is apparent from Fig. 2 that β coincides with ϕ so that $W_0(\beta) \equiv W_0(\phi)$. In the general case, the joint elementary probability $d^2 W(\phi, \gamma)$ of having the two angles within the intervals $(\phi, \phi + d\phi)$ and $(\gamma, \gamma + d\gamma)$ respectively, may be expressed as

$$d^2 W(\phi, \gamma) = 2 \sin\phi \cdot W(\gamma/\phi) \cdot W_0(\phi) \cdot d\phi \, d\gamma \tag{23}$$

where $W(\gamma/\phi)$ is the conditional probability density of having γ for a given ϕ. Obviously, since

$$\int_0^{2\pi} W(\gamma/\phi) \, d\gamma = 1 \tag{24}$$

for any ϕ, it is easy to see that the double integral of $d^2 W$ over ϕ and γ is unity, as it should be.

Using Eq. (22), it is possible to express γ in terms of β and ϕ; in particular, considering that $d\gamma$ appearing in Eq. (23) corresponds to fixed ϕ, upon differentiation of Eq. (22) we get

$$d\gamma \, (\phi = \text{const.}) = \frac{\sin\beta \, d\beta}{[(\sin\alpha \sin\phi)^2 - (\cos\beta - \cos\alpha \cos\phi)^2]^{1/2}} \tag{25}$$

With the aid of Eqs. (22) and (25) the double differential $d^2 W(\phi, \gamma)$ may be transformed into $d^2 W(\phi, \beta)$. Then integration over ϕ produces the elementary probability of having β in the interval $(\beta, \beta - d\beta)$, for all azimuthal directions around the Z axis (see Fig. 2). This probability may be expressed as $2\pi \sin\beta \cdot W_\alpha(\beta) \, d\beta$, where $W_\alpha(\beta)$ is the probability density we are looking for. Consequently, we get

$$2\pi \sin\beta \, W_\alpha(\beta) \, d\beta = 4\pi \int_{\phi=0}^{\phi=\pi} W(\gamma/\phi) \, W_0(\phi) \frac{\sin\phi \sin\beta \, d\phi \, d\beta}{[(\sin\alpha \sin\phi)^2 - (\cos\beta - \cos\alpha \cos\phi)^2]^{1/2}} \tag{26}$$

where an extra factor 2 is applied to the right-hand side because two opposite values for γ are possible with the same set of angles (ϕ, β). Eq. (26) gives

$$W_\alpha(\beta) = 2 \int_{\phi=0}^{\phi=\pi} W(\gamma/\phi) \, W_0(\phi) \frac{\sin\phi \, d\phi}{[(\sin\alpha \sin\phi)^2 - (\cos\beta - \cos\alpha \cos\phi)^2]^{1/2}} \tag{27}$$

In Eq. (27) we have modified the expression under the square root into a form equivalent to that appearing in Eq. (26) (the expression is symmetrical in the variables ϕ and β). Let us now introduce the angle γ_1 defined as

$$\cos\gamma_1 = \frac{\cos\phi - \cos\alpha \cos\beta}{\sin\alpha \sin\beta} \tag{28}$$

After comparison of Eq. (22) with Eq. (28), γ_1 is readily identified with the dihedral angle between the planes defined by (Z, OP) and (z, OP) (see Fig. 2). The differential $d\gamma_1$ (β = const) is obviously given by Eq. (25) except for interchanging ϕ and β. As a result, it is easy to verify that Eq. (27) reduces to

$$W_\alpha(\beta) = 2 \int_0^\pi W(\gamma/\phi) \cdot W_0(\phi)\, d\gamma_1 \tag{29}$$

where γ and ϕ must be considered as functions of γ_1 and β through Eqs. (22) and (28); in particular, from Eq. (28),

$$\phi = \cos^{-1}(\cos\gamma_1 \sin\alpha \sin\beta + \cos\alpha \cos\beta) \tag{30}$$

and it is possible to see that, for a given β, the possible corresponding values of $|\phi|$ are always comprised between $|\beta - \alpha|$ and $|\beta + \alpha|$. On the other hand, the symmetrical Eq. (22) shows that this statement remains correct after interchange between ϕ and β. Consequently, the total angular spread $\Delta\beta$ of X-ray intensities around the average angle α is given by $2\phi_{\lim}$.

The above equation requires the knowledge of the conditional probability density $W(\gamma/\phi)$, in addition to $W_0(\phi)$. Obviously enough, the simplest assumption corresponds to $W(\gamma/\phi) = 1/(2\pi)$, implying that the crystals are rotated around their c axes in a purely random manner no matter what is the angle ϕ. Consequently the above equation reduces to

$$W_\alpha(\beta) = \frac{1}{\pi} \int_0^\pi W_0(\phi)\, d\gamma_1 \tag{31}$$

In the following, we will adopt the above stated hypothesis thereby using Eqs. (31) and (30).

Comparison with Experimental Results

We have compared our theoretical results with the experimental data obtained on a high molecular weight, high steric purity cross-linked *cis*-1,4-polybutadiene by Cesari et al.[5]. More specifically, the most important data for our purposes are those giving the percent crystallinity α_w, the angular width within which crystallinity is observed ($2\phi_{\lim} = \Delta\beta$) and the X-ray intensity in the middle of the arc of the 110 reflection at different elongations and temperatures ($\alpha_{110} = 90°$). These data were all obtained by measuring the X-ray intensity diffracted by a stretched fiber. It is important to remark that the data appeared to be essentially reproducible, no matter whether the final temperature was reached moving towards increasing or decreasing values, at constant elongation. This should give reasonable confidence on the attainment of a close-to-equilibrium condition. Figs. 3 and 4 show the comparison between theory and experiment, on the basis of the three best-fitting parameters h_f, s_f and N reported in Tab. 1; we want to remind that these quantities refer to the statistical segment. The enthalpy and entropy of melting per monomeric unit[12] are also reported for reference. The corresponding limiting temperature $T_{\lim}$ (see Eq. (13)) is 62,4 °C. The incipient crystallization temperatures for the elongations considered in Fig. 3 are also given in Tab. 1, together with the calculated values. On the whole, agreement between observed and calculated data is rather rough; in particular, Fig. 4 shows that the

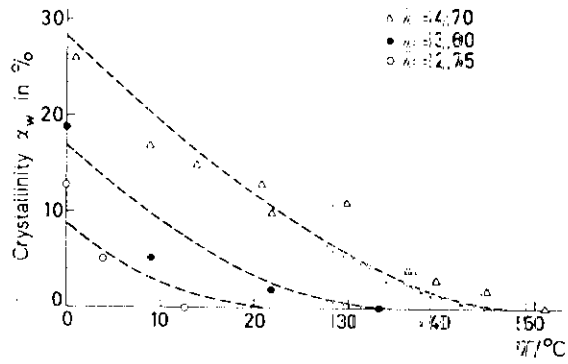

Fig. 3

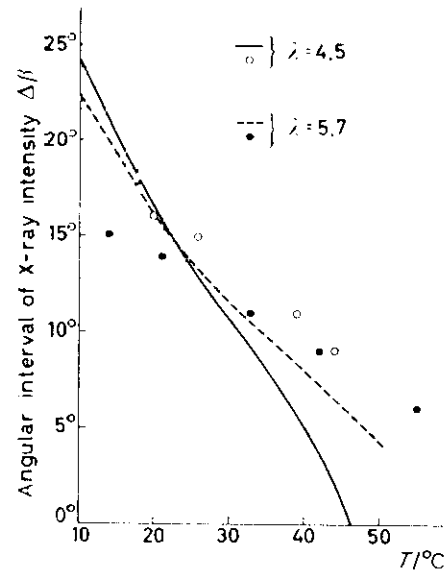

Fig. 4

Fig. 3. Overall crystallinity α_w of high-purity, cross-linked *cis*-1,4-polybutadiene for different temperatures and stretch ratios λ. Experimental points are taken from refs.[4] and [5], dashed lines are calculated from Eqs. (14) and (5')

Fig. 4. Angular width ($\Delta\beta = 2\phi_{1/2}$) of the crystallite distribution for different temperatures and two different stretch ratios λ. Lines correspond to data obtained from Eq. (12), circles to experimental values[5]

broadening of the X-ray reflections is much larger than calculated, at higher temperatures. Although the viscosimetric data in unperturbed solution are well interpreted on the basis of approximately two monomeric units per statistical segment[13], the best-fitting values of N, h_f and s_f shown in Tab. 1 would suggest that the statistical segment is better represented by about a single monomeric unit within the present theory.

From the data reported in Tab. 1, the temperature $T_m^* = h_f/s_f$ is 250 K, that is about 17 K lower than $T_m^0 = T_{m\lambda}(\lambda = 1) = 266{,}6$ K, i.e. the melting temperature of the undeformed sample. This is not surprising since T_m^* refers to an ideal state where the network is not only undeformed but also unconstrained to occupy a fixed volume, which leads to the necessary consequence that it should shrink to an infinite density[14, 15]. As long as λ is larger than unity — and smaller than $4\sqrt{2N/(3\pi)}$, otherwise most chains would be elongated at an essentially complete extension, contrary to our hypothesis — Eq. (11) leads to $T_{m\lambda} > T_m^0$.

Fig. 5 shows some calculated plots of the crystal probability distributions $W_0(\phi)$ and $W_{90°}(\beta)$, calculated from Eqs. (16), (17), (30) and (31). $W_{90°}(\beta)$ must be simply proportional to the X-ray intensity diffracted by any $hk0$ reflection (i.e., $\alpha = 90°$) for different angles β from the stretch direction. Tab. 2 shows the comparison between some X-ray intensities measured in the middle of the arc along the 110 reflection (i.e., $\beta = 90°$)[16], and the corresponding calculated values of $W_{90°}(90°)$ for different T's and λ's. The values have been obtained from the same sample and are

Tab. 1. Calculated and experimental values of N (number of statistical segments or monomeric units per chain connecting two different junctions), h_f and s_f (heat and entropy of fusion, respectively, per statistical segment or monomeric unit)

a)

	Best-fitting parameters referred to the statistical segment	Experimental values, referred to the monomeric unit
N	69	50 [4] (average value assuming 4 chains per crosslink)
h_f/(kcal/mol) [a]	2,48	2.21 [12]
s_f/(cal · mol^{-1} · K^{-1}) [a]	9,94	8.07 [12]

b)

Stretch ratio λ	Temperature of incipient crystallization $T_{m\lambda}$/°C	
	calc. from Eq. (11)	obs.[15]
1	−6,4 (= T_m^0)	−3
2,75	+21,2	+13
3,60	+33,1	+34
4,70	+46,2	+51

[a] In SI units: 1 kcal = 4,184 kJ.

Tab. 2. Comparison between properly scaled X-ray intensities in the middle of the arc of the 110 reflection[16] and the corresponding $W_{90°}(90°)$ values (see Eq. (31))

Stretch ratio λ	X-ray intensity at T =					
	10 °C		20 °C		30 °C	
	obs.	calc.	obs.	calc.	obs.	calc.
3,6	4,8	5,2	2,4	2,6	(undetectable)	0,4
4,7	14,4	14,1	9,6	10,1	6,6	5,9

given in arbitrary although uniform scale. Although the X-ray intensity profiles along the arcs corresponding to the Bragg reflections have not been obtained quantitatively, the qualitative agreement appears to be satisfactory.

Fig. 6 shows the calculated normalized tensile force (see Eq. (21)) vs. λ, for different temperatures. The incipient crystallization points are put into evidence; as anticipated, no discontinuity in the derivative of the force is obtained. In agreement with what has been observed by Smith[9] on some data obtained from Wildschut[17]

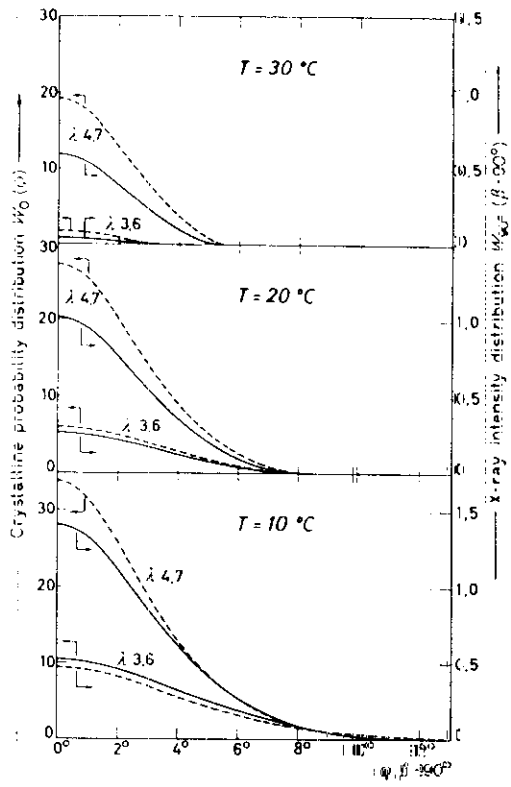

Fig. 5

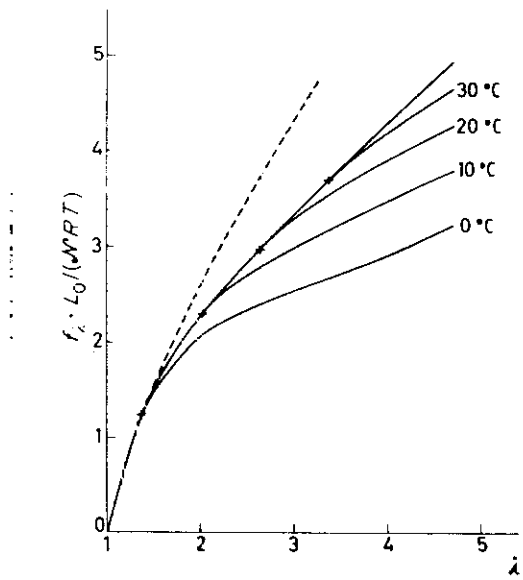

Fig. 6

Fig. 5. Probability distributions $W_\varphi(\varphi)$ (see Eq. (17)) and $W_{90°}(\beta)$ (see Eq. (31)) for different temperatures and for different stretch ratios λ

Fig. 6. The normalized retractile force $f_\lambda \cdot L_0/(\mathcal{N}RT)$ vs. λ (see Eq. (21)), for different temperatures as indicated. Crosses indicate points of incipient crystallization. The upper solid line corresponds to no crystallization, the dashed line corresponds to the ideal $(\lambda - \lambda^{-2})$ behaviour with the same initial slope

with natural rubber, the decrease on f_λ'/T is rather closely proportional to the induced amount of crystallinity. Some preliminary results obtained by Gargani and Giuliani from *cis*-polyisoprene at temperatures slightly above the normal melting point indicate that the tensile stress decrease due to sample crystallization is about of the same amount as calculated here[18].

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1) A. Keller, M. J. Machin, J. Macromol. Sci., Phys. **1**, 41 (1967); M. J. Hill, A. Keller, ibid. **3**, 153 (1969)
2) Von D. Göritz, F. H. Müller, W. Sietz, Colloid Polym. Sci. **252**, 330 (1974)
3) D. Luch, G. S. Y. Yeh, J. Macromol. Sci., Phys. **7**, 121 (1973)
4) M. Cesari, L. Gargani, G. P. Giuliani, G. Perego, A. Zazzetta, J. Polym. Sci., Polym. Lett. Ed. **14**, 107 (1976)
5) M. Cesari, G. Perego, A. Zazzetta, L. Gargani, Makromol. Chem. **180**, 1143 (1980)
6) R. J. Gaylord, D. J. Lohse, Polym. Eng. Sci. **16**, 163 (1976)
7) R. J. Gaylord, J. Polym. Sci., Polym. Phys. Ed. **14**, 1827 (1976)
8) P. J. Flory, J. Chem. Phys. **15**, 397 (1947)
9) K. J. Smith, Polym. Eng. Sci. **16**, 168 (1976)
10) P. J. Flory, Proc. R. Soc. London, Ser. A: **351**, 351 (1976)
11) G. Ronca, G. Allegra, J. Chem. Phys. **63**, 4990 (1975)
12) G. Natta, G. Moraglio, Makromol. Chem. **66**, 218 (1963)
13) G. Moraglio, Eur. Polym. J. **1**, 103 (1965); G. Allegra, Makromol. Chem. **110**, 58 (1967)
14) H. M. James, E. Guth, J. Chem. Phys. **15**, 669 (1947)
15) G. Ronca, G. Allegra, J. Chem. Phys. **63**, 4104 (1975)
16) G. Perego, M. Cesari, private communication
17) A. J. Wildschut, J. Appl. Phys. **17**, 51 (1946)
18) L. Gargani, G. P. Giuliani, private communication