

# Statistical Mechanics of Cross-Linked Polymer Networks I. Rubberlike Elasticity

Cite as: J. Chem. Phys. 11, 512 (1943); <https://doi.org/10.1063/1.1723791>

Submitted: 04 October 1943 . Published Online: 22 December 2004

Paul J. Flory, and John Rehner



View Online



Export Citation

## ARTICLES YOU MAY BE INTERESTED IN

### Thermodynamics of High Polymer Solutions

The Journal of Chemical Physics 10, 51 (1942); <https://doi.org/10.1063/1.1723621>

### Theory of the Elastic Properties of Rubber

The Journal of Chemical Physics 11, 455 (1943); <https://doi.org/10.1063/1.1723785>

### Kinetics of swelling of gels

The Journal of Chemical Physics 70, 1214 (1979); <https://doi.org/10.1063/1.437602>



**New**

## Your Qubits. Measured.

Meet the next generation of quantum analyzers

- Readout for up to 64 qubits
- Operation at up to 8.5 GHz, mixer-calibration-free
- Signal optimization with minimal latency

[Find out more](#)

 Zurich Instruments

Equation (12) was used to find the curves shown in Fig. 1.

The rate expression involving the acid chromate ion is

$$-d(\text{CrO}_3)/dt = k(\text{HCrO}_4^-)(\text{CH}_3\text{CHOHCH}_3)(\text{H}^+)^2. \quad (6)$$

The concentration of acid chromate ion can be calculated from the equilibrium expression

$$K' = (\text{HCrO}_4^-)^2/(\text{Cr}_2\text{O}_7^{--}) = 0.015 \text{ mole/liter} \quad (5)$$

where the parentheses indicate concentrations,

not activities. Using the notation defined above,

$$(\text{HCrO}_4^-) = \frac{-K' + [K'^2 + 8K'(b-x)]^{1/2}}{4}. \quad (13)$$

The integrated rate equation becomes

$$\frac{1}{6} \int_0^x \frac{dx}{(a-x)(c-x)^2[-K' + K'^2 + 8K'(b-x)]^{1/2}} = kt. \quad (14)$$

The indicated integration was performed graphically.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 11, NUMBER 11 NOVEMBER, 1943

## Statistical Mechanics of Cross-Linked Polymer Networks

### I. Rubberlike Elasticity<sup>1</sup>

PAUL J. FLORY AND JOHN REHNER, JR.

*Chemical Division, Esso Laboratories, Standard Oil Development Company, Elizabeth, New Jersey*

(Received October 4, 1943)

A model is proposed for the structure of a cross-linked network, such as exists in a vulcanized rubber, which is amenable to statistical treatment. Expressions are derived for the structural entropy of the network, and for the entropy change on deformation. The latter is in agreement with the relationship derived by Wall and others by a different treatment.

IT has been adequately demonstrated that the elastic retractive forces in rubber and rubberlike materials arise principally from the decrease in entropy accompanying deformation.<sup>2,3</sup> Only at high degrees of elongation, where crystallization may occur to a considerable degree, does the term  $(\partial\Delta H/\partial L)_T$  assume a magnitude comparable with  $T(\partial\Delta S/\partial L)_T$ ,  $L$  being the length of the sample in the direction of stretch. Hence, to an approximation which is good except for large deformations the retractive force is given by

$$f = (\partial\Delta F/\partial L)_T \cong -T(\partial\Delta S/\partial L)_T. \quad (1)$$

<sup>1</sup> A preliminary account of the work presented in this and the following paper was presented before the New York Academy of Sciences Conference on High Polymers, January 9, 1943.

<sup>2</sup> K. H. Meyer and C. Ferri, *Helv. Chim. Acta* **18**, 570 (1935); D. S. Ornstein, J. Wouda, and J. G. Eymers, *Proc. Akad. Wetensch. Amst.* **33**, 273 (1930); V. Hauk and W. Neumann, *Zeits. f. physik. Chemie* **A182**, 285 (1938); E. Guth, *J. Phys. Chem.* **46**, 826 (1942).

<sup>3</sup> L. R. G. Treloar, *Trans. Faraday Soc.* **38**, 293 (1942).

From the standpoint of polymer structure, a vulcanized rubber consists of a three-dimensional network composed of very long rubber molecules laterally attached to one another at occasional points along their lengths. The cross-linkages may consist of primary valence bonds connecting the chains directly, or of an intermediate group or atom such as sulfur which is bonded to each of the two chains. The precise nature of the cross-linkage is relatively unimportant here, aside from the stipulation that it be of a permanent nature. In the course of the cross-linking process (vulcanization) the original long polymer molecules can be considered to lose their identity, and there emerges a single giant network structure, the basic elements of which are the portions of the molecules reaching from one cross-linkage to the next. This basic element will be called a chain. (The term "chain" will not be applied to the long polymer molecules from which the network is formed.)

The cross-linkages bestow a degree of permanence on the network structure; the mid-portion of a chain is free to assume many configurations, but each end of the chain is constrained to join the ends of three other chains at the cross-linkage. When deformation occurs, the cross-linkages are shifted to new positions relative to one another in a manner paralleling the macroscopic deformation. Consequently the "displacement lengths" of the chains, i.e., the lengths of the vectors connecting the ends of the chains, are altered from their equilibrium distribution in the undeformed state. Since it may be assumed that the chains occupy most probable configurations in the undeformed state, deformation of the network forces them to assume less probable configurations; hence, the entropy decreases with deformation.<sup>4</sup>

Quantitative treatments of this problem have been based on the following expression derived by Guth and Mark<sup>5</sup> and by Kuhn<sup>6</sup> for the probability of a displacement length  $r$ .

$$W(r)dr = (4\beta^3/\pi^{\frac{1}{2}}) \exp(-\beta^2 r^2) r^2 dr. \quad (2)$$

Or, expressing  $r$  in rectangular coordinates

$$W(xyz)dx dy dz = (\beta^3/\pi^{\frac{1}{2}}) \times \exp[-\beta^2(x^2 + y^2 + z^2)] dx dy dz. \quad (2')$$

$\beta$ , the reciprocal of the most probable value of  $r$ , is dependent upon the contour length of the chain and its flexibility. If the chain possesses bonds about which there is only limited rotation, restricted perhaps by sterically interfering substituents, Kuhn has pointed out that its configurations in space may be replaced approximately by those assumed by a chain of the same contour length having a fewer number of bonds about which rotation is unhindered. These bonds will occur at correspondingly greater intervals along this chain of equivalent flexibility. For a chain containing  $Z$  bonds located at intervals of length  $l$  along the chain, successive segments of which meet at tetrahedral angles<sup>5-7</sup>

$$\beta^2 = 3/4Zl^2. \quad (3)$$

In deriving the modulus of elasticity of a rubber from (2), Kuhn<sup>8</sup> introduced the fundamental assumption that the deformation transforms the chain displacement lengths like macroscopic elements of a homogeneous isotropic medium. Thus, elongation of the sample in the  $z$  direction to a relative length  $\alpha$  times the initial length is assumed to increase the  $z$  component of the chain displacement vector  $\mathbf{r}$  (which connects one end of the chain with the other) by the factor  $\alpha$ ; since there is no appreciable change in volume, the  $x$  and  $y$  components are assumed to be decreased by the factor  $1/\alpha^{\frac{1}{2}}$ . Kuhn proceeded to apply his treatment to a system of independent molecular units whose dimensions were presumed to be restricted not only in the direction of  $r$ , but in the directions perpendicular to  $r$ , as well. He obtained for the modulus of elasticity at small deformations

$$\epsilon = 7(\nu/V)kT,$$

where  $\nu$  is the number of chains in the volume  $V$ . Recognition of the fact that in the network structure of a vulcanized rubber the "molecular unit" is the chain discussed above, and that only the ends of the chains are subject to constraints which depend on the degree of deformation, leads by the same procedure to

$$\epsilon = 3(\nu/\dot{V})kT = 3RT\rho/M_c, \quad (4)$$

where  $\rho$  is the density of rubber and  $M_c$  is the molecular weight of the chain.

Recently Wall<sup>9</sup> has shown by an improved mathematical treatment, based on Kuhn's fundamental assumption stated above, that the retractive force at any elongation is given by

$$f = (RTA_0\rho/M_c)(\alpha - 1/\alpha^2), \quad (5)$$

where  $A_0$  is the initial cross-sectional area. Or, for the modulus of elasticity

$$\epsilon = (RT\rho/M_c)(1 + 2/\alpha^3), \quad (6)$$

which reduces to (4) for small deformations. These same equations have been derived by Treloar<sup>10</sup> by an accurate reduction of Kuhn's equations.<sup>11</sup>

<sup>4</sup> K. H. Meyer, G. von Susich, and E. Valko, *Kolloid Zeits.* **59**, 208 (1932).

<sup>5</sup> E. Guth and H. Mark, *Monats.* **65**, 63 (1934).

<sup>6</sup> W. Kuhn, *Kolloid Zeits.* **68**, 2 (1934).

<sup>7</sup> H. Eyring, *Phys. Rev.* **39**, 746 (1932).

<sup>8</sup> W. Kuhn, *Kolloid Zeits.* **76**, 258 (1936).

<sup>9</sup> F. T. Wall, *J. Chem. Phys.* **10**, 485 (1942).

<sup>10</sup> L. R. G. Treloar, *Trans. Faraday Soc.* **39**, 36 (1943).

<sup>11</sup> Similar relationships have been derived by Guth and James. Full details of their treatment have only appeared

In postulating that the distribution of chain displacement lengths is transformed by the deformation in the simple manner assumed in the Kuhn-Wall treatment, the chains are treated essentially as independent elements transformed by the deformation. The interdependence of mutually connected chains is not specifically taken into account. In the treatment which we present here the introduction of an idealized network model obviates the basic assumption employed by Kuhn and Wall concerning the transformation of the chain displacement lengths during deformation. While we do not suggest that our treatment of deformations is preferable to those discussed above, it offers certain advantages in the treatment of swelling phenomena discussed in the following paper.<sup>12</sup>

#### THE MODEL AND ASSOCIATED ASSUMPTIONS

We consider a process whereby a three-dimensional network structure is formed by the introduction of occasional cross-linkages between very long polymer molecules. If, as ordinarily will be the case, the cross-linkages are introduced at random into the mass of randomly entangled molecules the distribution of chain contour lengths will be given by<sup>13</sup>

$$N_i = Np(1-p)^{i-1}, \quad (7)$$

the chain element of the network being defined as above. Here  $N_i$  is the number of chains composed of  $i$  units,  $N$  is the total number of chains in the network, and  $p$  is the probability that any particular chain unit (e.g.,  $C_5H_8$  in rubber) is cross-linked.

It can be imagined that the points at which cross-linking is destined to occur have been labeled before vulcanization. The chains so defined are free to assume any physically accessible configuration. Not only will the contour lengths  $i$  of the chains vary, in accordance with (7), but their displacement lengths  $r$  will exhibit further variation. The displacement lengths of

chains containing  $i$  units will be distributed about a root-mean-square  $r$  value in the manner described by Eq. (2). If we imagine that the cross-linkages are introduced instantaneously at the labeled points, the chain irregularity existing before cross-linking will be carried over into the network structure. The important difference between the vulcanized and the unvulcanized states may be set forth as follows. Each chain, which prior to vulcanization is designated as the molecular portion between two labeled points, can be characterized by the vector  $\mathbf{r}$  leading from one end of the chain to the other. Before vulcanization these vectors are entirely independent of one another; the directions they may assume are unrestricted and their lengths are independently distributed according to Eq. (1). After vulcanization, neither the length nor the direction of one of these vectors can be altered without affecting adjacently connected vectors.

In the analysis presented here, attention is focused on the points of cross-linkage rather than on the chains themselves. The cross-linkages may be regarded as centers of tetrafunctionality since the ends of four chains meet at each of these points. Surrounding a given cross-linkage there are four "nearest neighbor" cross-linkages at the other ends of the four chains meeting at the given central cross-linkage. These "nearest neighbor" cross-linkages will not, in general, be nearest in space; they are the nearest only with reference to the continuous network structure. The cross-linkages are not bound to fixed positions; they may diffuse through limited regions of the space. This is a consequence of the multiplicity of configurations which each chain may assume through bond rotations. However, displacements of the order of magnitude of the mean chain displacement length or greater are very improbable. They can be achieved only by imposing highly improbable displacement lengths on a few of the neighboring chains of the network, or by imposing slightly improbable displacement lengths on a great many chains including those more distantly removed. Thus, most probable configurations may be assigned to the nearest neighbor cross-linkages about a given cross-linkage. These four points will lie at the corners of a tetrahedron, which will be an irregular tetrahedron since the lengths of the four chains will differ.

after submission of this manuscript: H. M. James and E. Guth, *J. Chem. Phys.* **11**, 455 (1943). See also E. Guth and H. M. James, *Ind. Eng. Chem.* **33**, 624 (1941); **34**, 1365 (1942).

<sup>12</sup> P. J. Flory and J. Rehner, Jr., *J. Chem. Phys.* **11**, 521 (1943).

<sup>13</sup> P. J. Flory, *J. Am. Chem. Soc.* **58**, 1877 (1936).

In the treatment given here we have introduced the following assumptions and approximations:

(1) That the actual network can be replaced by one in which all of the chains are of the same contour length. Under this assumption, the most probable positions for the junctions surrounding a given cross-linkage may be assumed *on the average* to lie at the corners of a regular tetrahedron.

(2) That the properties of the network can be computed from those of this average "cell."

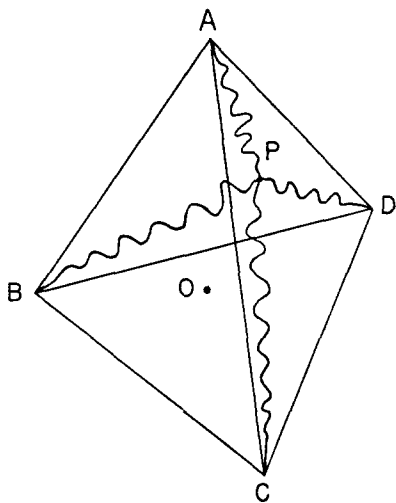


FIG. 1. Model for the elementary tetrahedral cell of tetrafunctional three-dimensional network.

(3) That the actual restraints imposed by the network on a given cross-linkage can be replaced by those obtained on fixing its nearest neighbor cross-linkages at their most probable average positions, i.e., by fixing the nearest neighbor cross-linkages at the corners of a regular tetrahedron.

(4) Finally, the distribution function [Eq. (2)] is assumed to apply to the independent chains prior to vulcanization. Validity of this assumption requires that the chains be long enough for Eq. (2) to be applicable with sufficient accuracy.

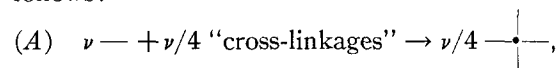
In introducing the concept of a regular tetrahedral "cell" as a representative unit of the network structure, it must be made clear that these cells are not mutually exclusive so far as occupancy of the space is concerned. Various tetrahedra, distantly connected along the network structure, will interpenetrate the same

region of space. This interpenetration which, fundamentally, is the result of the random intertwining of the chains must exist to the extent that within a single tetrahedron there will be many cross-linkages belonging to other tetrahedra. Consequently, it is impossible to conceive of a continuous array of regular tetrahedra such as occurs in the diamond lattice. The regular tetrahedral cell is introduced only as an average representative cell.

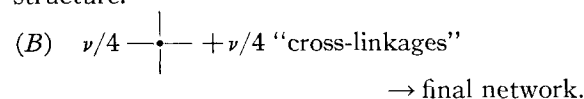
The average cell is shown in Fig. 1. The most probable positions of the four nearest neighbor cross-linkages lie at the corners *A*, *B*, *C*, and *D* of the tetrahedron. In accordance with assumption (3) these are considered to be fixed points. The four chains extending from *A*, *B*, *C*, and *D* to the central junction at *P* are indicated by wavy lines. (Their actual configurations will be much more irregular than is indicated by these lines.) The point *P* can occupy numerous positions, but points far from the center *O* of the tetrahedron can be occupied only by extending some (or all) of the four chains to improbable displacement lengths.

#### STRUCTURAL ENTROPY OF NETWORK FORMATION

We consider first the process of construction of the idealized network discussed above from  $\nu$  separate chains, instead of from a number of linear molecules of great length, each of which contains many chains. This process of network formation from separate chains can be divided into two steps represented schematically as follows:

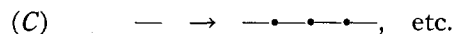


where each straight line segment represents a chain and  $\nu$  is the total number of chains. The "nuclei" resulting from step (A) then combine with one another, as indicated in the next step, the additional  $\nu/4$  cross-linkages combining the unattached chain ends to form the final network structure.



Next we consider the formation, from the chains, of long polymer molecules such as are actually

presumed to be present prior to the introduction of cross-linkages (i.e., prior to vulcanization). This may be represented by



The resultant of (A)+(B)-(C) represents the cross-linking process with which we are primarily concerned.

In step (A) three chains are constrained to meet within a volume element  $\Delta\tau$  located at the end of a fourth chain. The size of  $\Delta\tau$  will be dictated by the chemical structure of the cross-linkage, bond rigidities, etc.;  $\Delta\tau$  will be independent of deformation. The probability that the chains group themselves in this manner is

$$[\nu! 2^\nu / (4!)^{\nu/4}] (\Delta\tau/V)^{3\nu/4},$$

where  $V$  is the total volume of the system. The factor  $2^\nu$  is included in consideration of the identity of the two ends of each chain.

Step (A) requires also that the  $\nu/4$  cross-linkages be arranged in the vicinity of "lattice points" corresponding to the corners of the ultimate tetrahedral "cells" of the network. Hence, the additional factor  $(\Delta\tau'/V)^{\nu/4}$  is required, where  $\Delta\tau'$  is the size of the volume element to which each junction is assigned. Furthermore, in anticipation of step (B), we consider here the degeneracy in the orientations of the group of four chains which meets at each cross-linkage. There are twelve ways in which each of these groups may associate with its four neighboring junctions to be formed in step (B). For the probability of step (A) we write, therefore

$$W_A = \nu! (2\Delta\tau/V)^{3\nu/4} (\Delta\tau'/V)^{\nu/4}. \quad (8)$$

For the entropy change, we obtain upon introducing Stirling's approximations

$$\Delta S_A = k \ln W_A = k\nu [\ln (\nu/V) - 1 + (3/4) \ln (2\Delta\tau) + (1/4) \ln \Delta\tau']. \quad (9)$$

Having arranged  $\nu/4$  cross-linkages at the corners of  $\nu/4$  tetrahedral cells, step (B) involves the junction within each tetrahedron of the ends of four chains emanating from the corners of the tetrahedron. The probability that four such chain ends would meet spontaneously within the same volume element  $\Delta\tau = dx dy dz$  ( $\Delta\tau$  being defined

as above) of an average cell (regular tetrahedron) is

$$\Omega(xyz)(dx dy dz)^4 = \prod_{i=1}^4 W(x_i, y_i, z_i) dx_i dy_i dz_i,$$

where  $x_i, y_i, z_i$ , etc., are the coordinates of the same volume element  $\Delta\tau$  referred, respectively, to the four corners  $A, B, C, D$ , of the tetrahedron (see Fig. 1), and  $x, y$ , and  $z$  are coordinates of the volume element referred to the center  $O$  of the tetrahedron. On substituting for  $W$  from Eq. (2')

$$\Omega(xyz) = (\beta^{12}/\pi^6) \exp \left[ -\beta^2 \sum_{i=1}^4 r_i^2 \right]. \quad (10)$$

In Appendix I it is shown that for the undeformed network, i.e., for a regular tetrahedral "cell"

$$\sum_{i=1}^4 r_i^2 = 4(s^2 + \lambda^2), \quad (11)$$

where

$$s^2 = x^2 + y^2 + z^2,$$

$x, y$ , and  $z$  being referred to  $O$ , and  $\lambda$  is the distance  $AO$  from the center of the tetrahedron to one corner. The probability that all four chains terminate in the same volume element located *any place* becomes

$$\begin{aligned} \Omega_0(\Delta\tau)^3 &= \left[ \int_{\tau} \Omega(xyz) \Delta\tau \right] (\Delta\tau)^3 \\ &= (4\beta^{12}/\pi^6) \left\{ \int_0^\infty \exp [-4\beta^2(\lambda^2 + s^2)] s^2 ds \right\} (\Delta\tau)^3 \\ &= (\beta^9/8\pi^{9/2}) \exp (-4\beta^2\lambda^2) (\Delta\tau)^3. \end{aligned} \quad (12)$$

Hence, for the entropy change in step (B), involving  $\nu/4$  elementary tetrahedra,

$$\Delta S_B = (k\nu/4) [3 \ln (\beta^3/2\pi^3) - 4\beta^2\lambda^2 + 3 \ln \Delta\tau]. \quad (13)$$

For the third step (C) above, assuming that each polymer molecule contains many chains,

$$\begin{aligned} W_C &\cong \left( \frac{\Delta\tau''}{V} \right)^\nu 2^\nu \nu! \\ \Delta S_C &\cong k\nu [\ln (2\nu/V) + \ln \Delta\tau'' - 1]. \end{aligned} \quad (14)$$

Finally, for the structural entropy of vulcani-

zation, or cross-linking,

$$\begin{aligned} \Delta S_v &= \Delta S_A + \Delta S_B - \Delta S_C \\ &= k\nu \left[ \frac{3}{4} \ln(\beta^3/\pi^3) - \beta^2\lambda^2 + \frac{3}{2} \ln \Delta\tau \right. \\ &\quad \left. + \frac{1}{4} \ln \Delta\tau' - \ln \Delta\tau'' - \ln 2 \right]. \quad (15) \end{aligned}$$

Both  $\Delta\tau$  and  $\Delta\tau''$ , being determined by the chemical bond structure in the vicinity of the cross-linkage, are independent of network deformations, and we assume that this is true also of  $\Delta\tau'$ .<sup>13</sup> Consequently, for the purposes of the following development the magnitudes of the  $\Delta\tau$ 's are of no importance, and we may write

$$\Delta S_v = k\nu \left[ (3/4) \ln(\beta^3/\pi^3) - \beta^2\lambda^2 + \text{const.} \right]. \quad (16)$$

The dimension of the tetrahedron  $\lambda$  is to be taken equal to a mean chain displacement length, since at the instant vulcanization occurs the chains are assumed to exist in random configurations. Within the bounds of our assumptions concerning the representative tetrahedral cell, it is not possible to specify what type of average value of  $r$  should be used. If we let  $\lambda^2 = \bar{r}^2$ , then since according to Eq. (2)  $\bar{r}^2 = 3/2\beta^2$ ,  $\beta^2\lambda^2$  can be replaced by  $3/2$ .

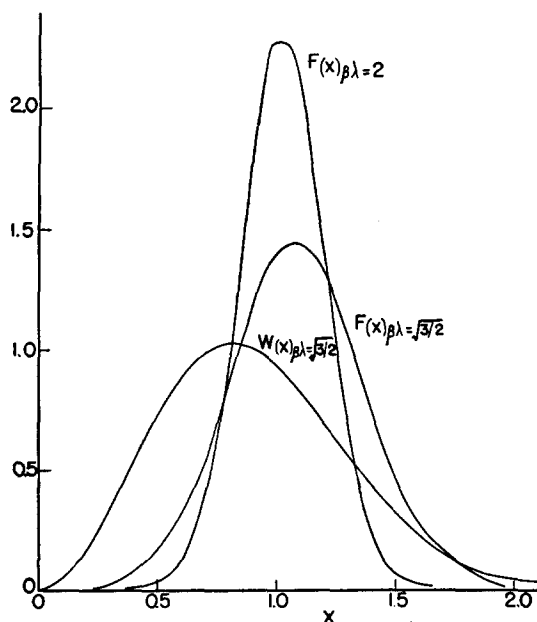


FIG. 2. Comparison of the distributions of chain displacement lengths for isolated chains ( $W(x)$ ) and for the cross-linked state ( $F(x)$ ).

<sup>13</sup> Possible moderate dependence of  $\Delta\tau'$  on deformation would have little effect on subsequent results.

## ENTROPY OF DEFORMATION

If the vulcanized rubber is deformed by an externally applied stress, the regular tetrahedral array of cross-linkages in the idealized model discussed above will be distorted. In other words, the most probable positions for a given set of four nearest neighbor cross-linkages will no longer lie at the corners of a regular tetrahedron. The manner in which a given tetrahedron is distorted will depend on its orientation with respect to the principal axes of the strain tensor. If, for example, the sample is elongated in a direction parallel to  $OA$  in Fig. 1, the tetrahedron will be converted to a regular pyramid,  $OA = \lambda$  being transformed to a length  $\alpha\lambda$ , where  $\alpha$  is the ratio of the deformed length to the initial length along the axis of strain. Since the change in density with deformation is negligible for rubber-like materials, except in the region where crystallization occurs, dimensions of the tetrahedron perpendicular to  $OA$  will change by the factor  $1/\alpha^{1/2}$ .

We now proceed to the deduction of the structural entropy of formation of the deformed network. Step (A) will differ only with respect to the spatial distribution of the  $\nu/4$  cross-linkages. The entropy change will be the same as was found previously. Step (C) also requires no modification. Step (B) will differ inasmuch as Eq. (11) no longer applies to the deformed tetrahedron.

In place of (11) we should average  $\sum r_i^2$  over all orientations of the direction of elongation with respect to the tetrahedron. An integration of this sort has not been carried out. However, it is shown in Appendix I that for orientations of the direction of the strain either perpendicular to or parallel to a face of the tetrahedron

$$\sum_{i=1}^4 r_i^2 = 4s^2 + 4\lambda^2(\alpha^2 + 2/\alpha)/3. \quad (17)$$

We assume that this equation represents the average resultant for all orientations.

Substitution of (17) in (10) leads ultimately to

$$\begin{aligned} \Delta S_v &= k\nu \left[ (3/4) \ln(\beta^3/\pi^3) \right. \\ &\quad \left. - \beta^2\lambda^2(\alpha^2 + 2/\alpha)/3 + \text{const.} \right] \quad (18) \end{aligned}$$

for the entropy of vulcanization. Equation (18) reduces to (16) for the undeformed state  $\alpha = 1$ .

Subtracting (16) from (18) there is obtained for the entropy of deformation

$$\Delta S_d = -k\nu\beta^2\lambda^2(\alpha^2 + 2/\alpha - 3)/3. \quad (19)$$

If we let  $\beta^2\lambda^2 = 3/2$ ,

$$\Delta S_d = -k\nu(\alpha^2 + 2/\alpha - 3)/2, \quad (19')$$

which is identical with Wall's<sup>9</sup> expression for the entropy of deformation. Taking  $\Delta H_d = 0$  and substituting  $T\Delta S_d = -\Delta F$  in Eq. (1), Eqs. (5) and (6) are obtained for the retractive force and for Young's modulus of elasticity, respectively.

### DISCUSSION

Both the Kuhn-Wall treatment and the one we have presented depend upon Eq. (2) for the probability distribution of chain lengths. The foundation for this relationship is reasonably secure, aside from the uncertainty in the magnitude of  $\beta$ , which does not enter into the elasticity calculations. The critical assumption involved in our treatment pertains to the use of the regular tetrahedron as a representative cell of the network structure. No specific model for the network is required in the Kuhn-Wall treatment. However, it has been necessary for them to postulate that the distribution of chain lengths is transformed directly as the macroscopic dimensions of the sample. No such postulate enters into our treatment.

It is of interest to inquire into the compatibility of this assumption with the restrictions imposed by the network structure, using the model we have assumed. If all cells of the network were regular tetrahedra, the corners of which are fixed with reference to their centers, a condition which goes beyond our actual assumptions,<sup>14</sup> then, as is shown in Appendix II, the distribution of chain lengths becomes

$$F(x) = (4\beta\lambda/\pi^{1/2}) \exp[-4\beta^2\lambda^2(1+x^2)] \times \sinh(8\beta^2\lambda^2x)xdx, \quad (20)$$

where  $x = r/\lambda$ . This function is shown in Fig. 2 in comparison with  $W(x)$  according to Eq. (2) for several values of  $\beta^2\lambda^2$ . The shapes of the distributions given by the two functions differ,  $F(x)$  being narrower than  $W(x)$ . This is due to the ordering resulting from adoption of the regular

tetrahedron cell. However, the distribution becomes sharper as  $\beta^2\lambda^2$  is increased; i.e., as the tetrahedron is isotropically enlarged. This magnification of the tetrahedron (increase in  $\lambda$ ) corresponds to the change in structure resulting from swelling, as discussed in the following paper. We conclude that swelling causes the distribution of chain lengths to become relatively narrower. The assumption made by Kuhn and Wall (for the case of deformations without change in volume) appears to be inapplicable to deformations accompanied by changes in volume.

Our method of treatment permits an estimate of the structural entropy change accompanying network formation from very long molecules which become cross-linked to one another at *specified points of reactivity* along their lengths. The actual magnitude of this entropy change, given by Eq. (15), is indeterminate to the extent of the arbitrariness in the values of the  $\Delta\tau$ 's. If we assume that each of the  $\Delta\tau$ 's is approximately equal to the volume of one of the  $Z$  chain elements, which will be of the order of  $l^3$ , and taking  $\beta^2\lambda^2 = 3/2$ ,

$$\Delta S_s = -k\nu[(9/8) \ln Z + 3.4]. \quad (21)$$

Or, for the entropy per mole of cross-linkages in the network

$$-R[(9/4) \ln Z + 6.8].$$

This entropy term becomes quite large when the lengths of the chain are great.

If the points at which cross-linking may occur cannot be specified in advance, as for example in the vulcanization of natural rubber, these expressions lose their significance. Thus, if cross-linking may occur wherever two molecules are in contact (as would very nearly be the case for natural rubber with its numerous unsaturated linkages), attachment of the chains to one another takes place without imposing on the system an increase in order. Consequently, there will be no structural entropy change. This will not hold true if the material possesses only a few reactive points, all, or nearly all, of which are to be utilized in the formation of cross-linkage. A typical example is found in the vulcanization of Butyl rubber,<sup>15</sup> an olefin-diolefin copolymer

<sup>14</sup> We have assumed only that the *average cell is a regular tetrahedron*.

<sup>15</sup> R. M. Thomas, I. E. Lightbown, W. J. Sparks, P. K. Frolich, and E. V. Murphree, *Ind. Eng. Chem.* **36**, 1283 (1940).



containing only a small proportion of the latter. In such instances Eq. (21) may be presumed to yield a significant estimate of the structural entropy of vulcanization.

We have assumed [assumption (1)] that our idealized network formed from regularly spaced points of cross-linkage will possess the same elastic properties as an actual completely random one. Although the actual magnitude of  $\Delta S_v$  given by Eq. (15) may be of little or no significance as pointed out above, we assume that the difference between Eqs. (18) and (15) represents correctly the change in entropy due to deformation.

The rather artificial approximations involved in steps (A) and (C) effectively cancel out in  $\Delta S_d$ , the entropy of deformation. Only step (B) contributes to the terms appearing in the deformation formulas. The equivalence of our results with those of Wall<sup>9</sup> and Treloar,<sup>10</sup> obtained by a fundamentally different procedure, adds considerable support to equations (19), (5), and (6) relating elastic properties to structure.

Similar treatments can be applied to networks in which either three or six chains (instead of four) are joined at the network junction points. For a network containing trifunctional junctions, the elementary cell becomes a triangle (instead of a tetrahedron) the corners of which represent the nearest neighbor junctions with respect to the given central junction. For a hexafunctional network, the elementary cell becomes an octahedron. In both cases the formula for the sum of the squares of the distances from the  $f$  neighboring junctions to the central junction located at a distance  $s$  from the center of the deformed cell can be expressed

$$\sum_{i=1}^f r_i^2 = fs^2 + f\lambda(\alpha^2 + 2/\alpha)/3, \quad (17')$$

which reduces to Eq. (17) for a tetrafunctional network ( $f=4$ ). Upon carrying through treatments paralleling that given above it is found that the entropy of deformation becomes

$$\Delta S_d = -(k/2)[\nu/(f/2)]\beta^2\lambda^2$$

$$\times \left\{ \left[ \sum_{i=1}^f r_i^2 \right]_{\alpha} - \left[ \sum_{i=1}^f r_i^2 \right]_{\alpha=1} \right\}.$$

Substitution of the more general expression (17')

into this equation gives Eq. (19) for the entropy of deformation. Since this equation does not contain  $f$ , we conclude that only the number of chains and not the functionality of their interconnecting linkages is important. The results which have been obtained therefore should be equally applicable to networks of functionality other than four.

We have been concerned primarily with networks formed by cross-linking of previously formed long molecules. It should be pointed out, however, that simultaneous linear growth and cross-linking or branching may produce equivalent network structures. Typical examples of polymers of this type include the products of copolymerization of a vinyl compound (e.g., styrene) with a small amount of a divinyl substance (e.g., divinyl benzene),<sup>16-18</sup> or of polycondensation of bi- and multifunctional reactants.<sup>19</sup> In order for the above treatment to apply, it is only necessary that the multifunctional linkages be introduced under conditions of random coiling. In any case the polymer must possess sufficient internal mobility to allow the chains to slip past one another during deformation; i.e., the polymer must be at a temperature such that it displays rubber-like behavior, or it must contain a sufficient quantity of a plasticizer to accomplish the same result.

## APPENDIX I

### Case 1

Consider a regular tetrahedron  $ABCD$ , as shown in Fig. 3. Let its center  $O$  be the origin of a set of rectangular coordinates of which the  $z$  axis passes through the apex  $A$ , the  $x$  axis is parallel to the edge  $BC$ , and the  $y$  axis is parallel to the bisector of the angle  $BDC$ . Let  $r_1, r_2, r_3$ , and  $r_4$  be the distances from the corners  $A, D, C$ , and  $B$ , respectively, to a point  $P(x, y, z)$  located at a distance  $s$  from the origin. Let  $\lambda$  be the distance from the origin to any of the corners. It can then be shown by simple geometry that

$$\begin{aligned} r_1^2 &= s^2 - 2\lambda z + \lambda^2, \\ r_2^2 &= s^2 - (4\sqrt{2}/3)\lambda y + \frac{2}{3}\lambda z + \lambda^2, \\ r_3^2 &= s^2 - 2(2/3)\lambda x + (2\sqrt{2}/3)\lambda y + \frac{2}{3}\lambda z + \lambda^2, \\ r_4^2 &= s^2 + 2(2/3)\lambda x + (2\sqrt{2}/3)\lambda y + \frac{2}{3}\lambda z + \lambda^2, \end{aligned}$$

<sup>16</sup> H. Staudinger and W. Heuer, Ber. **68**, 1618 (1935); Trans. Faraday Soc. **32**, 323 (1936).

<sup>17</sup> K. G. Blaikie and R. N. Crozier, Ind. Eng. Chem. **28**, 1155 (1936).

<sup>18</sup> R. G. W. Norrish and E. F. Brookman, Proc. Roy. Soc. (London) **A163**, 205 (1937).

<sup>19</sup> P. J. Flory, J. Am. Chem. Soc. **63**, 3083 (1941).

where  $s^2 = x^2 + y^2 + z^2$ . Adding these four equations one obtains

$$\sum_{i=1}^4 r_i^2 = 4(s^2 + \lambda^2)$$

which is Eq. (11).

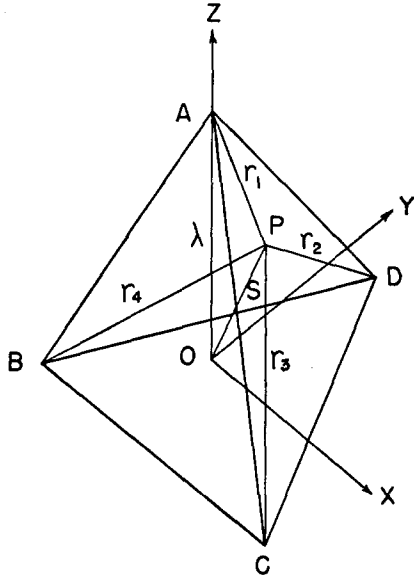


FIG. 3.

### Case 2

Let the tetrahedron of Fig. 3 be subjected to a homogeneous lateral compression in such a manner that the resulting irregular pyramid conforms to the following conditions: (1) its  $y$  and  $z$  dimensions are increased in the ratios  $\gamma$  and  $\alpha$ , respectively; (2) the vector  $AO$  remains perpendicular to the base; (3)  $YOZ$  remains a plane of symmetry; and (4) the volume of the pyramid is unchanged. The geometry of the distorted solid then leads to the following values:

$$\begin{aligned} r_1^2 &= s^2 - 2\alpha\lambda z + \alpha^2\lambda^2, \\ r_2^2 &= s^2 - (4\sqrt{2}/3\alpha^{\frac{1}{2}})\gamma\lambda y + (8/9\alpha)\gamma^2\lambda^2 + \frac{2}{3}\alpha\lambda z + \frac{1}{3}\alpha^2\lambda^2, \\ r_3^2 &= s^2 - (2(2/3)^{\frac{1}{2}}/\alpha^{\frac{1}{2}}\gamma)\lambda x + (2/3\alpha\gamma^2)\lambda^2 + (2\sqrt{2}/3\alpha^{\frac{1}{2}})\gamma\lambda y \\ &\quad + (2/9\alpha)\gamma^2\lambda^2 + \frac{2}{3}\alpha\lambda z + \frac{1}{3}\alpha^2\lambda^2, \\ r_4^2 &= s^2 + (2(2/3)^{\frac{1}{2}}/\alpha^{\frac{1}{2}}\gamma)\lambda x + (2/3\alpha\gamma^2)\lambda^2 + (2\sqrt{2}/3\alpha^{\frac{1}{2}})\gamma\lambda y \\ &\quad + (2/9\alpha)\gamma^2\lambda^2 + \frac{2}{3}\alpha\lambda z + \frac{1}{3}\alpha^2\lambda^2. \end{aligned}$$

Therefore

$$\sum_{i=1}^4 r_i^2 = 4[s^2 + \lambda^2(\alpha^2 + \gamma^2/\alpha + 1/\alpha\gamma^2)/3].$$

If  $\gamma = 1$ , this formula reduces to Eq. (17), while the condition  $\gamma = \alpha = 1$  gives Eq. (11). It is also seen that the stretch factors can be transposed in the above formula without changing its symmetry, as would be expected on the basis of an assumption of isotropy.

### APPENDIX II

According to Eqs. (10) and (11) the probability that the four chain ends terminate in the same volume element  $\Delta\tau$  is given by

$$\Omega(\lambda, x, y, z)(\Delta\tau)^4 = (\beta^{12}/\pi^6) \exp[-4\beta^2(x^2 + y^2 + z^2 + \lambda^2)](\Delta\tau)^4.$$

By translating the origin in Fig. 3 from the center  $O$  of the tetrahedron to the apex  $A$ , and changing to spherical coordinates, there is obtained

$$\begin{aligned} \Omega(\lambda, r, \theta, \varphi)dV &= (\beta^{12}/\pi^6) \\ &\quad \times \exp[-4\beta^2(r^2 + 2\lambda r \cos \varphi + 2\lambda^2)]r^2 \sin \varphi d\varphi d\theta dr, \end{aligned}$$

where  $\varphi$  is the angle  $OAP$ . Integration over the sphere of radius  $r$  gives the probability that the four chain ends lie at the point  $P$  at a distance  $r$  from  $A$ . It is found that

$$\int_{\text{sphere}} \Omega dS = (\beta^{10}/2\pi^5\lambda) \exp[-4\beta^2(r^2 + 2\lambda^2)] \cdot \sinh(8\beta^2\lambda r) r dr.$$

If this expression is divided by the probability  $\Omega_0$  [Eq. (12)] that the four chain ends terminate in the same volume element located any place, the ratio  $F(r)$  will give the probability that the volume element containing the chain termini lies in the spherical shell between  $r$  and  $r+dr$ ; in other words,  $F(r)$  is the probability that a constituent chain has a displacement length  $r$ . Therefore

$$\begin{aligned} F(r)dr &= \int_{\text{sphere}} \Omega dS / \Omega_0(\lambda) \\ &= (4\beta/\pi^{\frac{1}{2}}\lambda) \exp[-4\beta^2(r^2 + \lambda^2)] \cdot \sinh(8\beta^2\lambda r) r dr. \end{aligned}$$

Letting  $x = r/\lambda$ , the above expression gives Eq. (20).