the underlying mechanisms of these processes.

Appendix. Relationship between $\bar{M}_w$ and $\bar{M}_n$ during Association

The effect upon the weight-average molecular weight, $\bar{M}_w$, and number-average molecular weight, $\bar{M}_n$, due to the association between two component *molecules* with average molecular weights $\langle m_i\rangle$ and $\langle m_j\rangle$, respectively, at a given point during the process may be deduced in the following manner. (Note that the forms of the expressions for $\langle m_i\rangle$ and $\langle m_j\rangle$, which are appropriately averaged over all components present, will depend upon the nature of the governing molecular interactions.)

For the sample as a whole, $\delta(\sum_k c_k) = 0$ and $\delta(\sum_k n_k) = -N_A^{-1}$, where c_k is the weight in grams and n_k is the number of moles for the kth component. (N_A is Avogadro's number.) Furthermore

$$\delta(\sum_k c_k m_k) = N_A^{-1}[(\langle m_i\rangle + \langle m_j\rangle)^2 - \langle m_i\rangle^2 - \langle m_j\rangle^2] = 2N_A^{-1}\langle m_i\rangle\langle m_j\rangle = 2N_A^{-1}\langle m_i m_j\rangle$$

since, for a particular average component molecule, $\langle c_k\rangle = N_A^{-1}\langle m_k\rangle$. Thus

$$\delta(\bar{M}_w) = \delta\left(\frac{\sum_k c_k m_k}{\sum_k c_k}\right) = \frac{(\sum_k c_k)\delta(\sum_k c_k m_k) - (\sum_k c_k m_k)\delta(\sum_k c_k)}{(\sum_k c_k)^2} = \frac{2N_A^{-1}\langle m_i m_j\rangle}{\sum_k c_k}$$

and

$$\delta(\bar{M}_n) = \delta\left(\frac{\sum_k c_k}{\sum_k n_k}\right) = \frac{(\sum_k n_k)\delta(\sum_k c_k) - (\sum_k c_k)\delta(\sum_k n_k)}{(\sum_k n_k)^2} = \frac{N_A^{-1}(\sum_k c_k)}{(\sum_k n_k)^2}$$

The increments $\delta(\bar{M}_w)$ and $\delta(\bar{M}_n)$ are in effect limitingly small, and so the ratio of the two may be written

$$\partial\bar{M}_w/\partial\bar{M}_n = 2\langle m_i m_j\rangle(1/\bar{M}_n)^2$$

References and Notes

(1) Adler, E. *Wood Sci. Technol.* **1977**, *11*, 169.
(2) Obiaga, T. J.; Wayman, M. *J. Appl. Polym. Sci.* **1974**, *18*, 1943.
(3) Connors, W. J.; Sarkanen, S.; McCarthy, J. L. *Holzforschung* **1980**, *34*, 80.
(4) Benko, J. *Tappi* **1964**, *47*, 508.
(5) Brown, W. *J. Appl. Polym. Sci.* **1967**, *11*, 2381.
(6) Yaropolov, N. S.; Tishchenko, D. V. *Zh. Prikl. Khim.* **1970**, *43*, 1120.
(7) Yaropolov, N. S.; Tishchenko, D. V. *Zh. Prikl. Khim.* **1970**, *43*, 1351.
(8) Lindström, T. *Colloid Polym. Sci.* **1979**, *257*, 277.
(9) Hüttermann, A. *Holzforschung* **1978**, *32*, 108.
(10) Forss, K. G.; Stenlund, B. G.; Sågfors, P.-E. *Appl. Polym. Symp.* **1976**, *28*, 1185.
(11) Teller, D. C. *Methods Enzymol.* **1973**, *27*, 346–441.
(12) Yphantis, D. A. *Biochemistry* **1964**, *3*, 297.
(13) Lansing, W. D.; Kraemer, E. O. *J. Am. Chem. Soc.* **1935**, *57*, 1369.
(14) McNaughton, J. G.; Yean, W. Q.; Goring, D. A. I. *Tappi* **1967**, *50*, 548.
(15) Gelotte, B. *J. Chromatogr.* **1960**, *3*, 330.
(16) Porath, J. *Svensk. Kem. Tidskr.* **1962**, *74*, 6.
(17) Porath, J. *Svensk. Kem. Tidskr.* **1962**, *74*, 306.
(18) Flodin, P. Dissertation, Uppsala, 1962.
(19) Lundquist, K.; Lundgren, R. *Acta Chem. Scand.* **1972**, *26*, 2005.
(20) Smith, D. C. C. *J. Chem. Soc.* **1955**, 2347.
(21) Smith, D. C. C. *Nature (London)* **1955**, *176*, 267.
(22) Kratzl, K.; Gratzl, J.; Claus, P. *Adv. Chem. Ser.* **1966**, *No. 59*, 157.
(23) Kratzl, K.; Schafer, W.; Claus, P.; Gratzl, J.; Schilling, P. *Monatsh. Chem.* **1967**, *98*, 891.
(24) Wallis, A. F. A. In "Lignins"; Sarkanen, K. V., Ludwig, C. H., Eds.; Wiley: New York, 1971; pp 345–72.
(25) Doty, P.; Wagner, H.; Singer, S. J. *J. Phys. Colloid Chem.* **1947**, *51*, 32.
(26) Strauss, U. P.; Gershfeld, N. L.; Crook, E. H. *J. Phys. Chem.* **1956**, *60*, 577.
(27) Gregor, H. P.; Frederick, M. *J. Polym. Sci.* **1957**, *23*, 451.
(28) Quadrifoglio, F.; Crescenzi, V.; Delben, F. *Macromolecules* **1973**, *6*, 301.
(29) Rinaudo, M.; Pierre, C. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1969**, *269*, 1280.
(30) Rinaudo, M.; Milas, M. *J. Chim. Phys.* **1969**, *66*, 1489.
(31) Zana, R.; Tondre, C.; Rinaudo, M.; Milas, M. *J. Chim. Phys.* **1971**, *68*, 1258.
(32) Strauss, U. P.; Ross, P. D. *J. Am. Chem. Soc.* **1959**, *81*, 5295.
(33) Eisenberg, H.; Mohan, G. R. *J. Phys. Chem.* **1959**, *63*, 671.
(34) Chu, P.; Marinsky, J. A. *J. Phys. Chem.* **1967**, *71*, 4352.
(35) Harkin, J. M. *Adv. Chem. Ser.* **1966**, *No. 59*, 65.
(36) Takahashi, A.; Kato, T.; Nagasawa, M. *J. Phys. Chem.* **1967**, *71*, 2001.
(37) Gardon, J. L.; Mason, S. G. *Can. J. Chem.* **1955**, *33*, 1491.
(38) Rezanowich, A.; Goring, D. A. I. *J. Colloid Sci.* **1960**, *15*, 452.
(39) Ekman, K. H.; Lindberg, J. J. *Pap. Puu* **1966**, *48*, 241.

Rubber Elasticity Theory. A Network of Entangled Chains

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ABSTRACT: Following Edwards, the effect of entanglements on the chains of a concentrated polymeric system is described by means of "tubes" endowed with a harmonic potential. The elastic free energy of the entangled network is then calculated by assuming that the tube constraints deform affinely. The resulting expressions predict various nonclassical effects. Some of them qualitatively coincide with the predictions of the modern theories of rubber elasticity by Ronca and Allegra and by Flory which are based on the restrictions of junction fluctuations due to entanglements. However, the value of the shear modulus predicted here is significantly different and it is related to the plateau modulus of the un-cross-linked polymer.

Introduction

Recent network theories which account for the effect of entanglements can be grouped in two categories. Those advanced by Ronca and Allegra[1] and Flory[2-5] emphasize the role of entanglements in restricting the fluctuations of the junctions. They are successful in qualitatively explaining the various departures of the behavior of real networks from that predicted by classical theories of phantom networks. In particular, the well-known Mooney effect is accounted for and even the maximum in the

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product of the diluent chemical potential times the extension ratio in swollen rubbers is qualitatively predicted.[5] However, the largest possible value of the shear modulus which is predicted by these theories is νkT, where ν is the concentration of active chains.

This result seems at variance with some experimental findings. For example, in a recent work by Pearson and Graessley[6] which deals with networks prepared by cross-linking ethylene–propylene copolymers, values of the shear modulus much larger than νkT are found. These values appear to be closely related to that of the plateau modulus of the copolymer prior to cross-linking, thus supporting the conclusion that the role of entanglements is more comprehensive than accounted for in the above theories. At least in some cases, a direct effect of entanglements on the network chains, and not just on the network junctions, appears to be present.

Theories based on the latter concept have been developed recently, mainly after Edwards and co-workers. The original idea that the accessible chain conformations are somehow reduced by the confining action of other chains[7] developed into quantitative treatments based either on knot theory and topological invariance—cf., e.g., Deam and Edwards[8]—or on "tube" models endowed with a harmonic potential.[9] Whereas theories of topological invariance are very difficult and still not fully developed, tube models are relatively simple and look promising in their predictive abilities. For the case of concentrated polymeric liquids, tube models were used successfully by de Gennes,[10] Doi and Edwards,[11] and Marrucci and Hermans.[12] A simple model of a cross-linked network, using tubes with "reflecting" walls, was advanced also by Gaylord,[13] based on statistical calculations by Gaylord and Lohse.[14]

In this paper, a detailed model of a cross-linked network made up of entangled chains is developed. The basic unit of the network, i.e., the entangled chain, is treated as a chain in a tube endowed with a harmonic potential. The problem of the fluctuations of the junctions, which is essential for networks of phantom chains, is treated here consistently with the tube model. One of the main differences with respect to the result by Edwards[9] is in the assumption that the tube cross section deforms affinely. Whereas Edwards, in either the cross-linked[9] or the liquid case,[11] seems to prefer the assumption of a constant cross section, de Gennes[15] and Gaylord[13] adopt the affine assumption. Though the question is ultimately deferred to a comparison with experimental results, we think, consistent with previous work,[12,16] that the affine assumption should be preferred, especially in the cross-linked case, where very large deformations are seldom considered. The point may be related to whether the length scale of the topological confinements (tube diameter) is or is not much larger than the monomer dimension even in dense systems. If the former choice is made—and Edwards himself appears to do so[9,11]—then the affine assumption looks more appropriate on an intuitive basis.

Throughout the paper, calculations of the Helmoltz free energy will be made by direct evaluation of configuration integrals. Some of the results, especially in the next two sections, essentially coincide with those reported in the works quoted above and are repeated here for the sake of clarity. Since most configuration integrals can be factorized in three terms, one for each coordinate axis, only one of them will be considered in the next section.

Partition Function of a Chain in a Harmonic Potential

Consider a chain made up of $n + 1$ Rouse beads (chain monomers) numbered sequentially from 0 to n and call b the root-mean-square distance between consecutive beads. Some economy in the notation is achieved if the coordinates of the beads, as well as all other lengths, are made dimensionless by taking the ratio with $(^2/_3)^{1/2}b$. Thus the partition function of the free chain, Q, is proportional to the configuration integral (x coordinate only)

$$Q \propto \int \dots \int \exp\{-[x_1^2 + (x_1 - x_2)^2 + \dots + (x_{n-1} - x_n)^2]\}\, \mathrm{d}x_1 \dots \mathrm{d}x_n = \pi^{n/2} \quad (1)$$

where x_i is the coordinate of the ith bead and the zeroth bead has been placed at the origin so as to locate the chain in space.

Let us assume now that a harmonic potential centered at $x = 0$ acts on the beads. The partition function will depend on the strength of this potential, indicated by s^2, as well as on the constraints imposed on the end points of the chain, if any are present. We first consider the case where both ends are fixed at $x = 0$. The partition function $Q_0(s)$ for this case is given by

$$Q_0(s) = Q\Big[\int \dots \int \exp\{-[x_1^2 + (x_1 - x_2)^2 + \dots + x_{n-1}^2 + s^2(x_1^2 + \dots + x_{n-1}^2)]\}\, \mathrm{d}x_1 \dots \mathrm{d}x_{n-1}\Big] \Big/ \Big[\int \dots \int \exp\{-[x_1^2 + (x_1 - x_2)^2 + \dots + (x_{n-1} - x_n)^2]\}\, \mathrm{d}x_1 \dots \mathrm{d}x_n\Big] = Q\pi^{-1/2} A_{n-1}{}^{-1/2} \quad (2)$$

where $A_{n-1}(s)$ is the determinant of the quadratic form appearing in the numerator of eq 2

$$A_{n-1} = \begin{vmatrix} 2 + s^2 & -1 & 0 & \cdots \\ -1 & 2 + s^2 & -1 & \cdots \\ 0 & -1 & 2 + s^2 & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix} \quad (3)$$

This determinant is well-known; cf., e.g., Eichinger and Martin.[17] It is given by

$$A_{n-1} = \sinh(n\theta)/\sinh\theta \quad (4)$$

where

$$\theta = 2 \sinh^{-1}(s/2) \quad (5)$$

If $s \ll 1$, then $\theta \simeq s$. If, together with $s \ll 1$, we have also $\exp(ns) \gg 1$, eq 4 reduces to

$$A_{n-1} \simeq \frac{1}{2s} \exp(ns) \quad (6)$$

When the nth bead is free to fluctuate, instead of being fixed at $x = 0$, an expression similar to eq 2 gives

$$Q_{\mathrm{f}}(s) = QB_n{}^{-1/2} \quad (7)$$

with B_n given by

$$B_n = \begin{vmatrix} 1 + s^2 & -1 & 0 & \cdots \\ -1 & 2 + s^2 & -1 & \cdots \\ 0 & -1 & 2 + s^2 & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix} = \cosh(n\theta) + (\coth\theta - \operatorname{csch}\theta)\sinh(n\theta) \quad (8)$$

which, for $s \ll 1$ and $\exp(ns) \gg 1$, becomes

$$B_n \simeq \tfrac{1}{2} \exp(ns) \quad (9)$$

Since the chain is now autonomously located in space, i.e., since it is kept close to $x = 0$ by the effect of the harmonic potential, we can consider also the case where both ends are free. We obtain

$$Q_{\mathrm{ff}}(s) = Q\pi^{1/2} C_{n+1}{}^{-1/2} \quad (10)$$

$$C_{n+1} = (1+s^2)B_n - B_{n-1} = 2(\coth\theta - \operatorname{csch}\theta)\sinh(n+1)\theta \qquad (11)$$

Again, for $s \ll 1$ and $\exp(ns) \gg 1$, eq 11 reduces to

$$C_{n+1} \simeq (s/2)\exp(ns) \qquad (12)$$

By comparing eq 6, 9, and 12, one can see that, provided $s \ll 1$ and $\exp(ns) \gg 1$, the partition functions Q_0, Q_f, Q_{ff} are proportional to $\exp(-ns/2)$, irrespective of the constraints which are imposed on the chain ends. End effects only change the power of s in the preexponential factor. A similar result will be found later for network junctions.

We finally consider the case where the zeroth bead is held fixed at $x = 0$ and the nth bead is placed at some arbitrary value $x_n = x$. From the result of Appendix A, for the case $s \ll 1$, we obtain

$$Q_x(s) = Q\pi^{-1/2}\left[\frac{\sinh(ns)}{s}\right]^{-1/2}\exp\left[-\frac{s}{\tanh(ns)}x^2\right] \qquad (13)$$

For $s = 0$, eq 13 reduces to the well-known result

$$Q_x(0) = Q(\pi n)^{-1/2}\exp(-x^2/n) \qquad (14)$$

whereas, for $\exp(ns) \gg 1$, it simplifies to

$$Q_x(s) \simeq Q\left(\frac{2s}{\pi}\right)^{1/2}\exp\left(-\frac{ns}{2} - sx^2\right) \qquad (15)$$

We conclude this section by recalling that, as shown, e.g., in ref 11 and 12, the strength s of the harmonic potential and the average fluctuation of the beads are simply related to one another. If the chain is sufficiently long so as to make $\exp(ns) \gg 1$, the average fluctuation is independent of end effects and is given by

$$\langle x_i^2\rangle = 1/4s \qquad (16)$$

The approximation adopted henceforth of considering small values of s is then justified by the fact that fluctuations of the beads much larger than b^2 are expected even for entangled chains in dense systems; i.e., in dimensionless form $\langle x_i^2\rangle \gg 1$.

Free Energy of an Entangled Chain

Following the suggestion by Edwards, we now assume that a chain belonging to a concentrated system behaves as if it were constrained in a tubelike region, taken to represent the topological hindrance of the surrounding chains. These lateral constraints are arbitrarily described by a harmonic potential centered at the tube axis.

Though the tube is certainly not straight and indeed its center line—called the "primitive chain"—can itself be considered as a random coil, we shall calculate the partition function of the enclosed chain as if the tube were a straight cylinder. This, however, introduces an approximation which is very good when the chain is either very long ($ns \gg 1$) or very short ($ns \ll 1$) with respect to the lateral fluctuations.

We take the z axis of a Cartesian coordinate system along the axis of the cylinder. If the cylinder has a circular cross section, orientation of the x and y axes is irrelevant. Since we shall deal also with deformed cylinders having an elliptic cross section, we align the x and y axes along those of the ellipse in such a case.

We place one of the chain ends at the origin and the other at the arbitrary point $P(x,y,z)$. In the z direction there is no harmonic potential and an equation like eq 14 is to be used whereas along x and y, eq 13 holds true. For a circular cross section, the partition function then becomes

$$Q_{xyz}(s) = Q\pi^{-3/2}n^{-1/2}\frac{s}{\sinh(ns)}\exp\left[-\frac{s}{\tanh(ns)}(x^2+y^2) - \frac{z^2}{n}\right] \qquad (17)$$

Again it can be verified that eq 17 degenerates into the classical result when $ns \ll 1$. However, henceforth we shall be mainly interested in the other extreme case, i.e., when $ns \gg 1$. Thus, eq 17 becomes

$$Q_{xyz}(s) = 2Q\pi^{-3/2}n^{-1/2}s\exp\left[-ns - s(x^2+y^2) - \frac{z^2}{n}\right] \qquad (18)$$

It should be noted that, if x and y are within the fluctuation range and $ns \gg 1$, in view of eq 16, the second term in the exponential of eq 18 is negligible with respect to the first. This somehow justifies considering a straight tube, since the transverse coordinates of the end points provide a minor contribution. The only coordinate which matters is the longitudinal one. In eq 18, z should be interpreted as the end-to-end curvilinear distance of the chain measured along the tube center line. In most of the following equations, this point will be stressed by using the symbol l in place of z.

Setting $x = y = 0$, we write eq 18 as

$$Q_{00l}(a) = 2Q\pi^{-3/2}n^{-1/2}\frac{1}{a^2}\exp\left(-\frac{n}{a^2} - \frac{l^2}{n}\right) \qquad (19)$$

where, in view of eq 16, s has been replaced for convenience by the "radius of the cross section of the tube", arbitrarily defined as

$$a^2 = 4\langle x_i^2\rangle = 4\langle y_i^2\rangle = 1/s \qquad (20)$$

If the tube cross section is elliptic, i.e., if the potential is of the form $s_1{}^2x^2 + s_2{}^2y^2$, eq 19 becomes

$$Q_{00l}(a_1,a_2) = 2Q\pi^{-3/2}n^{-1/2}\frac{1}{a_1a_2}\exp\left[-\frac{n}{2}\left(\frac{1}{a_1{}^2} + \frac{1}{a_2{}^2}\right) - \frac{l^2}{n}\right] \qquad (21)$$

where a_1 and a_2 are the semiaxes of the ellipse defined similarly to eq 20. It may be noted that eq 21 is equivalent to the equation given by Gaylord (eq 3b of ref 13) for cylinders of rectangular cross section with reflecting walls, under the same limiting conditions as considered here.

From eq 19, the following expression for the Helmoltz free energy, A_c, of an entangled chain is obtained:

$$\frac{A_c}{kT} = c(T) + \frac{l^2}{n} + \frac{n}{a^2} + 2\ln a \qquad (22)$$

Here the partition function of the free chain and other terms which do not depend on deformation have been included in the function $c(T)$. This function, being irrelevant, is disregarded henceforth.

The coefficient of the logarithmic term appearing in eq 22 is related to the conditions of the chain ends. As previously noted, this coefficient (and only it) would change by changing the constraints at the ends of the chain. The inverse dependence of free energy on the square of the tube diameter as given by eq 22 is in agreement with the result by de Gennes.[15]

Contribution of the Junctions

Before considering the network as a whole, we need to establish the contribution to the free energy due to the special constraints at the chain ends as given by the

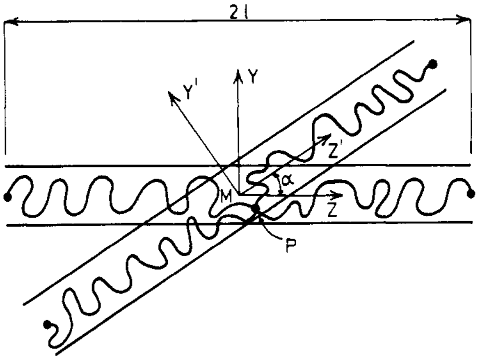

Figure 1. Formation of a tetrafunctional junction P by cross-linking two entangled chains fixed at the ends.

junctions of the network. Each junction is free to fluctuate, yet it is restricted by the walls of the tubes in which the chains emanating from the junction are confined.

Let us examine the case schematically depicted in Figure 1. Two chains are considered, each made up of $2n$ monomers, fixed at their ends which are separated by a distance $2l$. The tubes which host the chains have equal diameters; their center lines are coplanar and meet at their middle point, M, forming an angle α. Two coordinate systems are used, one for each tube, with the origin at M and the x axis orthogonal to the plane determined by the tube axes.

We now assume that a cross-link is formed, generating four equal chains made up of n monomers. Each chain has one end fixed and the other, P, fluctuating in common with the other chains.

The partition function of this system is calculated as

$$Q = \int\int\int Q_1Q_2Q_3Q_4 \, \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z \qquad (23)$$

where, according to eq 18 and neglecting constant factors, the individual Q's are given by

$$Q_1 = s \exp\left[-ns - s(x^2 + y^2) - \frac{1}{n}(l + z)^2\right]$$

$$Q_2 = s \exp\left[-ns - s(x^2 + y^2) - \frac{1}{n}(l - z)^2\right]$$

$$Q_3 = s \exp\left[-ns - s(x'^2 + y'^2) - \frac{1}{n}(l + z')^2\right]$$

$$Q_4 = s \exp\left[-ns - s(x'^2 + y'^2) - \frac{1}{n}(l - z')^2\right] \qquad (24)$$

and the coordinates of P in the two systems are related by

$$x' = x$$

$$y' = y \cos \alpha - z \sin \alpha$$

$$z' = y \sin \alpha + z \cos \alpha \qquad (25)$$

Performing the integration, we obtain

$$Q = s^{5/2}(\sin^2 \alpha + 4/ns)^{-1/2} \exp(-4ns - 4l^2/n) \qquad (26)$$

where the α dependence has been simplified by using the inequality $ns \gg 1$.

On the other hand, the two original chains without the cross-link would have, collectively, a partition function given by

$$Q = s^2 \exp(-4ns - 4l^2/n) \qquad (27)$$

Thus, introduction of the cross-link provides the contribution

$$Q(s,\alpha) = s^{1/2}(\sin^2 \alpha + 4/ns)^{-1/2} \qquad (28)$$

which reduces to $Q_{90} = s^{1/2}$ and $Q_0 = s$ for orthogonal and parallel tubes, respectively. These extreme cases are readily understood by considering that, for orthogonal chains, the fluctuation in the y direction of one chain is not opposed by the harmonic potential of the other. Only fluctuations in the x direction are opposed by both potentials simultaneously. Conversely, for parallel chains, both the x and y fluctuations are doubly impeded.

From eq 28, the contribution to the free energy due to the junction is written as

$$A_j/kT = \ln a + \tfrac{1}{2} \ln (\sin^2 \alpha + \delta) \qquad (29)$$

where we have replaced s by $1/a^2$ and the small quantity $4/ns$ by δ. The latter term has been kept in the expression of A_j to avoid degeneracy for $\alpha = 0$. However, it plays no role since it disappears in the averaging procedure. For example, if the tube directions are randomly distributed, the appropriate average is

$$\int_0^{\pi/2} \sin \alpha \ln (\sin^2 \alpha + \delta) \, \mathrm{d}\alpha = (1 + \delta)^{1/2} \ln \frac{(1 + \delta)^{1/2} + 1}{(1 + \delta)^{1/2} - 1} + \ln \delta - 2 \simeq 2(\ln 2 - 1) \qquad (30)$$

The result of eq 29 is more general than it might appear from the way it was obtained. As shown by Doi and Edwards,[11] for a chain trapped in a tube the line density of monomers is uniform along the tube and its value depends upon the tube radius a and the monomer length b. In dimensionless form, it is given by (cf. also ref 12)

$$n/l = a \qquad (31)$$

Equation 31 applies to a concentrated polymeric liquid such as the un-cross-linked polymer. As discussed in the following section, after cross-linking and even more so after a deformation, eq 31 will no longer be valid but the line density of monomers along the tubes will nevertheless be uniform. Now, if n/l is a constant, eq 29 is obtained also if the four chains meeting at P have four different lengths.

Similarly irrelevant are the conditions at the other end points of the chains, previously assumed to be fixed on the axes of the tubes. They may well fluctuate instead; as long as $ns \gg 1$ for all four chains, these fluctuations do not interfere with that of point P.

Depicting a tetrafunctional junction as occurring at the crossing of two cylinders is consistent with the model. Although the tubes in reality are not straight, they may be so approximated in the region of the junction. Finally, it is not necessary to assume that the axes of the cylinders are coplanar as they will not be so in general. Accounting of this fact introduces another term into eq 29, but this turns out to be independent of deformation.

Equation 29 is limited by the assumption that the two cylinders have a circular cross section of equal diameter. The result for two different diameters could be readily obtained, but it would represent an undue complication at this stage. Elliptic cross sections are similarly ignored.

Elastic Free Energy of the Network

Case 1. Tubes with a Circular Cross Section. An un-cross-linked rubber polymer is made up of long entangled chains. Following Doi and Edwards, we envisage the chains as transversally constrained by tubes of radius a_0 along which the chains slowly diffuse by a reptation motion. As previously recalled, the line density of monomers along the tubes is constant and equal to a_0.

After cross-linking the reptation motion is suppressed and each chain of the network becomes a distinct entity with a fixed number of monomers n. We shall here restrict the analysis to the case where all active chains are made up of a number of monomers such that $ns = n/a^2 \gg 1$. This being the case, the analysis may be further simplified by assuming that all chains have the same number of monomers. In fact, similarly to the classical theory, the results do not change if we consider a distribution of n values instead.

We call l_0 the curvilinear length of the tubes which contain the chains at the moment of the network formation. Since the monomer line density is a constant and n is assumed equal for all chains, l_0 will be the same for all chains and the following relationship will hold true:

$$n/l_0 = a_0 \tag{32}$$

After the network is formed but in the absence of a deformation, we may expect that the tube radius has become a_r, with $a_r \geq a_0$. In fact, in a liquid polymer the concept of entanglements is a dynamic one and the chains may be thought to be enclosed in tubes of a given diameter only to the effect of phenomena which take place over a time scale which does not extend to infinity. Conversely, in the case of networks, we are interested in the elastic response under equilibrium conditions. Thus, defects of the network such as loose chain ends or sol material do not participate in the equilibrium elastic response and act as a diluent. We may therefore expect a value of the tube radius in the network as formed somewhat larger than a_0, depending on the fraction of material which has actually gone in the active chains.

The effect of dilution on the value of the tube radius in a liquid polymer has been considered by Daoud et al.[18] and Edwards.[19] Their results could perhaps be applied to this case as well. However, in the following we shall use the parameter

$$r = a_0^2/a_r^2 \qquad r \leq 1 \tag{33}$$

to indicate this structural difference of the network with respect to the parent polymer.

As mentioned in the Introduction, we shall assume that the tubes, i.e., the constraints exerted upon each chain or junction by the neighboring material, deform affinely. This immediately implies that

$$\langle l^2 \rangle = l_0^2 \frac{\lambda_1^2 + \lambda_2^2 + \lambda_3^2}{3} \tag{34}$$

where λ_1, λ_2, and λ_3 are the principal extension ratios.

In this section of the paper, we shall make the additional assumption that the tube cross section will stay circular (case 1), though the tube diameter will change with the deformation.

From eq 22 and 29, we write for the free energy of the network in this case

$$\frac{A}{kT} = \nu\left(\frac{1}{n}\langle l^2 \rangle + n\left\langle \frac{1}{a^2} \right\rangle\right) + \mu\left(\langle \ln a \rangle + \frac{1}{2}\langle \ln(\sin^2 \alpha + \delta) \rangle\right) \tag{35}$$

where ν is the number of active chains and μ that of active junctions. Equation 35 was obtained by summing the contributions of the chains as given by eq 22 without the logarithmic term due to fixed ends together with those of the fluctuating junctions as given by eq 29. Beyond the assumptions inherent in eq 29, we are here considering a network made up entirely of tetrafunctional junctions which would have $\mu = \nu/2$.

The first simple application of eq 35 is that of a purely dilational deformation defined by the extension ratio $\lambda = (V/V_0)^{1/3}$. Since both l and a will change proportionally to λ in this case, eq 35 becomes

$$\frac{A}{kT} = \nu\frac{l_0}{a_0}\left(\lambda^2 + \frac{r}{\lambda^2}\right) + \mu \ln \lambda \tag{36}$$

where, in view of eq 30, we have dropped the rightmost term of eq 35 and use has been made of eq 32 and 33.

Equation 36 shows that the network as formed ($V = V_0$) is not under conditions of minimum free energy. Without effects of excluded volume, the network would shrink to a value of λ given by

$$\lambda = \left\{\left[r + \left(\frac{\mu a_0}{4\nu l_0}\right)^2\right]^{1/2} - \frac{\mu a_0}{4\nu l_0}\right\}^{1/2} < 1 \tag{37}$$

which, as $\mu a_0/4\nu l_0$ is small, can be approximated by $\lambda \simeq r^{1/4}$ or, if $r = 1$, by $\lambda \simeq 1 - \mu a_0/8\nu l_0$.

From eq 36, we can calculate the change in chemical potential $\bar{\mu} - \bar{\mu}_0$ of a diluent in the swollen rubber due to the elasticity of the network. In particular, we consider the product

$$\lambda(\bar{\mu} - \bar{\mu}_0) \propto \frac{1}{\lambda}\frac{\mathrm{d}}{\mathrm{d}\lambda}\left(\frac{A}{kT}\right) \propto 2\nu\frac{l_0}{a_0}\left(1 - \frac{r}{\lambda^4}\right) + \frac{\mu}{\lambda^2} \equiv \varphi(\lambda) \tag{38}$$

It is noteworthy that $\varphi(\lambda)$ reaches a maximum when

$$\lambda = 2\left(\frac{\nu}{\mu}\frac{l_0}{a_0}r\right)^{1/2} \tag{39}$$

A maximum in $\varphi(\lambda)$ has been found experimentally in some cases[20,21] and discussed theoretically by Flory.[5] We do not dwell on more quantitative aspects of this result because of the many assumptions that we have used. Particularly, the assumption that $ns \gg 1$ for all chains is hardly true in most cases and it is reconsidered in a later section.

The next case we examine is that of a simple extension or compression at constant volume, $V = V_0$. For a constant-volume deformation in general, the tube length always increases on the average since

$$\frac{\lambda_1^2 + \lambda_2^2 + \lambda_3^2}{3} > 1 \qquad \text{if } \lambda_1\lambda_2\lambda_3 = 1 \tag{40}$$

Affinity then requires that the tube diameter decreases on the average so as to preserve the tube volume; i.e.

$$\langle a^2 \rangle = \text{cost}\left\langle \frac{1}{l} \right\rangle \simeq a_r^2\left(\frac{\lambda_1^2 + \lambda_2^2 + \lambda_3^2}{3}\right)^{-1/2} \tag{41}$$

In a simple extension or compression, defined by the extension ratio λ, we write eq 35 as

$$\frac{A}{kT} = \nu\frac{l_0}{a_0}\left[\frac{\lambda^2 + 2\lambda^{-1}}{3} + r\left(\frac{\lambda^2 + 2\lambda^{-1}}{3}\right)^{1/2}\right] \tag{42}$$

where we have temporarily ignored the logarithmic terms and taken $\langle 1/a^2 \rangle = 1/\langle a^2 \rangle$ for simplicity.

From eq 42, the retractive force is obtained as

$$\frac{F}{S_0} = \frac{1}{V}\frac{\mathrm{d}A}{\mathrm{d}\lambda} = \frac{l_0}{a_0}\nu kT\left[\frac{2}{3} + \frac{r}{3}\left(\frac{\lambda^2 + 2\lambda^{-1}}{3}\right)^{-1/2}\right](\lambda - \lambda^{-2}) \tag{43}$$

where S_0 is the initial cross section of the sample and ν has to be interpreted as the number of chains per unit volume.

Equation 43 describes a nonideal behavior of the network. The ratio $F/(\lambda - \lambda^{-2})$ decreases with increasing deformation for both extension and compression with a maximum at $\lambda = 1$. However, the drop is less steep in compression. In fact, the behavior is close to that found by Ronca and Allegra.[1] Also the physical interpretation is similar to that indicated by those authors as well as by Flory,[2] with the difference that it refers to the fluctuation of the chains rather than junctions. Indeed, as the chains elongate the line density of monomers along the tubes decreases proportionally to $(\lambda^2 + 2\lambda^{-1})^{-1/2}$. At the same time, the tube diameter decreases only proportionally to $(\lambda^2 + 2\lambda^{-1})^{-1/4}$ so that eq 31 no longer holds and the chains become progressively less sensitive to the tube constraints. Relatively, more conformations become available and the rubber softens.

If the coefficients of the two terms of eq 41 are interpreted as C_1 and C_2, one would obtain a ratio

$$C_2/C_1 = 0.5r \tag{44}$$

However, what is more important in eq 43 is the front factor, which gives the shear modulus G of the network as

$$G = \frac{l_0}{a_0}\nu kT\left(\frac{2}{3} + \frac{r}{3}\right) \tag{45}$$

With respect to the maximum value predicted by the classical theories, $G = \nu kT$, we find the amplifying factor $(2/3 + r/3)l_0/a_0$.

Actually, the value of G given by eq 45 is virtually independent of ν and essentially represents a property of the parent polymer. Considering a perfect network for which $r = 1$, by the use of eq 32 we rewrite eq 45 as

$$G_{\max} = \frac{1}{a_0^2}n\nu kT \tag{46}$$

and note that the product $n\nu$ is constant with increasing extent of cross-linking and equal to the monomer concentration, c. In an imperfect network, it varies only inasmuch as the proportion of inactive material may also vary with ν.

By reverting to dimensional quantities, we finally write eq 46 as

$$G_{\max} = \frac{2}{3}\frac{b^2}{a_0^2}ckT \tag{47}$$

Within a numerical factor of order unity, this is the expression of the plateau modulus of the un-cross-linked polymer as given by the theory of Doi and Edwards.[22]

The fact that G is virtually independent of ν should not be considered as a negative result. Apart from the influence of network imperfections, it should be remembered that we have assumed $ns \gg 1$ for all chains. Now, even if $ns \gg 1$ on the average, a proportion of shorter chains will exist for which this inequality does not hold. These chains behave "classically" and their number increases with increasing extent of cross-linking. A more complete theory should use eq 17 instead of eq 18, together with the appropriate distribution of chain lengths. An approximation in this direction will be considered in a later section.

We finally calculate the contribution of the logarithmic terms of eq 35. We recall that they were obtained by assuming that the tubes converging into the junction were of the same diameter. After deformation this will not be true in general since the tubes are differently oriented and thus differently deformed. However, also the assumption that the tubes are straight is not true in reality so that, if the tubes are sufficiently long, many different orientations of the tube center line exist in the same tube. We then assume that the cross section of *each* tube has a radius equal to the average value $\langle a^2\rangle^{1/2}$.

Consistent with this assumption, the term $\langle \ln a\rangle = {}^1/_2 \ln \langle a^2\rangle$ gives the following contribution to the retractive force in a simple extension or compression:

$$\frac{F'}{S_0} = -\frac{1}{6}\mu kT\left(\frac{\lambda^2 + 2\lambda^{-1}}{3}\right)^{-1}(\lambda - \lambda^{-2}) \tag{48}$$

Here μ is the number of junctions per unit volume.

The second logarithmic term in eq 35 appears difficult to handle exactly. We have approximated it by taking

$$\langle \ln (\sin^2 \alpha + \delta)\rangle \simeq \ln \langle \sin^2 \alpha\rangle = \ln (1 - \langle \cos^2 \alpha\rangle) \tag{49}$$

By using spherical angles θ and φ with the polar axis in the direction of the extension, we calculate $\langle \cos^2 \alpha\rangle$ as

$$\langle \cos^2 \alpha\rangle = \frac{1}{8\pi}\int_0^\pi \mathrm{d}\theta \int_0^\pi \mathrm{d}\theta' \int_0^{2\pi} \mathrm{d}\varphi' \frac{(\lambda^2 \cos\theta \cos\theta' + \lambda^{-1} \sin\theta \sin\theta' \cos\varphi')^2}{(\lambda^2 \cos^2\theta + \lambda^{-1}\sin^2\theta)(\lambda^2\cos^2\theta' + \lambda^{-1}\sin^2\theta')} \times \sin\theta \sin\theta' \tag{50}$$

where θ,φ and θ',φ' are the angles of the tubes in the isotropic state and φ (or φ') can be set equal to zero in view of the axial symmetry of the deformation. This gives

$$\langle \cos^2 \alpha\rangle = \left[\frac{1 - g(\lambda)}{1 - \lambda^{-3}}\right]^2 + \frac{1}{2}\left[\frac{g(\lambda) - \lambda^{-3}}{1 - \lambda^{-3}}\right]^2 \tag{51}$$

where

$$g(\lambda) = (\lambda^3 - 1)^{-1/2} \tan^{-1} (\lambda^3 - 1)^{1/2} \tag{52}$$

or

$$g(\lambda) = (1 - \lambda^3)^{-1/2} \tanh^{-1} (1 - \lambda^3)^{1/2} \tag{52'}$$

for tension or compression, respectively.

The contribution of the second logarithmic term of eq 35 to the retractive force is then calculated as

$$\frac{F''}{S_0} = -\frac{1}{2}\mu kT\frac{1}{1 - \langle \cos^2\alpha\rangle}\frac{\mathrm{d}}{\mathrm{d}\lambda}\langle \cos^2 \alpha\rangle \tag{53}$$

By letting $\epsilon = \lambda - 1$ and expanding eq 51 around $\epsilon = 0$, we obtain

$$\langle \cos^2 \alpha\rangle = \frac{1}{3} + \frac{6}{25}\epsilon^2 + ... \tag{54}$$

From eq 53 and 54, we then calculate a shear modulus contribution of $-3\mu kT/25$.

It may be noted that the contribution of the junctions to the shear modulus is small and negative in sign. Collectively, it is given by (cf. also eq 48)

$$G_j \simeq -\left(\frac{1}{6} + \frac{3}{25}\right)\mu kT \tag{55}$$

Case 2. Tubes with an Elliptic Cross Section. In the previous section we have approximated the deformed tubes as cylinders of circular cross section on the basis of the fact that the tubes are actually curved. The circular cross section was taken to represent an average of the various different sections which exist along the tube. Nevertheless, individual segments of the tubes will assume an elliptic cross section as a consequence of anisotropic deformations. It is therefore interesting to estimate the influence of this change in shape upon the deformation dependence of the elastic free energy.

We shall then consider straight tubes which in the isotropic reference state have a circular cross section of radius a_r and are randomly oriented. After deformation, the cross section becomes an ellipse with semiaxes a_1 and a_2.

The free energy of this system is obtained from eq 21 as

$$\frac{A}{\nu kT} = \frac{1}{n}\langle l^2 \rangle + \frac{n}{2}\left\langle \frac{1}{a_1^2} + \frac{1}{a_2^2} \right\rangle \tag{56}$$

where, in view of the results of the previous section, the small contribution of the junctions is altogether neglected.

The quantity $1/a_1^2 + 1/a_2^2$ has a quite complex expression in the general case. It is calculated in Appendix B; the result is

$$\frac{1}{a_1^2} + \frac{1}{a_2^2} = \frac{1}{a_r^2}\,\frac{B + C}{D}$$

$$B = (\lambda_1\lambda_2\lambda_3)^{-2}[L^2M^2(\lambda_1^2 - \lambda_2^2)^2 + M^2N^2(\lambda_2^2 - \lambda_3^2)^2 + N^2L^2(\lambda_3^2 - \lambda_1^2)^2]$$

$$C = (L^2\lambda_1^2 + M^2\lambda_2^2 + N^2\lambda_3^2)\left[L^2M^2\left(\frac{1}{\lambda_1^2} - \frac{1}{\lambda_2^2}\right)^2 + M^2N^2\left(\frac{1}{\lambda_2^2} - \frac{1}{\lambda_3^2}\right)^2 + N^2L^2\left(\frac{1}{\lambda_3^2} - \frac{1}{\lambda_1^2}\right)^2\right]$$

$$D = L^2M^2\left(\frac{\lambda_1}{\lambda_2} - \frac{\lambda_2}{\lambda_1}\right)^2 + M^2N^2\left(\frac{\lambda_2}{\lambda_3} - \frac{\lambda_3}{\lambda_2}\right)^2 + N^2L^2\left(\frac{\lambda_3}{\lambda_1} - \frac{\lambda_1}{\lambda_3}\right)^2 \tag{57}$$

where L, M, and N are the direction cosines of the cylinder axis in the isotropic state with respect to the principal directions of strain and λ_1, λ_2, and λ_3 are, in the same order, the principal extension ratios.

In simple extension or compression, eq 57 reduces to

$$\frac{1}{a_1^2} + \frac{1}{a_2^2} = \frac{1}{a_r^2}\left(\lambda + \frac{\sin^2\theta + \lambda^3\cos^2\theta}{\lambda^2}\right) \tag{58}$$

where θ is the angle that the cylinder axis forms with the extension direction under isotropic conditions.

By taking the average we obtain in such a case

$$\left\langle \frac{1}{a_1^2} + \frac{1}{a_2^2} \right\rangle = \frac{2}{3}\,\frac{1}{a_r^2}(2\lambda + \lambda^{-2}) \tag{59}$$

so that the retractive force is given by

$$\frac{F}{S_0} = \frac{2}{3}\,\frac{l^0}{a_0}\nu kT(1 + r\lambda^{-1})(\lambda - \lambda^{-2}) \tag{60}$$

where we have used also eq 32 and 33.

It is noteworthy that the Mooney–Rivlin equation is predicted exactly in this case, with a C_2/C_1 ratio and a modulus given by

$$C_2/C_1 = r \qquad G = \frac{2}{3}\,\frac{l_0}{a_0}\nu kT(1 + r) \tag{61}$$

It is well-known, however, that the Mooney correction does not extend to the compression case, where the ratio $F/(\lambda - \lambda^{-2})$ is found to be almost constant. We are tempted in this regard to somehow combine the results of eq 43 and 60, corresponding to circular and elliptic cross sections, respectively. Because of the curvature of the tubes, eq 60 is approximate since each tube segment is too short for the assumption $ns \gg 1$ to be valid. On the other hand, because of the noncircular cross section on a local basis, eq 43 is also approximate. It may be noted that the deviations from the classical form predicted by eq 43 and 60 are in the same direction in the tension region whereas they give opposite effects in the case of a compression.

We conclude this section by comparing our result with that obtained by Gaylord.[13] As mentioned previously, Gaylord uses cylinders with a rectangular cross section which are equivalent to the elliptic cylinders used here. However, as a model for the whole network, only three representative cylinders are taken by Gaylord, each aligned along one of the principal directions of strain. The nonclassical term which is then obtained in the free energy expression is of the form $\lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2}$.

Although this result coincides with that of eq 59 for simple extension or compression, a significant difference is found in the general case. We have not found the average of the expression given by eq 57 but it appears unlikely that it is simply $\lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2}$.

Influence of a Distribution of Chain Lengths

All results obtained so far are subject to the restriction $ns \gg 1$ for all chains, a condition which is hardly fulfilled in most cases. Removing this restriction would imply, as previously noted, the use of eq 17 instead of eq 18, which is no simple matter. Furthermore, if many shorter chains exist in the network, a significant proportion of junctions are subject to fluctuations which are of the same order of the end-to-end distance of the shorter chains, thus contributing significantly to the free energy of the system. It appears very difficult to calculate this contribution in a mixed situation, where chains of different length, i.e., variously encumbered by the entanglements, exist simultaneously.

Lacking a better theory, we take here a very simple approach in order to estimate the influence of a distribution of chain lengths. We totally ignore the problem of the junctions. Furthermore, we separate the chains into two categories only. Those for which $ns > 1$ are taken to behave in the way described in the previous sections; those which have $ns < 1$ obey the classical theory.

If the network was formed by cross-linking in a random fashion a single giant macromolecule, the distribution $P(n)$ of chain lengths may be written as

$$P(n) = \frac{1}{\bar{n}}\exp\left(-\frac{n}{\bar{n}}\right) \tag{62}$$

where the average value of n is related to the monomer concentration c and chain concentration ν by

$$\bar{n} = c/\nu \tag{63}$$

If the network contains loose ends, sol material, etc. in a significant proportion, eq 63 is replaced by

$$\bar{n} = (c/\nu)p \tag{64}$$

where p is the fraction of monomers which belong to the active chains. Though the distribution of chain lengths will be somewhat different in such a case,[23] we keep eq 62 for simplicity.

We now call f the fraction of chains for which $ns = n/a^2 > 1$. From eq 62 and 64, this fraction is obtained as

$$f = \int_{a^2}^{\infty} P(n)\,\mathrm{d}n = \exp\left(-\frac{\nu a^2}{cp}\right) \tag{65}$$

In the network as formed f takes the value f_r given by

$$f_r = \exp\left(-\frac{a_0^2}{c}\,\frac{\nu}{rp}\right) \tag{66}$$

which depends on the parent polymer through $c/a_0^2 = G_{\max}/kT$ (cf. eq 47) as well as on the network structure through ν, p, and r. As previously mentioned, the latter two quantities could perhaps be related to one another by dilution theories.[18,19] For well-characterized networks, ν and p can also be determined.[6]

Equation 65 shows that f also depends on deformation. As the network swells, f decreases according to

$$f = f_r^{\lambda^2} \tag{67}$$

Conversely, a constant-volume deformation increases f. If a^2 is preaveraged in eq 65, one obtains

$$f = f_r^{[(\lambda_1^2+\lambda_2^2+\lambda_3^2)/3]^{-1/2}} \tag{68}$$

The elastic free energy of the composite network, made up of short as well as of longer entangled chains, is written as

$$A = \nu\int_0^{a^2} A'P(n)\,\mathrm{d}n + \nu\int_{a^2}^{\infty} A''P(n)\,\mathrm{d}n \tag{69}$$

where a^2 depends on deformation according to

$$a^2 = \frac{a_0^2}{r}\,\frac{V}{V_0}J^{-1} \qquad J^2 = \frac{I_1}{3} = \frac{1}{3}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2) \tag{70}$$

λ_1, λ_2, and λ_3 being defined with respect to the reference isotropic state at $V = V_0$ when the network was formed.

In eq 69, A' is the free energy of a phantom chain and A'' that of an entangled one. A possible choice for A' and A'' is made by taking the partition functions of eq 14 and 19, respectively, and neglecting the preexponential factors

$$\frac{A'}{kT} = \left\langle\frac{x^2 + y^2 + z^2}{n}\right\rangle = \frac{3}{2}J^2 \tag{71}$$

$$\frac{A''}{kT} = \left\langle\frac{l^2}{n} + \frac{n}{a^2}\right\rangle = \frac{n}{a_0^2}\left(J^2 + r\frac{V_0}{V}J\right) \tag{72}$$

Substituting eq 71 and 72 into eq 69 gives

$$\frac{A}{\nu kT} = \frac{3}{2}J^2(1 - f) + \left(1 + \frac{1}{r}\,\frac{V}{V_0}J\right)f + \frac{\bar{n}}{a_0^2}\left(J^2 + r\frac{V_0}{V}J\right)f \tag{73}$$

Crude as it is, eq 73 is already quite complex and gives rise to various nonclassical results, including the possibility of a maximum in $\lambda(\bar{\mu} - \bar{\mu}_0)$ for swollen rubbers, depending on values of the parameters. By way of example, we write here the expression for the shear modulus in the reference state

$$G = \nu kT\left(1 + \frac{2}{3}\,\frac{1-r}{r}f_r + \frac{\nu kT}{pG_{\max}}\,\frac{2-r}{6r^2}f_r\right) + \frac{2+r}{3}pf_rG_{\max} \tag{74}$$

If $r = p = 1$, eq 74 simplifies to

$$G = \nu kT\left(1 + \frac{\nu kT}{6G_{\max}}f_r\right) + f_rG_{\max} \tag{75}$$

Further analysis of eq 69 and 73 and possible comparisons with existing data on real networks are deferred to a later paper.

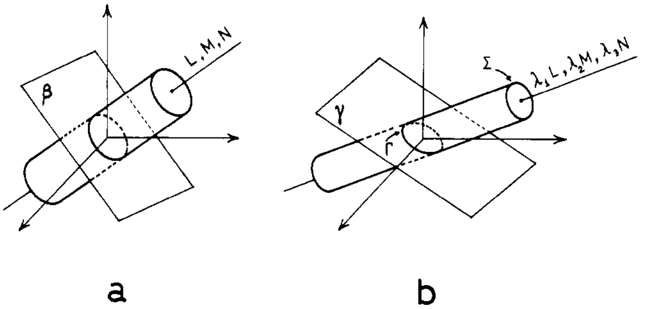

Figure 2. (a) Undeformed circular cylinder. The plane β is orthogonal to the cylinder axis. (b) Deformed elliptic cylinder. The plane γ is the deformed of β. Σ, not Γ, is the cross section.

Conclusions

We have shown that accounting for the effect of entanglements on the chains of a network by means of tube constraints which deform affinely gives rise to expressions for the elastic free energy which are able to predict the various nonclassical effects normally observed in real networks. Particularly, the Mooney effect and the maximum in the group $\lambda(\bar{\mu} - \bar{\mu}_0)$ for swollen networks arise naturally from the theory.

What appears to be more important is the prediction of a shear modulus which, contrary to classical and more modern theories, may result larger than νkT and closely related to the plateau modulus of the un-cross-linked polymer.

The theory is approximate and incomplete but it has the advantage of providing simple analytical expressions for the relevant quantities. The hope is that the model contains the most significant ingredients of that complex recipe which is a real network.

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Appendix A

We want to find the partition function $Q(x_0,x_n;s)$ of a chain in a harmonic potential when the zeroth bead is placed at x_0 and the nth bead at x_n. This requires calculation of the integral (x_0 and x_n excluded from the integration)

$$F = \int\ldots\int \exp(-\psi)\,\mathrm{d}x_1\ldots\mathrm{d}x_{n-1} \tag{A1}$$

where

$$\psi = (x_1 - x_0)^2 + \ldots + (x_{n-1} - x_n)^2 + s^2(x_0^2 + \ldots + x_n^2) \tag{A2}$$

First consider the integrals

$$\phi_k = \int\ldots\int x_k \exp(-\psi)\,\mathrm{d}x_1\ldots\mathrm{d}x_{n-1} \tag{A3}$$

For $k = 0$ and $k = n$, one finds trivially

$$\phi_0 = x_0F \qquad \phi_n = x_nF \tag{A4}$$

For any other k, the terms in ψ which contain x_k add up to

$$\psi_k = (2 + s^2)x_k^2 - 2x_k(x_{k-1} + x_{k+1}) \tag{A5}$$

so that

$$x_k = \frac{1}{2(2 + s^2)}\,\frac{\partial\psi_k}{\partial x_k} + \frac{1}{2 + s^2}(x_{k-1} + x_{k+1}) \tag{A6}$$

Since the integration over x_k of $\partial\psi_k/\partial x_k \exp(-\psi_k)$ gives zero, eq A3 becomes

$$\phi_k = \frac{1}{2 + s^2}(\phi_{k-1} + \phi_{k+1}) \tag{A7}$$

so that

$$\phi_k = C_1 \cosh (k\theta) + C_2 \sinh (k\theta) \qquad \theta = 2 \sinh^{-1} (s/2) \tag{A8}$$

where C_1 and C_2 are independent of the running index k. They are found from the "boundary conditions", eq A4, as

$$C_1 = x_0 F \qquad C_2 = x_n F \operatorname{csch} (n\theta) - x_0 F \coth (n\theta) \tag{A9}$$

On the other hand, from eq A1 we may write

$$\frac{\partial F}{\partial x_0} = -2(1 + s^2)x_0 F + 2\phi_1$$

$$\frac{\partial F}{\partial x_n} = -2(1 + s^2)x_n F + 2\phi_{n-1} \tag{A10}$$

Substituting from eq A8 and A9 and integrating gives

$$F \propto \exp(-W)$$

$$W = [\sinh \theta \coth (n\theta) + \cosh \theta - 1](x_0^2 + x_n^2) - 2 \sinh \theta \operatorname{csch} (n\theta) x_0 x_n \tag{A11}$$

By normalizing, we obtain the probability of finding the chain ends at x_0 and x_n

$$P(x_0,x_n;s) = \pi^{-1}\left[2\frac{\coth \theta - \operatorname{csch} \theta}{\coth \theta - \coth (n + 1)\theta}\right]^{1/2} \exp(-W) \tag{A12}$$

Finally, the required partition function is obtained through that of the chain with free ends (cf. eq 10 and 11 of the text)

$$Q(x_0,x_n;s) = Q_{ff}(s)P(x_0,x_n;s) = Q\pi^{-1/2}\left[\frac{\sinh (n\theta)}{\sinh \theta}\right]^{-1/2} \exp(-W) \tag{A13}$$

Equation A13 extends the result reported (with obvious misprints) by Edwards[9] to arbitrary values of the strength of the harmonic potential.

Appendix B

Take a Cartesian coordinate system with the axes along the principal directions of strain and consider a cylinder with the axis through the origin. Before deformation, the cylinder has a circular cross section of radius $a = 1$ and the direction cosines of the axis are L,M,N. We want to find the semiaxes a_1 and a_2 of the elliptic cross section of the deformed cylinder.

Consider the plane β through the origin which is orthogonal to the cylinder axis before deformation (cf. Figure 2). After deformation, this becomes the plane γ with the equation

$$\lambda_2\lambda_3 Lx + \lambda_3\lambda_1 My + \lambda_1\lambda_2 Nz = 0 \tag{B1}$$

The points which formed the circular cross section of the undeformed cylinder in the plane β will now form an ellipse Γ which is obtained by intersecting the plane γ with the ellipsoid

$$\frac{x^2}{\lambda_1^2} + \frac{y^2}{\lambda_2^2} + \frac{z^2}{\lambda_3^2} = 1 \tag{B2}$$

However, this ellipse is no longer the cross section of the deformed cylinder.

Since the axis of this cylinder now has direction cosines proportional to $\lambda_1 L,\lambda_2 M,\lambda_3 N$, the deformed cylinder is described by the set of straight lines

$$\frac{x - \xi}{\lambda_1 L} = \frac{y - \eta}{\lambda_2 M} = \frac{z - \zeta}{\lambda_3 N} \tag{B3}$$

passing through points ξ,η,ζ of the ellipse Γ. Making ξ,η,ζ to satisfy eq B1 and B2 and eliminating ξ,η,ζ from eq B1 to B3 give the equation of the deformed cylinder as

$$\frac{(x - \lambda_1 Lw)^2}{\lambda_1^2} + \frac{(y - \lambda_2 Mw)^2}{\lambda_2^2} + \frac{(z - \lambda_3 Nw)^2}{\lambda_3^2} = 1$$

$$w = \frac{L}{\lambda_1}x + \frac{M}{\lambda_2}y + \frac{N}{\lambda_3}z \tag{B4}$$

To find the semiaxes of the elliptic cross section Σ of this cylinder, it is now sufficient to perform a change to coordinates x',y',z' which put eq B4 in canonical form.

We choose, say, the z' axis to be parallel to the cylinder axis. Its direction cosines with respect to x,y,z are thus proportional to $\lambda_1 L,\lambda_2 M,\lambda_3 N$. The direction cosines of x' and y', so far unknown, are indicated as l_1,m_1,n_1 and l_2,m_2,n_2. They must obey the orthogonality conditions

$$l_1 l_2 + m_1 m_2 + n_1 n_2 = 0$$

$$\lambda_1 L l_1 + \lambda_2 M m_1 + \lambda_3 N n_1 = 0$$

$$\lambda_1 L l_2 + \lambda_2 M m_2 + \lambda_3 N n_2 = 0 \tag{B5}$$

The fourth relationship which is needed for their determination is provided by the condition that, after the change of coordinates has been performed in eq B4, the cross term in $x'y'$ must vanish. Of course, all terms in z' also vanish identically.

Cumbersome calculations then provide the result

$$a_1^2 = D/B \qquad a_2^2 = D/C \tag{B6}$$

where B, C, and D are the expressions reported in eq 57 of the text.

References and Notes

(1) Ronca, G.; Allegra, G. *J. Chem. Phys.* **1975**, *63*, 4990.
(2) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1976**, *351*, 351.
(3) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.
(4) Erman, B.; Flory, P. J. *J. Chem. Phys.* **1978**, *68*, 5363.
(5) Flory, P. J. *Macromolecules* **1979**, *12*, 119.
(6) Pearson, D. S.; Graessley, W. W. *Macromolecules* **1980**, *13*, 372.
(7) Edwards, S. F. *Proc. Phys. Soc.* **1967**, *92*, 9.
(8) Deam, R. T.; Edwards, S. F. *Philos. Trans. R. Soc. London, Ser. A.* **1976**, *280*, 317.
(9) Edwards, S. F. *Br. Polym. J.* **1977**, *9*, 140.
(10) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.
(11) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818.
(12) Marrucci, G.; Hermans, J. J. *Macromolecules* **1980**, *13*, 380.
(13) Gaylord, R. J. *Polym. Eng. Sci.* **1979**, *19*, 263.
(14) Gaylord, R. J.; Lohse, D. J. *J. Chem. Phys.* **1976**, *65*, 2779.
(15) de Gennes, P. G. *J. Phys., Lett.* **1974**, *35*, L-133.
(16) Marrucci, G.; de Cindio, G. *Rheol. Acta* **1980**, *19*, 68.
(17) Eichinger, B. E.; Martin, J. E. *J. Chem. Phys.* **1978**, *69*, 4595.
(18) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, J.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.
(19) Quoted in ref 11, p 1792.
(20) Yen, L. Y.; Eichinger, B. E. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 121.
(21) Gee, G.; Herbert, J. B. M.; Roberts, R. C. *Polymer* **1965**, *6*, 541.
(22) Cf. eq 5.8 in ref 11, p 1825. The monomer concentration is there written as the product of the polymer concentration c times the degree of polymerization N_0.
(23) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953.