

Viscoelasticity of Networks Consisting of Crosslinked or Entangled Macromolecules. I. Normal Modes and Mechanical Spectra

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A molecular theory is developed to describe quantitatively the mechanical behavior of entanglement networks of linear, randomly coiling molecules. The theory is based on the model of Rouse for a single molecule and is a generalization of the theory of Duiser and Staverman for chemically crosslinked networks.

A new model for an "entanglement point" is suggested, which accounts for the frictional force due to the velocity difference between two entangled molecules at that point. This leads to a modification of the diffusion equation in the Rouse theory.

It turns out that the relaxation spectrum of a network corresponds to that of an assembly of "decoupled" equivalent molecules in which the ends of some submolecules have a mobility which is smaller by a slip factor δ . This parameter may have values from zero (crosslinked molecules) to unity (free molecules in dilute solution).

The relaxation spectra of the decoupled equivalent molecules can be obtained by applying a property of the Sturm sequence in a computer program, without actually solving for the eigenvalues of the modified matrix in the Rouse diffusion equation.

Application of the theory to experimental data yields the number of elastically effective network chains of an entanglement network by integration of the area under the curve in the long-time region of the relaxation spectrum.

INTRODUCTION

IN the literature dealing with the mechanical behavior of polymers and polymer solutions, several theories can be found which attempt to describe this behavior on a molecular basis.¹⁻⁵ In most cases, these theories concentrate on a rather narrow field of interest. Many molecular theories are still restricted to linear viscoelastic behavior of linear, randomly coiling polymer chains. Furthermore they must still be extended in order to explain the long-time regions where entanglements affect the viscoelastic properties. Entanglements

are present in concentrated polymer solutions as well as in bulk polymers, whether chemically crosslinked or not. Characterization of such entanglement networks as well as chemically crosslinked, permanent networks involves the determination of the number of entanglements and/or permanent crosslinks. Permanent crosslinks give rise to an equilibrium rubber elastic modulus, which can be viewed as resulting from a number of molecular relaxation times which have become infinite. Entanglements give rise to a series of relaxation times, which are not infinite but very long. Entanglement networks therefore do not show an equilibrium modulus but behave rubber elastically in a certain time scale.

The dearth of precise knowledge in this field, reflected in several controversies in current polymer network theories, provides the main impetus for research in this area. One of the present authors (J.A.D.) has recently⁶ extended the molecular model of Rouse⁷ for linear

¹ A. J. Staverman, in *Handbuch der Physik*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1962), Vol. 13, pp. 432-451.

² L. R. G. Treloar, in *Die Physik der Hochpolymeren*, H. A. Stuart, Ed. (Springer-Verlag, Berlin, 1956), Vol. 4, pp. 295-372.

³ J. D. Ferry, *Viscoelastic Properties of Polymers* (John Wiley & Sons, Inc., New York, 1961), pp. 151ff.

⁴ A. V. Tobolsky, *Properties and Structure of Polymers* (John Wiley & Sons, Inc., New York, 1960), pp. 160ff.

⁵ A. V. Tobolsky and J. J. Aklonis, *J. Phys. Chem.* **68**, 1970 (1964).

⁶ J. A. Duiser, Ph.D. thesis, Leiden, The Netherlands, 1965.

⁷ P. E. Rouse, Jr., *J. Chem. Phys.* **21**, 1272 (1953).

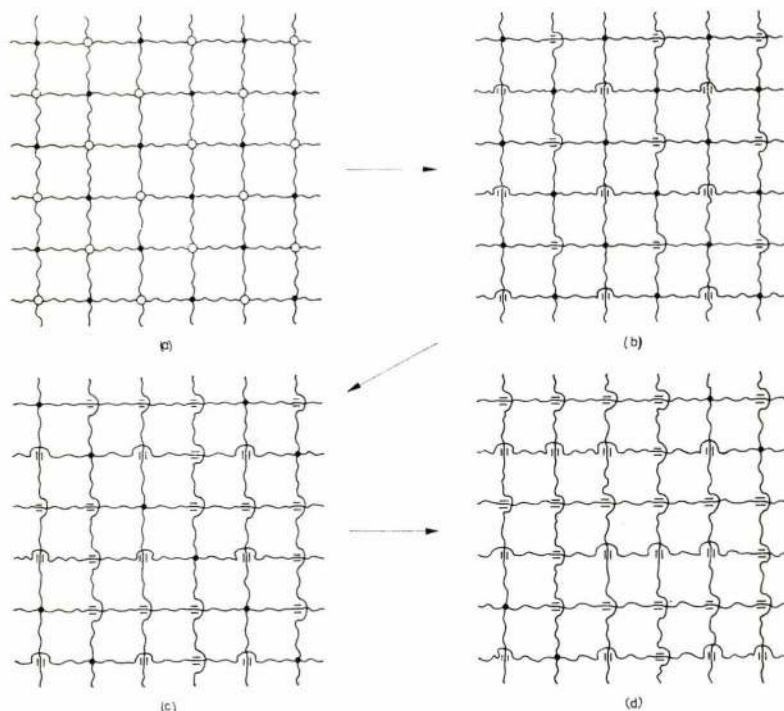


FIG. 3. The stepwise "decoupling" of chains in a regular network.

ment $a_{ij} = a_{(N-j+1)(N-i+1)}$. This means that if two chains are entangled as shown in Fig. 4(a), where the chains are divided into two pairs of equal chain segments, they can be represented by their mathematical equivalence as in Fig. 4(a).

This also means that a mathematical equivalence may be found for two entangling chains containing only two fixed points and two free ends as shown in Fig. 4(b), provided the entanglement divides the chains into two pairs of equal chain segments.

It has not yet been found possible to apply the above treatment to the general case where all four segments AP, BP, CP, and DP are different.

The physical meaning of these transformations can be illustrated as follows:

The chain AC can move with almost complete freedom. Once it has chosen a configuration, however, the point P appears to the chain BD as if it were fixed in

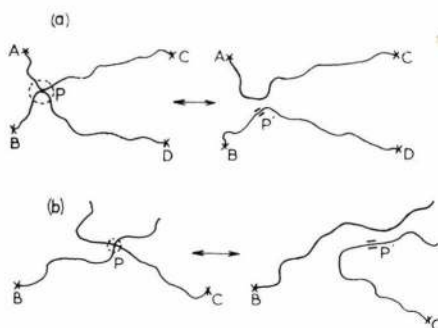


FIG. 4. The "decoupling" of somewhat irregularly entangled molecules.

the case of a permanent crosslink, or as if it were a slow point in the case of an entanglement. The sections BP and PD then choose their own configuration independently. The system of four chain sections, therefore—instead of the commonly accepted four degrees of freedom in which elastic energy can be stored—has only three degrees of freedom in the case of a permanent crosslink and a variable number between 2 and 3 in the case of an entanglement depending on the time scale of the experiment.

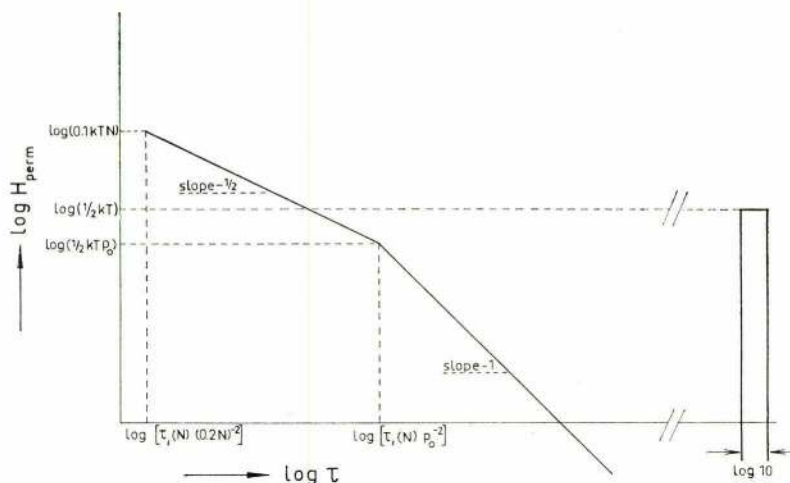
There seems to be no obvious reason why this physical interpretation should not also apply to a case where P is not at the center of the chains AC and BD, although it is not easy to prove this mathematically.

It is therefore assumed that the relaxation spectrum H_{ent} of an entanglement network with random distribution of chain lengths between entanglements, is also represented by Eq. (23). Each term $H[(m-1)/2^k]$ in this equation then represents an average of all possible entanglement distributions for a molecule with $(m-1)/2^k$ slow points. In actual calculations, however, for each term $H[(m-1)/2^k]$, one of the many possible distributions must be chosen and an average spectrum calculated from five to 10 such choices, depending on the accuracy which is desired.

PERMANENTLY CROSSLINKED NETWORKS

For the limiting case of a chemically crosslinked network where $\delta=0$, Eq. (23) may be simplified by writing the determinant of the characteristic equation of Eq. (24) as a product of smaller determinants. Then the relaxation spectrum H_{perm} per elastically effective

FIG. 5. The relaxation spectrum per network chain in a permanently crosslinked network.



network chain is found to be

$$H_{\text{perm}} = \frac{1}{4}H(N) + \frac{3}{4} \sum_{k=1,2,\dots}^{\infty} (4^k)^{-1}H(2^kN), \quad (25)$$

in which $H(y)$ is the relaxation spectrum of a chain with fixed ends and with a length of y submolecules. It should be noted that the spectra represented by Eqs. (23) and (25) are no longer series of lines of equal height.

At infinite relaxation time, the summation of Eq. (25) can easily be carried out, because each $H(y)$ is associated with one mechanism with an infinite relaxation time. It is found that the total number of these mechanisms is half the number of elastically effective chains because

$$\frac{1}{4} + \frac{3}{4} \sum_{k=1,2,\dots}^{\infty} (4^k)^{-1} = \frac{1}{2}.$$

As follows from Eqs. (6) and (7), the longest finite relaxation time of a chain is proportional to the square of the number of submolecules. So, if the longest finite relaxation time for a chain with y submolecules is represented by $\tau_1(y)$, then

$$\tau_1(2^kN) = 2^{2k}\tau_1(N). \quad (26)$$

From Eq. (25) the following spectrum is obtained:

(a) At short times, where $\tau_{0,2N}(N) < \tau \leq \tau_1(N)p_0^{-2}$, substitution of Eqs. (11) and (26) in Eq. (25) and summation gives

$$H_{\text{perm}} = \frac{1}{2}kT[\tau_1(N)/\tau]^{\frac{1}{2}}, \quad (27)$$

which is equal to H of a free molecule, represented by Eq. (11).

(b) At longer times, where $\tau > \tau_1(N)p_0^{-2}$, some terms of Eq. (25) become zero, as is shown by Eq. (11). A value k_0 may be defined in such a way, that only chains of 2^kN submolecules in length for which $k \geq k_0$ will contribute to the spectrum. Then in the region of the relaxation spectrum where

$$\tau_1(2^{k_0-1}N)p_0^{-2} < \tau \leq \tau_1(2^{k_0}N)p_0^{-2}, \quad (28)$$

the summation of Eq. (25) must be carried out starting from k_0 . With the use of Eq. (26), Eq. (28) can be written

$$\frac{1}{4}2^{2k_0}\tau_1(N)p_0^{-2} < \tau \leq 2^{2k_0}\tau_1(N)p_0^{-2}. \quad (29)$$

So, the value of k_0 is related to τ in such a way that

$$4p_0^2\tau/\tau_1(N) > 2^{2k_0} \geq p_0^2\tau/\tau_1(N). \quad (30)$$

Defining a number q_0^2 lying between $\frac{1}{4}$ and 1, one may write

$$2^{2k_0} = p_0^2\tau/q_0^2\tau_1(N). \quad (31)$$

Substitution of Eqs. (11) and (26) in Eq. (25) as before, but now carrying out the summation from a value k_0 determined by Eq. (31), yields

$$\begin{aligned} H_{\text{perm}} &= \frac{1}{2}kT \left[\frac{\tau_1(N)}{\tau} \right]^{\frac{1}{2}} \sum_{k_0, k_0+1, \dots}^{\infty} 2^{-k} \\ &= \frac{1}{2}kT \left[\frac{\tau_1(N)}{\tau} \right]^{\frac{1}{2}} \left(\frac{3}{4} \right)^{\frac{1}{2}} 2^{-k_0} \sum_{0,1,2,\dots}^{\infty} 2^{-k} \\ &= \frac{1}{2}kT [\tau_1(N)/\tau]^{\frac{1}{2}} \left(\frac{3}{2} \right)^{\frac{1}{2}} [q_0^2\tau_1(N)/p_0^2\tau]^{\frac{1}{2}} \\ &= \frac{1}{2}kT [\tau_1(N)/\tau] (3q_0/2p_0). \end{aligned} \quad (32)$$

The value of q_0 is somewhat arbitrary; if it is taken to be $\frac{2}{3}$ the two parts of the spectrum derived in (a) and (b) will fit at $\tau = \tau_1(N)p_0^{-2}$.

The physical meaning of Eqs. (27) and (32) lies in the representation of two kinds of movements performed by the network. That part of the spectrum which is proportional to τ^{-1} [given by Eq. (27)] refers to movements of chains between neighboring crosslinks. At longer times it is followed by a part where the spectrum is proportional to τ^{-1} [given by Eq. (32)] corresponding to movements in which crosslinks participate. These movements may be extended over chain lengths larger than that of a primary molecule before crosslinking. Indeed extremely long relaxation times have been found experimentally.¹⁴ It should be empha-

¹⁴ Reference 3, pp. 189 and 198.

sized, however, that in a crosslinked polymer network additional entanglements also cause very long relaxation times. The theoretical relaxation spectrum per elastically effective network chain thus obtained, is illustrated in Fig. 5. The form of the peak at infinite time may be chosen arbitrarily provided the condition

$$\int_{\text{peak}} H d \ln \tau = G_e = \frac{1}{2} k T$$

is fulfilled. The theoretical relaxation spectrum per network chain thus obtained, is illustrated in Fig. 5.

ENTANGLEMENT NETWORKS

For the case of an entanglement network where δ is not equal to zero, Eq. (23) cannot be simplified further. To calculate the relaxation spectra of all the terms $H[x]$, a method has to be found to obtain the eigenvalues of a matrix like the one given in Eq. (24). Since the relaxation spectra obtainable from experiment are always continuous, the eigenvalues or consequently the relaxation times themselves do not have to be calculated, but only the density of relaxation times along the τ axis. This affords a short cut to the calculation of a continuous relaxation spectrum of each $H[x]$ by applying a property of the Sturm sequence.¹⁵

Moreover, random distribution of entanglement points over the entire molecule can now also be easily introduced.

The method is based on the fact that, given a tri-diagonal determinant in the characteristic equation

$$\begin{vmatrix} c_1 - \lambda & b_1 & & & \\ b_1' & c_2 - \lambda & b_2 & & \\ & b_2' & c_3 - \lambda & b_3 & \\ & & b_3' & c_4 - \lambda & b_4 \\ & & & & \ddots & \ddots \\ & & & & & b_{N-1}' & c_N - \lambda \end{vmatrix} = 0, \quad (33)$$

the subdeterminants (H_{11} , $H_{22} \dots$) indicated by dotted lines form the following sequence:

$$\begin{aligned} H_{00} &= +1, \\ H_{11} &= (c_1 - \lambda)H_{00}, \\ H_{22} &= (c_2 - \lambda)H_{11} - b_1' b_1 H_{00}, \\ H_{33} &= (c_3 - \lambda)H_{22} - b_2' b_2 H_{11}, \\ H_{ii} &= (c_i - \lambda)H_{i-1, i-1} - b_{i-1}' b_{i-1} H_{i-2, i-2}. \end{aligned} \quad (34)$$

A theorem exists which proves that if a certain value of λ is substituted into this "Sturm sequence," the number of agreements (a_i) in sign between consecutive members of the sequence is equal to the number of

eigenvalues greater than that λ . If a $H_{ii} = 0$ occurs, its sign is defined to be opposite to that of $H_{i-1, i-1}$.

For instance, for $\lambda = 4$ in the matrix **A** of Eq. (24) all the H_{ii} will alternate in sign, giving no eigenvalues larger than +4. This maximum value for λ of +4 follows obviously from Eq. (7) for $p = N$. For $\lambda = 0$ all the H_{ii} will be positive and thus all the eigenvalues will be larger than zero, as they should be.

At this point the lengthy calculations must be taken over by a computer, which is given the following instructions:

(1) Determine the number of agreements a_1 for a certain λ_1 .

(2) Determine the number of agreements a_2 for $\lambda_1 - \Delta \lambda_1 = \lambda_2$ (where Δ is a multiplying factor, rather than an arithmetic increment, so as to give equal increments on a logarithmic scale).

(3) Find $a_2 - a_1$ and repeat the process until $a_i = mN$, the order of the matrix.

(4) Give the results converted into $\log \tau_R$ values, where $\tau_R = 1/\lambda_i$.

As a result of such a calculation it was found that δ must be very small (10^{-3} to 10^{-6}) in order to affect significantly the spectrum obtained with the unmodified Rouse matrix. For instance if $\delta = 0.1$ the change is so slight as to be undetectable by experiment.

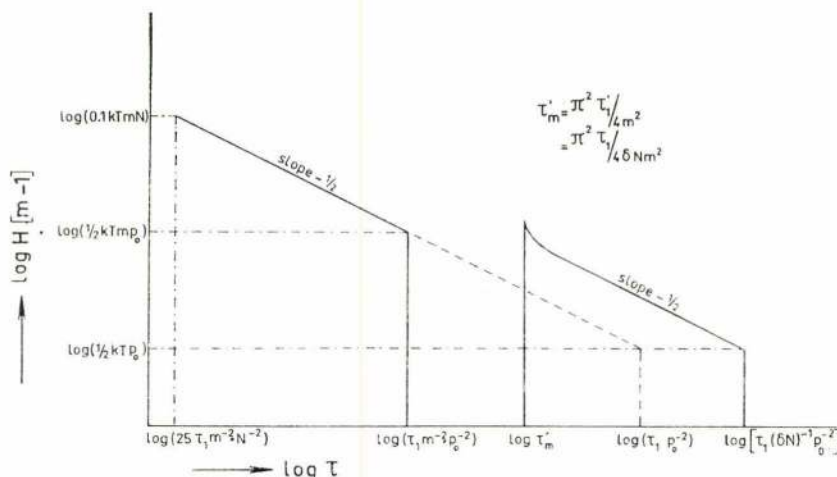
Clearly this result does not only apply to a chain with free ends, i.e., a matrix with 3's in the corners, but also to a chain with fixed ends, i.e., a matrix with 1's in the corners containing such perturbations as appear in Eq. (24). The results of these calculations will be given in a forthcoming article.

An approximate solution can be given for each term $H[x]$ of Eq. (23), provided δ is very small, by applying a method used by Kronig and Penney¹⁶ for the calculation of energy levels in a metal. A qualitative explanation for this approximation can be given as follows: At short times, where movements of chain segments occur which are much shorter than the average number of submolecules between entanglements, there is hardly any slip. The entanglements may then be considered as permanent crosslinks, or conversely the slow points may be considered as fixed points. This results in the type of relaxation spectrum discussed in the previous section. In the viscoelastic behavior at long times, however, the viscous properties of the molecule are mainly determined by the x slow points, while the $(x+1)$ almost rubbery behaving chain segments between the slow points take care of the elastic properties of the molecule. In this long-time region the molecule may be considered as a series of slow points coupled by rubbery chain portions, which behave like giant "submolecules." The mobilities at the slow points are then taken as δ times the mobility of a normal submolecule.

¹⁵ J. H. Wilkinson, *Numerische Mathematik* **4**, 362 (1962).

¹⁶ R. de L. Kronig and W. G. Penney, *Proc. Roy. Soc. (London)* **A130**, 499 (1931).

FIG. 6. The approximate relaxation spectrum $H[m-1]$ for a "decoupled" molecule of mN submolecules.



According to Eqs. (6) and (7) the relaxation times are inversely proportional to the mobilities at the junctions and are proportional to the square of the number of "submolecules" and to their average square end-to-end distance. Thus, in the long-time region of $H[x]$ the approximation predicts a longest finite relaxation time τ_1' of a molecule with x slow points of

$$\tau_1' = \langle r_e^2 \rangle (x+1)^2 / (6\pi^2 k T \delta B), \quad (35)$$

where $\langle r_e^2 \rangle$ is the average square end-to-end distance of the giant "submolecule" between slow points. The longest finite relaxation time of a molecule with the same length but without slow points is, according to Rouse,

$$\tau_1 = \langle r_e^2 \rangle (mN)^2 / (6\pi^2 k T B). \quad (36)$$

Since

$$\langle r_e^2 \rangle = \langle r_s^2 \rangle mN / (x+1),$$

Eqs. (35) and (36) yield

$$\tau_1' / \tau_1 = (x+1) / mN \delta. \quad (37)$$

This result indicates that the very long-time region of

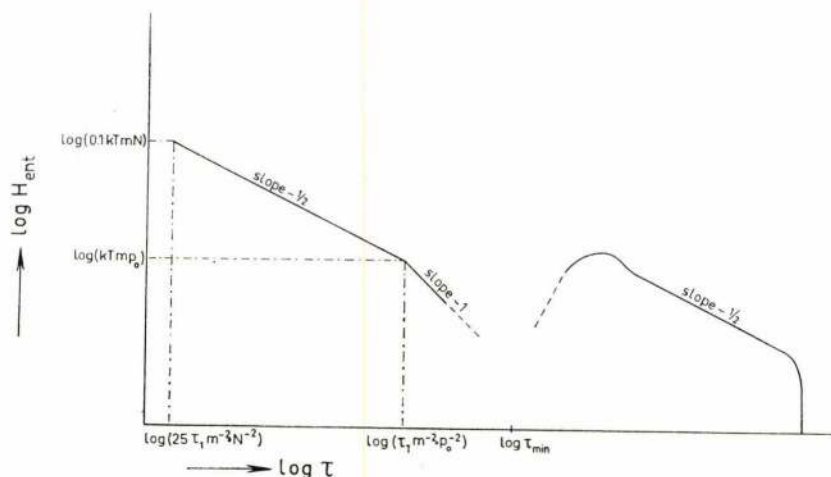
the spectrum $H[x]$ should approximately correspond to a shift of part of the Rouse spectrum to higher values of τ by a factor of $(x+1)/(mN\delta)$. This is illustrated for the spectrum $H[m-1]$ in Fig. 6.

A similar type of relaxation spectrum has already been suggested intuitively by Ferry and co-workers¹⁷ for a real entangled molecule. In the present article, however, the spectrum of Fig. 6 is only valid for a molecule in the transformed equivalent system of molecules. The real spectrum H_{ent} has to be assembled from a large number of such spectra according to Eq. (23).

Combining the results from the previous section for the short-time region with the above, yields a relaxation spectrum H_{ent} of a shape as shown in Fig. 7.

The hump in the long-time region of the spectrum has a shape which is difficult to predict exactly, but the area under it is more important. Interpretation of the relaxation spectrum of Fig. 6 in terms of discrete line spectra, yields for $H[m-1]$ in the long-time region $(m-2)$ lines of equal height. Similarly, $H[\frac{1}{2}(m-1)]$ has in the long-time region $\frac{1}{2}(m-1)-1$ lines of equal height, and $H[\frac{1}{4}(m-1)]$ has in the same region

FIG. 7. Expected relaxation spectrum for molecule in an entanglement network.



¹⁷ J. D. Ferry, R. F. Landel, and M. L. Williams, *J. Appl. Phys.* **26**, 359 (1955).

$\frac{1}{4}(m-1)-1$ lines of equal height, etc. It is then obvious that the summation of all these lines in the long-time region, using Eq. (23), yields in Fig. 7 an area under the hump equal to half the number of elastically effective network chains (ν_e) multiplied by kT because

$$\frac{1}{4}(m-2) + \frac{3}{4} \sum_{k=1,2,\dots} (1/2^k) \{ [(m-1)/2^k] - 1 \} \\ = \frac{1}{2} [(m-1) - 2], \quad (38)$$

which is exactly equal to half the number of elastically effective network chains per molecule.

Thus the long-time region of the relaxation spectrum of an entanglement network replaces the infinite-time region of a chemically crosslinked network (the "block" at infinite time in Fig. 5).

CONCLUSIONS

The theory of Rouse thus permits an extension which describes the viscoelastic relaxation spectrum of networks consisting of crosslinked or entangled macromolecules. The extension is performed by modification of the mobility-coefficient matrix in the configuration-diffusion equation, to give account of the frictional phenomena at an entanglement point between two entangled molecules.

It turns out that such a friction may be expressed mathematically by introducing a slip parameter δ . Application of a decoupling process yields a system of two chains, where the mobility at the former point of contact on one of the two chains must be multiplied with this factor δ , whereas the mobility at the same point on the other chain is kept unchanged.

Extension of this principle to a whole network yields also a mathematical equivalence, which is an assembly of decoupled molecules containing various amounts of "slow points." Since the relaxation spectra are assumed to be additive, the spectrum of the whole network can be obtained by appropriate summation of the different spectra of the decoupled molecules times their respective mole fractions.

A simplification can be achieved in the case where the molecules are permanently crosslinked ($\delta=0$). Then the spectrum can be split into two regions: (1) At short times the slope of the logarithmic relaxation spectrum is $-\frac{1}{2}$, changing to -1 at a time corresponding to the longest relaxation time of a chain between two neighboring crosslinks; (2) at infinite time a peak in H appears, corresponding to a number of mechanisms

equal to half the number of elastically effective network chains. Both regions are illustrated in Fig. 5.

If $0 < \delta < 1$ the entanglements can be considered more or less similar to crosslinks. The long-time region of the relaxation spectrum no longer lies at infinite time. Instead, a hump in H appears at fairly long relaxation times. The position of this hump depends on the value of δ . Only for very low values of δ an approximate solution is applicable. Quite generally, however, the relaxation spectrum can be obtained by means of a computer using a property of the Sturm sequence. The relaxation spectrum thus obtained is schematically shown in Fig. 7. It has the following characteristic properties:

(a) In the short-time region the spectrum is identical with the spectrum for a crosslinked network, i.e., the slope of $-\frac{1}{2}$ is followed by a slope of -1 .

(b) A rather low minimum in the curve is followed by a hump, representing a group of long relaxation times. The integral of H as a function of $\ln \tau$, corresponding to the hump, yields

$$\int_{\min}^{\infty} H d \ln \tau = \frac{1}{2} \nu_e k T. \quad (39)$$

Therefore, the number of elastically effective chains ν_e , can be calculated directly from the spectrum derived from experiments. Examples of these calculations will be given in a forthcoming article.

(c) Beyond the maximum in the hump the slope is practically constant and equal to $-\frac{1}{2}$ up to the highest relaxation time. Relative to the short-time region where the slope is also equal to $-\frac{1}{2}$, this part of the spectrum may be considered as if the relaxation times of part of the Rouse spectrum have been shifted to higher values of τ over a distance proportional to $-\log(\delta N)$ along the time axis.

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