Relaxation Spectra of Nonlinear Polymers

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ABSTRACT: A method is presented to calculate the relaxation spectra of nonlinear polymers. Actual calculations are made for the star, comb, and Cayley tree type molecules, and also for the regular network of polymer chains. Sum rules for the eigen relaxation times are proved. It is found that none of the calculated relaxation spectra exhibit a box-type spectrum.

KEY WORDS   Relaxation Spectrum / Eigenvalue Problems / Branching / Random Network / Sum Rules /

It is now well known that the relaxation spectrum $H(\tau)$ of undiluted polymer solutions has a characteristic shape very different from that of dilute solutions. For the short time region the shape is the same as that of the linear chain, called a wedge type spectrum, but in the long time region there is a hump sometimes approximated to be a box-type spectrum. The box-type spectrum is considered to arise from the entanglement effect, but no successful theory has been given to explain the shape of the spectrum.

The entanglement effect is the topological constraint that the chains cannot intersect each other. However, the effect is often discussed on the basis of "nontopological" models. For instance, Ham[1] investigated the possibility of a permanent cross-linkage model to describe the entanglement effect. Yamamoto[2] proposed a constitutive equation of undiluted polymer solutions based upon a temporary cross-linkage model. Chompff, Duiser, and Prins considered a system in which the polymer chains are interacting on each other at fixed imperfect slipping points.[3,4] Very recently Yamamoto[6] calculated the relaxation spectrum of a linear chain whose friction coefficient varies along the chain.

In any case, when we adopt these models, we encounter the problem of nonlinear and inhomogeneous polymer chains whose structure is in general random. The detailed calculation of the relaxation spectrum of such polymers is a very difficult problem, but in general the fine structure of the spectrum is not of interest since it cannot be obtained from experiments so accurately. In the present paper we attempt to clarify the following two points: (i) Can we obtain the box-type relaxation spectrum based upon such nontopological models? (ii) How can we calculate the longest relaxation time, which plays the dominant role in the viscoelastic properties of the chain?

First we present a method to calculate the relaxation spectrum and next apply it to the problem of some typical branched polymers. Some general properties of the relaxation spectrum are discussed and sum rules of the relaxation spectrum are proved. Finally we shall discuss whether the permanent cross-linkage model can exhibit the box-type spectrum.

FORMULATION

In this section we present a method to calculate the relaxation spectra of branched polymers. Our method is a direct extension of the Rouse—Zimm theory.[12,13] We neglect the hydrodynamic interaction between the submolecules throughout this paper so as to avoid additional difficulty.

First, let us consider a linear chain. Let r_1, r_2, ..., r_{N_t} be the coordinates of the submolecules. To find the normal mode, we consider the equations of motion of the submolecules:

$$\zeta_\sigma \frac{\partial r_\sigma}{\partial t} = -F_\sigma + F_{\sigma+1} \qquad (\sigma = 1, 2, \ldots, N_t) \quad (1)$$

where ζ_σ is the friction coefficient of the σ-th submolecule (here we consider a general polymer whose friction coefficient and bond length vary along the chain), and F_σ is the thermodynamic force exerted by the $(\sigma-1)$-th submolecule on the σ-th one. These can be explicitly written as

$$F_\sigma = \frac{3kT}{b_\sigma^2}(r_\sigma - r_{\sigma-1}) \qquad (\sigma = 2, 3, \ldots, N_t) \quad (2)$$

and

$$F_1 = F_{N_t+1} = 0 \qquad (3)$$

where k is the Boltzmann constant, T is the temperature, and b_σ is the bond length between the $(\sigma-1)$-th and σ-th submolecules. Let us now regard the parameter σ as a continuous variable. Then eq 1 and 2 are rewritten as

$$\zeta(\sigma)\frac{\partial}{\partial t}r(\sigma, t) = \frac{\partial}{\partial\sigma}F(\sigma, t) \qquad (4)$$

$$F(\sigma, t) = \frac{3kT}{b^2(\sigma)}\frac{\partial}{\partial\sigma}r(\sigma, t) \qquad (5)$$

Let the relaxation time be τ and put $r(\sigma, t) = \phi(\sigma)e^{-t/\tau}$; then from eq 4 and 5, we obtain

$$\frac{d}{d\sigma}\frac{3kT}{b^2}\frac{d\phi}{d\sigma} = -\frac{\zeta}{\tau}\phi \qquad (6)$$

In the above equation, we have simply written the vector $\boldsymbol{\phi}(\sigma)$ as $\phi(\sigma)$ because the three components of ϕ are equivalent and independent. The boundary condition at the chain end is also rewritten as

$$\frac{d\phi}{d\sigma} = 0 \qquad \text{(at the chain end)} \qquad (7)$$

In case that $b(\sigma)$ and $\zeta(\sigma)$ are constant along the chain, eq 6 reduces to a simple form

$$\frac{d^2\phi}{d\sigma^2} = -Q^2\phi \qquad (8)$$

where

$$Q^2 = \frac{1}{D\tau} \qquad (9)$$

$$D = \frac{3kT}{b^2\zeta} \qquad (10)$$

Therefore the normal mode, which we shall call the eigenfunction from now on, is readily obtained by considering the boundary condition 7.

$$\phi_p(\sigma) = \cos Q_p\sigma \qquad (11)$$

with

$$Q_p = \frac{p\pi}{N_t} \qquad (12)$$

and the eigen relaxation time is

$$\tau_p = \frac{\tau_{\max}}{p^2} \qquad (13)$$

with

$$\tau_{\max} = \frac{N_t^2}{D\pi^2} \qquad (14)$$

These results agree with those of the Rouse theory for long relaxation times.

Now let us turn to the problems of nonlinear polymers. In contrast to linear polymers, the submolecules of the nonlinear polymer cannot be designated by a single continuous parameter, so we must employ another appropriate way of designation. Let us define the "subchain" of the nonlinear polymer as the portion between the two branching points (or chain ends). We specify the submolecule by two parameters $\sigma = (\alpha, s)$, where α and s indicate respectively the subchain and the submolecule of the subchain. Then an argument similar to that for the linear chain can be made and eq 4—7 also hold, if we understand that $d\phi(\sigma)/d\sigma$ now means $d\phi(\alpha, s)/ds$.

The effect of the branching is taken into account by the boundary conditions. Let $\sigma_1, \sigma_2, \ldots, \sigma_n$ be the submolecules meeting at a branching point. Then we obtain the following two boundary conditions at the branching points. The first condition is that all the submolecules must be at the same point

$$\phi(\sigma_1) = \phi(\sigma_2) = \cdots = \phi(\sigma_n) \qquad (15)$$

The second is that the sum of the forces acting on the branching point must vanish

$$\pm\frac{1}{b^2}\frac{d\phi}{d\sigma}\bigg|_{\sigma=\sigma_1} \pm \frac{1}{b^2}\frac{d\phi}{d\sigma}\bigg|_{\sigma=\sigma_2} \pm \cdots \pm \frac{1}{b^2}\frac{d\phi}{d\sigma}\bigg|_{\sigma=\sigma_n} = 0 \qquad (16)$$

The sign in eq 16 should be chosen either plus or minus corresponding to the case that the branching point is the starting point ($s=0$), or the end point ($s=$ length of the subchain*).

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* In this paper, the term "length" means the number of the submolecules contained between the two points of the chain.

Equation 6 with the boundary conditions 7, 15, and 16 determines completely the eigenfunction $\phi_p(\sigma)$ and the corresponding eigen relaxation time τ_p. According to the normal mode analysis,[7] the intrinsic viscosity is given by

$$[\eta(\omega)] = \frac{N_A kT}{M\eta_0} \sum_p \frac{\tau_p/2}{1+i\omega\tau_p/2} \qquad (17)$$

where M is the molecular weight, N_A is Avogadro's number and η_0 is the viscosity of the solvent. Then the relaxation spectrum $h(\tau)$ defined by

$$[\eta(\omega)] = \int_0^\infty \frac{h(\tau)}{1+i\omega\tau} d\tau \qquad (18)$$

is given as

$$h(\tau) = \frac{N_A kT}{M\eta_0} \sum_p \frac{\tau_p}{2} \delta\left(\tau - \frac{\tau_p}{2}\right) \qquad (19)$$

However, to avoid unnecessary complications, we introduce a simplified function

$$H(\tau) = \tau \sum_p \delta(\tau - \tau_p) \qquad (20)$$

and call this also the relaxation spectrum.

In case that $b(\sigma)$ and $\zeta(\sigma)$ are constant along the chain, eq 8 gives the eigenfunction

$$\phi(\alpha, s) = A_\alpha \cos Qs + B_\alpha \sin Qs \qquad (21)$$

Substituting this into the boundary conditions 7, 15, and 16, we obtain a homogeneous linear equations for the A_α and B_α's. By setting the determinant of the coefficient matrix equal to zero, we obtain an eigenvalue equation for Q. This equation is a transcendental equation consisting of $\cos QN_\alpha$ and $\sin QN_\alpha$'s. In the following section we will attempt to solve the eigenvalue equations. Here we will show that the relaxation spectrum $H(\tau)$ takes a universal form, irrespective of the type of branching, in the short time region.

Let us denote the density of the eigenvalues of Q by $\Omega(Q)$

$$\Omega(Q) = \sum_p \delta(Q - Q_p) \qquad (22)$$

where the Q_p's are the solutions of the above mentioned eigenvalue equation. By using $\Omega(Q)$, $H(\tau)$ is expressed as

$$H(\tau) = \tau \left[\Omega(Q) \frac{dQ}{d\tau} \right]_{Q=(D\tau)^{-1/2}}$$
$$= \frac{[\Omega(Q)]_{Q=(D\tau)^{-1/2}}}{2(D\tau)^{1/2}} \qquad (23)$$

Since the eigenvalue equation contains only $\cos QN_\alpha$ and $\sin QN_\alpha$'s, the eigenvalues Q_p's are distributed almost periodically. Therefore $\Omega(Q)$ is also an almost periodic function, the period of which can be approximated by $2\pi/N_s$, where N_s is the characteristic length of the subchain. Then from eq 23 we find that $H(\tau)$ is also an oscillatory function. As τ approaches zero, the oscillation period decreases according to the law

$$\text{the oscillation period} = \left| \frac{d\tau}{dQ} \right| \cdot \frac{2\pi}{N_s} \propto \tau^{3/2}$$

Therefore in the short time region, we can replace the rapidly oscillating function $H(\tau)$ by the smooth function

$$H(\tau) = \frac{\overline{\Omega(Q)}}{2(D\tau)^{1/2}} \qquad (\tau \ll N_s^2/D) \qquad (24)$$

where $\overline{\Omega(Q)}$ is the averaged function of $\Omega(Q)$ in the interval of $2\pi/N_s$, which is estimated from the following consideration.

Let us consider the following three types of boundary conditions for ϕ:

(a) The first are the pertinent ones given by eq 7, 15, and 16.

(b) The second are those for the free chain end

$$\frac{d\phi}{d\sigma} = 0 \qquad \text{(at the branching points and chain ends)} \qquad (25)$$

(c) The third are for the fixed chain end

$$\phi = 0 \qquad \text{(at the branching points and chain ends)} \qquad (26)$$

We denote the set of the eigenvalues determined from the above boundary conditions by $\{\tau_p^{(a)}\}$, $\{\tau_p^{(b)}\}$, and $\{\tau_p^{(c)}\}$, respectively. We may assume that these are ordered as

$$\tau_1^{(a)} \geq \tau_2^{(a)} \geq \cdots, \qquad \tau_1^{(b)} \geq \tau_2^{(b)} \geq \cdots,$$
$$\tau_1^{(c)} \geq \tau_2^{(c)} \geq \cdots$$

Then the following inequality can be proved by using the variational principle associated with eigenvalue problems.[8]

$$\tau_p^{(c)} \leq \tau_p^{(a)} \leq \tau_p^{(b)} \qquad (p=1, 2, 3, \ldots) \qquad (27)$$

This inequality can be rewritten into a more convenient form. Let $H_a(\tau)$, $H_b(\tau)$, and $H_c(\tau)$ be the relaxation spectra obtained from these

eigen relaxation times. Then eq 27 is equivalent to the following inequality, which holds for any time τ.

$$\int_{\tau}^{\infty} H_{\mathrm{c}}(\tau')\,\mathrm{d}\ln\tau' \leq \int_{\tau}^{\infty} H_{\mathrm{a}}(\tau')\,\mathrm{d}\ln\tau'$$

$$\leq \int_{\tau}^{\infty} H_{\mathrm{b}}(\tau')\,\mathrm{d}\ln\tau' \qquad (28)$$

because

$$\int_{\tau}^{\infty} H(\tau')\,\mathrm{d}\ln\tau' = \int_{\tau}^{\infty} \sum_{p}\delta(\tau'-\tau_{p})\,\mathrm{d}\tau'$$

$$=\text{number of eigenvalues}$$

larger than τ .

The relaxation spectra $H_{\mathrm{b}}(\tau)$ and $H_{\mathrm{c}}(\tau)$ are easily obtained because they are the sums of those for the independent subchains. Since

$$\overline{\Omega_{\mathrm{b}}(Q)}=\overline{\Omega_{\mathrm{c}}(Q)}= \sum_{\alpha}\frac{N_{\alpha}}{\pi}=\frac{N_{\mathrm{t}}}{\pi}$$

we obtain

$$H_{\mathrm{b}}(\tau)=H_{\mathrm{c}}(\tau)=\frac{N_{\mathrm{t}}}{2\pi(D\tau)^{1/2}} \qquad (29)$$

where N_{t} is the total length of the branched polymer.

Therefore by comparing eq 24, 28, and 29, we reach the final result:

$$H(\tau)=\frac{N_{\mathrm{t}}}{2\pi(D\tau)^{1/2}} \qquad (\tau \ll N_{\mathrm{s}}^{2}/D) \qquad (30)$$

This property will be used in the following section.

Before ending this section, we show that our formulation is equivalent to Ham's. To prove this, we consider the function defined by

$$f(\sigma)=\frac{\mathrm{d}\phi}{\mathrm{d}\sigma} \qquad (31)$$

Then from eq 8, $f(\sigma)$ satisfies the differential equation

$$\frac{\mathrm{d}^{2}f}{\mathrm{d}\sigma^{2}}=-Q^{2}f \qquad (32)$$

together with the following boundary conditions; at the chain end

$$f(\sigma)=0 \qquad (33)$$

and at the branching point

$$\left.\frac{\mathrm{d}f}{\mathrm{d}\sigma}\right|_{\sigma=\sigma_{1}} = \left.\frac{\mathrm{d}f}{\mathrm{d}\sigma}\right|_{\sigma=\sigma_{2}} = \cdots = \left.\frac{\mathrm{d}f}{\mathrm{d}\sigma}\right|_{\sigma=\sigma_{n}} \qquad (34)$$

$$\pm f(\sigma_{1})\pm f(\sigma_{2})\pm \cdots \pm f(\sigma_{n})=0 \qquad (35)$$

Equations 33—35 are derived from eq 7, 15, and 16 respectively. Equations 32—35 are just the same as those given by Ham.

CALCULATION OF THE RELAXATION SPECTRUM

In this section the relaxation spectrum is calculated for some typical branched polymers.

Star Molecule

First we consider the star molecule shown in Figure 1. The relaxation spectrum of this polymer has been calculated by many authors,[1,5,9] but we consider it here as the simplest application of our method. Let $N_1, N_2, \ldots, N_f$ be the lengths of the subchains. We choose the chain end as the starting point of each subchain. Then the solution of eq 8 satisfying the boundary condition at the chain end is written as

$$\phi(\alpha,\,s)=A_{\alpha}\cos Qs \qquad (35)$$

The boundary conditions at the branching point give the equations

$$\left.\begin{array}{l} A_1\cos QN_1=A_2\cos QN_2= \cdots =A_f\cos QN_f \\ A_1\sin QN_1+A_2\sin QN_2+ \cdots +A_f\sin QN_f=0 \end{array}\right\} \qquad (36)$$

By eliminating A_{α}'s, we obtain

$$\sum_{\alpha=1}^{f}\tan QN_{\alpha}=0 \qquad (37)$$

This equation can be solved graphically. The solution $Q=0$ corresponds to the uniform translation mode. The smallest positive solution $Q_{\min}$, which gives the longest relaxation time, is estimated as follows. Let N_1 and N_2 be the lengths of the longest two subchains. By considering the graph of the left hand side of eq
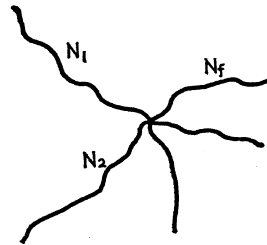

Figure 1. The star molecule.

37, the following inequality can readily be verified:

$$\frac{\pi}{2N_1} < Q_{\min} < \mathrm{Min}\left[\frac{\pi}{N_1}, \frac{\pi}{2N_2}\right]$$

We also find that when $N_1 \gg N_2$, $Q_{\min}$ approaches π/N_1, and when $N_1 \simeq N_2$, $Q_{\min}$ becomes approximately $\pi/2N_1$. From these observations we evaluate $Q_{\min}$ by $\pi/(N_1+N_2)$. Therefore it is concluded that the longest relaxation time of the star molecule is nearly equal to that of the linear chain consisting of the longest two subchains of the star molecule. Note that this longest relaxation time is not so much longer than that of each subchain. Then it is also concluded that the relaxation spectrum of the star molecule is given by eq 30 for almost the whole time region.

Caylay Tree Molecule

Next let us consider the molecule shown in Figure 2. We call a molecule of this type Caylay tree molecule. This molecule has a center denoted by 0 in Figure 2, which we call the branching point of "zero rank." The center is connected with f subchains of "first rank" and each first rank subchain is connected with f "second rank" subchains and so on. When all the subchains are of equal length, the eigenvalues are obtained by the transfer matrix method.

For convenience, we indicate the subchain by two parameters $\alpha = (k, a)$, where k and a indicate respectively the rank and the subchain belonging to the same rank, (hence $1 \leq a \leq f^k$). The solution of eq 8 in the (k, a)-th subchain in written as

$$\phi(k, a, s) = A_{k,a} \cos Qs + B_{k,a} \sin Qs \quad (38)$$

Let n be the rank of the subchain containing the chain end. Then from eq 7, the boundary condition at the chain ends is
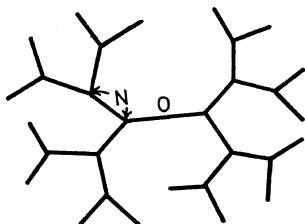

Figure 2. The Cayley tree molecule.

$$B_{n,a} = 0 \quad (a = 1, 2, \ldots, f^n) \quad (39)$$

At the branching point of the $(n-1, 1)$-th subchain, the boundary conditions give the equations

$$A_{n-1,1} = A_{n,1} \cos QN$$
$$= A_{n,2} \cos QN = \cdots = A_{n,f} \cos QN \quad (40)$$

$$B_{n-1,1} = -(A_{n,1} + A_{n,2} + \cdots + A_{n,f}) \sin QN \quad (41)$$

where N is the length of the subchain. Similar equations to the above ones should be written for the branching point of the $(n-1, 2)$, $(n-1, 3)$, $\ldots$ $(n-1, f^{n-1})$-th subchains.

Here different analyses are necessary according to the following two cases:

(i) The case that $A_{n-1,1} \neq 0$. In this case, from eq 40 and 41, we obtain

$$A_{n,1} = A_{n,2} = \cdots = A_{n,f} \quad (42)$$

$$A_{n-1,1} = A_{n,1} \cos QN \quad (43)$$

$$B_{n-1,1} = -f A_{n,1} \sin QN \quad (44)$$

We call this the symmetric case.

(ii) The case that $A_{n-1,1} = 0$. In this case we find

$$\cos QN = 0 \quad (45)$$

and $A_{n,i}$'s ($i = 1, 2, \ldots, f^n$) are independent of each other. We call this the nonsymmetric case.

In the nonsymmetric case, we obtain an eigenvalue equation without considering any other boundary conditions, whereas in the symmetric case we must take into account the boundary conditions at the lower rank branching points. To continue our analysis in the symmetric case, we consider the boundary conditions at the branching point of the $(n-2, 1)$-th subchain. Then the same circumstance arises: We encounter the nonsymmetric case and the symmetric one. In the former case, the eigenvalue equation is obtained and no further analysis is necessary. But in the latter case we must again consider the boundary conditions at the branching point of the $(n-3, 1)$-th subchain and so forth.

Therefore let us consider the general case where the symmetric case occurs at the $(n-1)$, $(n-2)$, $\ldots$, $(p+1)$-th rank branching points. Then we can prove by mathematical induction that all A's and B's of the same rank are equal.

$$A_{k,1}=A_{k,2}=\cdots=A_{k,f^k} \tag{46}$$

$$B_{k,1}=B_{k,2}=\cdots=B_{k,f^k} \tag{47}$$

$$(k=n,\ n-1,\ \ldots,p+2)$$

Further it can be proved that these values are proportional to $A_{n,1}$. To show this, we consider the boundary conditions at the k-th rank branching point, which are written as

$$A_{k,1}=\cos QNA_{k+1,1}+\sin QNB_{k+1,1} \tag{48}$$

$$B_{k,1}=-f\sin QNA_{k+1,1}+f\cos QNB_{k+1,1} \tag{49}$$

where we have used the relations 46 and 47. Equations 48 and 49 can be conveniently written in a matrix form as

$$\begin{pmatrix} A_{k,1} \\ B_{k,1} \end{pmatrix}=\mathbf{T}\begin{pmatrix} A_{k+1,1} \\ B_{k+1,1} \end{pmatrix}=\mathbf{T}^{n-k}\begin{pmatrix} A_{n,1} \\ 0 \end{pmatrix} \tag{50}$$

where $\mathbf{T}$ is a matrix defined by

$$\mathbf{T}=\begin{pmatrix} \cos QN, & \sin QN \\ -f\sin QN, & f\cos QN \end{pmatrix} \tag{51}$$

The boundary conditions at the p-th rank branching points are

$$A_{p,1}=\cos QNA_{p+1,1}+\sin QNB_{p+1,1}=\cdots$$
$$=\cos QNA_{p+1,f}+\sin QNB_{p+1,f} \tag{52}$$

$$B_{p,1}=-(A_{p+1,1}+\cdots+A_{p+1,f})\sin QN$$
$$-(B_{p+1,1}+\cdots+B_{p+1,f})\cos QN \tag{53}$$

If the nonsymmetric case occurs at this point, we have $A_{p,1}=0$. This condition can be written as

$$A_{p,1}=\cos QNA_{p+1,1}+\sin QNB_{p+1,1}$$
$$=\mathbf{T}_{1,1}(\mathbf{T}^{n-p-1})_{1,1}A_{n,1}+\mathbf{T}_{1,2}(\mathbf{T}^{n-p-1})_{2,1}A_{n,1}$$
$$=(\mathbf{T}^{n-p})_{1,1}A_{n,1}=0 \tag{54}$$

hence

$$(\mathbf{T}^{n-p})_{1,1}=0 \tag{55}$$

The eigenvalues determined by this equation are f^p-fold degenerate because there are f^p degrees of freedom in the choice of the coefficients A_α and B_α's. On the other hand, if the symmetric case occurs, we find from eq 52 and 53 that

$$A_{p+1,1}=A_{p+1,2}=\cdots=A_{p+1,f^{p+1}} \tag{56}$$

$$B_{p+1,1}=B_{p+1,2}=\cdots=B_{p+1,f^{p+1}} \tag{57}$$

This argument provides a proof of eq 46 and 47.

Thus we find that the eigenvalue equation is given by eq 55 if the first nonsymmetric case

occurs at the p-th rank branching point. If the symmetric case occurs at all the branching points, the eigenvalue equation is obtained from the boundary condition at the center. This condition is written as $B_{0,1}=0$; hence from eq 53, we obtain

$$(\mathbf{T}^n)_{2,1}=0 \tag{58}$$

The above eigenvalue eq 55 and 58 are explicitly written in terms of Q, by diagonalizing the matrix $\mathbf{T}$. Let λ_1 and λ_2 be the eigenvalues of $\mathbf{T}$. From eq 51, we obtain

$$\left.\begin{aligned} \lambda_1&=[(1+f)+\{(1+f)^2\cos^2 QN-4f\}^{1/2}]/2 \\ \lambda_2&=[(1+f)-\{(1+f)^2\cos^2 QN-4f\}^{1/2}]/2 \end{aligned}\right\} \tag{59}$$

After some calculations, we find that eq 55 and 58 reduce respectively to

$$\left(\frac{\lambda_1}{\lambda_2}\right)^{n-p}=\frac{\lambda_1-\sin QN}{\lambda_2-\cos QN} \tag{60}$$

$$\left(\frac{\lambda_1}{\lambda_2}\right)^n=1 \tag{61}$$

Since we are interested only in small eigenvalues, we calculate the solution by expanding eq 60 and 61 in terms of Q. From eq 59, we obtain

$$\lambda_1=f\left(1+\frac{1}{2}\frac{f+1}{f-1}(NQ)^2\right) \tag{62}$$

$$\lambda_2=1+\frac{1}{2}\frac{f+1}{f-1}(NQ)^2 \tag{63}$$

where we have assumed $NQ\ll 1$. Equation 61 does not have such a solution, but eq 60 does. Substituting eq 62 and 63 into eq 60, we obtain

$$Q_p{}^2=\frac{(f-1)^2}{N^2 f^{n-p+1}} \tag{64}$$

$$\tau_p=\tau_{\max}\cdot f^{-p} \tag{65}$$

where

$$\tau_{\max}=\frac{N^2 f^{n+1}}{D(f-1)^2} \tag{66}$$

Let us now consider the relaxation spectrum. For the long time region, the eigen relaxation times are given by eq 65, which is f^p-fold degenerate. Then the relaxation spectrum is calculated as

$$H(\tau)=f^p\tau\left|\frac{\mathrm{d}p}{\mathrm{d}\tau_p}\right|_{\tau_p=\tau}$$
$$=\frac{f}{\ln f}\frac{\tau_{\max}}{\tau}\qquad\left(\tau\gg\frac{N^2}{D}\right) \tag{67}$$
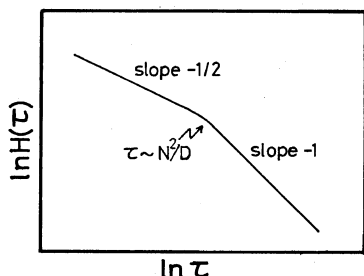
Figure 3. The relaxation spectrum of the Cayley tree molecule.

On the other and for $\tau \ll N^2/D$, the relaxation spectrum is given by eq 30, where $N_t = N(f+f^2+\cdots+f^n)=[(f^{n+1}-f)/(f-1)]N$, then

$$H(\tau)=\frac{(f^{n+1}-f)}{2\pi(f-1)}\frac{1}{(D\tau)^{1/2}} \quad (68)$$

Note that eq 67 and 68 give almost the same value at $\tau \sim N^2/D$. In Figure 3 the relaxation spectrum is illustrated schematically.

Comb Molecule

As the final example, we discuss the comb molecule shown in Figure 4. This molecule consists of one main chain and several side chains. For the sake of convenience, we do not divide the main chain into subchains. The submolecule in the main chain is denoted by $\sigma=(m, s)$, where s is the length measured from the chain end of the main chain, and m is the suffix to denote the main chain.

Let (m, s_α) be the branching point where the α-th side chain branches. The submolecule in the side chain is designated by (α, s), where s
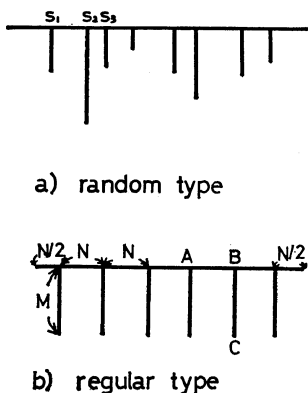

a) random type

b) regular type

Figure 4. The comb molecule.

is the length measured from the chain end of the side chain. The solution of eq 8 in the α-th side chain can be written as

$$\phi(\alpha, s)=A_\alpha \cos Qs \quad (69)$$

Then the boundary conditions at the branching point give

$$\phi(m, s_\alpha)=A_\alpha \cos QN_\alpha \quad (70)$$

$$\frac{d\phi(m, s)}{ds}\bigg|_{s=s_\alpha+0} - \frac{d\phi(m, s)}{ds}\bigg|_{s=s_\alpha-0}$$
$$=-QA_\alpha \sin QN_\alpha \quad (71)$$

where N_α is the length of the α-th side chain. By eliminating A_α, we obtain

$$\frac{d\phi}{ds}\bigg|_{s=s_\alpha+0} - \frac{d\phi}{ds}\bigg|_{s=s_\alpha-0} = -Q \tan QN_\alpha\phi(m, s_\alpha) \quad (72)$$

Therefore $d\phi/ds$ is discontinuous at the branching point. This discontinuity is included in the differential eq 6 by adding a "potential term" of delta function form:

$$\left[Q^2+\frac{d^2}{ds^2}+\sum_\alpha Q \tan QN_\alpha\delta(s-s_\alpha)\right]\phi(m, s)=0 \quad (73)$$

Thus our problem is reduced to the eigenvalue problem of the electron gas under the effect of the random potential of delta functions, which is well known as the random Kronig-Penny model. This problem is in general a difficult one and is now being widely investigated.[10] Here we are interested only in the long wave length mode and in that case the following simple treatment is possible.

For the long wavelength mode, where the wavelength is much longer than the interval between the neighbouring branching points, the local structure of the random potential is not important, and the random potential is approximated by an averaged potential $\bar{V}$ defined by

$$\bar{V}=\frac{1}{N_m}\int_0^{N_m} ds \sum_\alpha Q \tan QN_\alpha\delta(s-s_\alpha)$$

$$=\frac{1}{N_m}\sum_\alpha Q \tan QN_\alpha \cong \frac{Q^2}{N_m}\sum_\alpha N_\alpha \quad (74)$$

where N_m is the length of the main chain. The above approximation will be good if the length of the side chain is short enough compared with that of the main chain. Substituting eq 74 into eq 73, we obtain

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$$\left[Q^2\left(1+\frac{\sum N_\alpha}{N_m}\right)+\frac{d^2}{ds^2}\right]\phi=0 \qquad (75)$$

The eigenvalue is then readily obtained. The results is

$$\tau_p=\frac{\tau_{\max}}{p^2} \qquad (76)$$

with

$$\tau_{\max}=N_m(N_m+\sum_\alpha N_\alpha)/\pi^2 D \qquad (77)$$

This result can be intuitively understood as follows. As is shown by Rouse,[12] the choice of the submolecule does not affect the long eigen relaxation times. So we may divide the comb molecule into two submolecules. Then the friction coefficient of each submolecule is $\zeta(N_m+\sum N_\alpha)/2$, and the bond length between them is $N_m b^2$. Then the longest relaxation time can be estimated as

$$\tau_{\max}\sim\frac{\zeta(N_m+\sum N_\alpha)}{2}\cdot\frac{N_m b^2}{3kT}=\frac{N_m(N_m+\sum N_\alpha)}{2D} \qquad (78)$$

This agrees with eq 77 except for the numerical factor.

The relaxation spectrum is now easily obtained. Let N_s be the characteristic length of the side chain. For $\tau\gg N_s^2/D$, the relaxation spectrum is obtained from eq 76:

$$H(\tau)=\tau\left|\frac{dp}{d\tau_p}\right|_{\tau_p=\tau}=\frac{1}{2}\left[\frac{N_m(N_m+\sum N_\alpha)}{\pi^2 D\tau}\right]^{1/2} \qquad (79)$$

On the other hand, for $\tau\ll N_s^2/D$, $H(\tau)$ is given by the general formula 30

$$H(\tau)=\frac{N_t}{2(\pi^2 D\tau)^{1/2}}=\frac{N_m+\sum N_\alpha}{2(\pi^2 D\tau)^{1/2}} \qquad (80)$$

Therefore, it is seen that the relaxation spectrum suffers a rather abrupt change at $\tau\sim N_s^2/D$. Note that the relaxation spectrum cannot have a hump for the comb molecule. In Figure 5, the relaxation spectrum is schematically illustrated.

If the side chains branch regularly, an exact treatment is possible by the use of Bloch's theorem. Let n be the number of the branching points. We denote the length of the side chain by M and the interval between the neighbouring branching points by N. According to Bloch's theorem, the eigenfunction in the main chain can be written as follows:
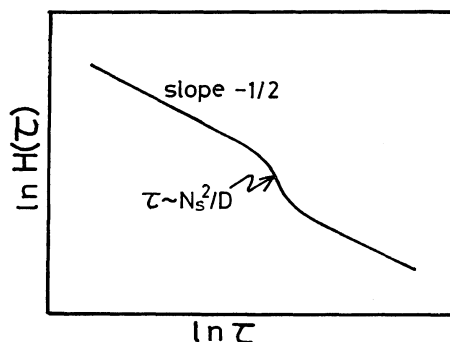
Figure 5. The relaxation spectrum of the comb molecule.

$$\phi(m,\ s)=f(s)e^{iK_p s} \qquad (81)$$

where

$$K_p=\frac{\pi p}{nN} \qquad (p=0,\ 1,\ 2,\ \ldots,\ (n-1)) \qquad (82)$$

and the function $f(s)$ is periodic

$$f(s+N)=f(s) \qquad (83)$$

From eq 8 and 81, $f(s)$ is given as

$$f(s)=f_1 e^{i(Q-K_p)s}+f_2 e^{-i(Q+K_p)s} \qquad (84)$$

Then from eq 70, 71, and 83, we obtain

$$f_1+f_2=f_1 e^{i(Q-K_p)N}+f_2 e^{-i(Q+K_p)N}=A\cos MQ \qquad (85)$$

$$f_1-f_2=iA\sin QM+f_1 e^{i(Q-K_p)N}-f_2 e^{-i(Q+K_p)N} \qquad (86)$$

By eliminating f_1, f_2, and A, we obtain the following eigenvalue equation:

$$\cos K_p N=\cos QN-\frac{1}{2}\sin QN\tan QM \qquad (87)$$

To check the calculation, let us put $M=0$, then eq 87 is readily solved, giving

$$Q_{p,k}=K_p\pm\frac{2k\pi}{N}=\frac{(2pn\pm k)\pi}{nN} \qquad (k=0,\ 1,\ 2,\ \ldots) \qquad (88)$$

The result agrees with that of the linear chain.

For the case $M\neq 0$, the long relaxation times are obtained by expanding both sides of eq 87 with respect to Q and K. The result is

$$Q_p=\frac{NK_p}{\{N(N+M)\}^{1/2}}=\frac{\pi p}{\{N(N+M)n^2\}^{1/2}} \qquad (89)$$

$$\tau_p=\frac{\tau_{\max}}{p^2} \qquad (90)$$

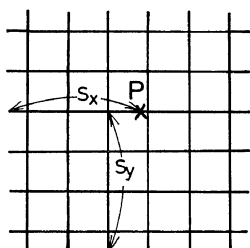$$\tau_{\max}=n^2 N(N+M)/\pi^2 D \qquad (91)$$

Figure 6. The two-dimensional network of polymer chains. A submolecule P is designated by (s_x, s_y) shown in the figure.

which agrees with the general one given by eq 77, where $N_m = nN$ and $\sum N_\alpha = nM$.

The above treatment can readily be extended to the case of the regular network of the polymer chain. Here we shall briefly discuss the relaxation spectrum of the network.

As an example of the two dimensional network, we consider a "network of square lattices," obtained by connecting the lattice points of the square lattice by subchains (see Figure 6). Let N be the "lattice constant" of the network. According to Bloch's theorem, the eigenfunction of the network is written as follows:

$$\phi(s_x, s_y) = f(s_x, s_y) e^{i(K_x s_x + K_y s_y)} \qquad (92)$$

$$K_x = \frac{\pi p_x}{nN} \qquad K_y = \frac{\pi p_y}{nN}$$

$$(p_x, p_y = 1, 2, \ldots, (n-1)) \qquad (93)$$

where (s_x, s_y) is the (x, y) coordinate in the network space. For the long wavelength mode $(Q \ll \pi/N)$, $f(s_x, s_y)$ can be regarded as almost constant. Therefore the eigenvalues are determined by the lattice momenta, K_x and K_y

$$Q^2 \cong K_x{}^2 + K_y{}^2 = \frac{\pi^2}{(nN)^2}(p_x{}^2 + p_y{}^2) \qquad (94)$$

Then the state density $\Omega(Q)$ is given by

$$\Omega(Q) \cong \frac{(nN)^2}{2\pi} \cdot Q \qquad (95)$$

Therefore from eq 23, we obtain

$$H(\tau) = \frac{(nN)^2}{2\pi D\tau} \qquad (96)$$

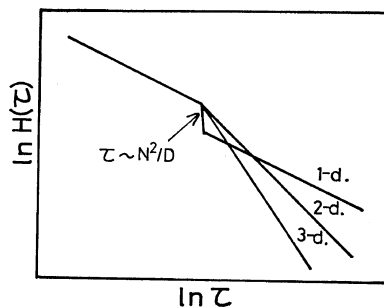On the other hand, for $Q \gg \pi/N$, $H(\tau)$ is given by eq 27

Figure 7. The relaxation spectra of the regular network of the polymer chain: 1-d, regular comb molecule; 2-d, two-dimensional regular network; and 3-d, three-dimensional regular network.

$$H(\tau) = \frac{n^2 N}{2\pi(D\tau)^{1/2}} \qquad (97)$$

Note that the right-hand-sides of eq 96 and 97 are equal at $\tau \sim N^2/D$. Therefore the relaxation spectrum is continuous at $\tau \sim N^2/D$.

In the case of a three-dimensional network, the relaxation spectrum is also calculated in a way similar to that given above. The result is

$$H(\tau) \cong \frac{(nN)^3}{2\pi(D\tau)^{3/2}} \qquad (\tau \gg N^2/D) \qquad (98)$$

$$H(\tau) \cong \frac{n^3 N}{2\pi(D\tau)^{1/2}} \qquad (\tau \ll N^2/D) \qquad (99)$$

These relaxation spectra are shown in Figure 7.

It is seen that in all cases, the relaxation spectrum of the branched polymer has no hump. Therefore we may conclude that the characteristic shape of the relaxation spectrum cannot be explained on the basis of the permanent cross-linkage model.

SUM RULES

In the previous section, we calculated the longest relaxation time by solving the eigenvalue problem. We can estimate the longest relaxation time much more simply as

$$\tau_{max} \sim \frac{N_t}{Db^2} \langle S^2 \rangle \qquad (100)$$

where $\langle S^2 \rangle$ is the mean square radius of gyration.

The foundation of eq 100 is the following sum rule.

$$\sum_p \tau_p = \frac{N_t \zeta}{3kT} \langle S^2 \rangle \qquad (101)$$

In this section we shall discuss sum rules of this type.

A physical proof of eq 100 was given by Chompff,[5] based upon the assumption that the steady state intrinsic viscosity calculated by the Rouse theory[12] should be equal to that given by Debye.[14] Mathematical proof was also given by Ham for molecules which contain no loops. Here we shall give a complete proof of eq 101 in a generalized form. The polymer we consider here may contain loops and the friction coefficient and the bond length may vary along the chain.

The sum rule which we shall prove is

$$\sum_p \tau_p = \frac{\xi}{3kT} \langle S^2 \rangle_\zeta \qquad (102)$$

where ξ is the translational friction constant of the polymer

$$\xi = \int d\sigma \zeta(\sigma) \qquad (103)$$

and $\langle S^2 \rangle_\zeta$ is the mean square radius of gyration, the weighting factor of which is not the mass, but the friction coefficient of the submolecules

$$\langle S^2 \rangle_\zeta = \frac{1}{\xi} \int d\sigma \zeta(\sigma) \langle (r(\sigma) - r_\xi)^2 \rangle \qquad (104)$$

$$r_\xi = \frac{1}{\xi} \int d\sigma \zeta(\sigma) r(\sigma) \qquad (105)$$

In the above equations, the integral $\int d\sigma$ means the sum of the integrals contributed from each subchain, that is

$$\int d\sigma \zeta(\sigma) = \sum_\alpha \int_0^{N\alpha} ds \zeta(\alpha, s) \qquad (106)$$

Before going into the proof of eq 102, we shall first prove an important relation. Consider a static correlation function of the positions of the submolecules defined by

$$\psi(\sigma; \sigma_1, \sigma_2) = \langle (r(\sigma) - r(\sigma_2)) \cdot (r(\sigma_1) - r(\sigma_2)) \rangle \qquad (107)$$

then it can be proved that ψ satisfies the following differential equation

$$\frac{\partial}{\partial \sigma} \frac{1}{b^2} \frac{\partial}{\partial \sigma} \psi(\sigma; \sigma_1, \sigma_2) = -\delta(\sigma - \sigma_1) + \delta(\sigma - \sigma_2) \qquad (108)$$

together with the boundary conditions;
at the chain end

$$\frac{\partial \psi}{\partial \sigma} = 0 \qquad (109)$$

at the branching point where the submolecules $\sigma_b, \sigma_b', \ldots$ meet

$$\psi(\sigma_b) = \psi(\sigma_b') = \cdots \qquad (110)$$

$$\pm \frac{1}{b^2} \frac{\partial \psi}{\partial \sigma}\bigg|_{\sigma=\sigma_b} \pm \frac{1}{b^2} \frac{\partial \psi}{\partial \sigma}\bigg|_{\sigma=\sigma_b'} \pm \cdots = 0 \qquad (111)$$

and at the point σ_2

$$\psi(\sigma_2; \sigma_1, \sigma_2) = 0 \qquad (112)$$

The sign in eq 111 must be chosen in the same way as in eq 16. Note that the boundary conditions for $\psi(\sigma)$ are just the same as for $\phi(\sigma)$, except eq 112.

The above equations are proved by using the fluctuation theorem. Since the correlation function $\psi(\sigma; \sigma_1, \sigma_2)$ is invariant under the uniform translation of the chain, we can assume without loss of generality that the position of the submolecule σ_2 is fixed. Let us consider a weak force F, directing along the z-axis and acting on the submolecule σ_1. In the absence of an external force, the mean position of the submolecule is equal to $r(\sigma_2)$, but the force displaces the submolecule to a new position. The displacement of the submolecule, which we denote by $u(\sigma)$, is proportional to F and can be written

$$u(\sigma) = \chi(\sigma; \sigma_1, \sigma_2) F \qquad (113)$$

According to the fluctuation theorem, $\chi(\sigma; \sigma_1, \sigma_2)$ is related to the static correlation function

$$\chi(\sigma; \sigma_1, \sigma_2)$$
$$= \frac{1}{kT} \langle (r_z(\sigma) - \langle r_z(\sigma) \rangle) \cdot (r_z(\sigma_1) - \langle r_z(\sigma_1) \rangle) \rangle$$
$$= \frac{1}{3kT} \langle (r(\sigma) - r(\sigma_2)) \cdot (r(\sigma_1) - r(\sigma_2)) \rangle \qquad (114)$$

where we have used the fact that all of the three components of the Cartesian coordinates are equivalent.

To determine $\chi(\sigma)$, we consider the force balance equation. We must note that the external force is acting not only on σ_2 but also on σ_1 to keep the position of σ_2 fixed. The force acting on σ_2 is equal to $-F$, and the

tensile force of the chain is given by $(3kT/b^2)(\partial u/\partial \sigma)$. Therefore the force balance equation is written as

$$\frac{\partial}{\partial \sigma}\frac{3kT}{b^2}\frac{\partial u}{\partial \sigma}=-F\delta(\sigma-\sigma_1)+F\delta(\sigma-\sigma_2) \quad (116)$$

By using eq 113 and 114, we obtain eq 108. Further, repeating the same argument as discussed in connection with the equation of motion, we can easily verify the boundary conditions 109—111. The condition 112 is self-evident.

It is of interest to consider the above results in comparison with electrical network theory. Consider an electrical network whose topological structure is equal to the pertinent branched polymer, and whose network element is a resistance equal to the square of the effective bond-length of the corresponding submolecule. Then eq 108 is nothing but the equations satisfied by the electrical potential of the network, when there exists a unit source of electrical current at σ_1 and a unit absorption sink of current at σ_2. The boundary condition 109 means that the electrical current vanishes at the chain end. Equation 110 is the continuity condition of the electrical potential at the branching point and eq 111 is the conservation condition of the electrical current. Thus it is proved that $\psi(\sigma; \sigma_1, \sigma_2)$ is equal to the electrical potential at point σ. In particular, it is proved that the mean square of the separation between the two submolecules is equal to the driving point impedance, because $\langle(r(\sigma_1)-r(\sigma_2))^2\rangle=\psi(\sigma_1; \sigma_1, \sigma_2)$ is equal to the potential difference between the two source points of the electrical current.

Now let us prove the sum rule. Following Ham,[1] we shall make use of the Green's function. Let $\{\phi_p\}$ be the orthonormal set of the eigenfunctions of eq 6. The orthonormal conditions are written as

$$\int d\sigma \zeta(\sigma)\phi_p{}^*(\sigma)\phi_{p'}(\sigma)=\delta_{p,p'} \quad (117)$$

$$\sum_p \zeta(\sigma)\phi_p{}^*(\sigma)\phi_p(\sigma')=\delta(\sigma-\sigma') \quad (118)$$

Among these eigenfunctions, we must pay special attention to the uniform translational mode $\phi_0(\sigma)$ because its relaxation time is infinite, corresponding to the vanishing eigenvalue. From the normalization condition we obtain

$$\phi_0(\sigma)=\xi^{-1/2} \quad (119)$$

Let us now introduce a Green's function defined by

$$g(\sigma, \sigma')=\sum_{p\neq 0} \tau_p\phi_p{}^*(\sigma)\phi_p(\sigma')\zeta(\sigma') \quad (120)$$

From eq 117 and 120, we obtain

$$\sum_p \tau_p=\int d\sigma g(\sigma, \sigma) \quad (121)$$

From eq 6, it is found that $g(\sigma, \sigma')$ satisfies the differential equation

$$\frac{\partial}{\partial \sigma}\frac{3kT}{b^2}\frac{\partial}{\partial \sigma}g(\sigma, \sigma')=-\sum_{p\neq 0}\zeta(\sigma)\zeta(\sigma')\phi_p{}^*(\sigma)\phi_p(\sigma')$$

$$=-\zeta(\sigma')\left(\delta(\sigma-\sigma')-\frac{\zeta(\sigma)}{\xi}\right) \quad (122)$$

together with the boundary conditions of eq 7, 15, and 16.

Let us first prove that $g(\sigma, \sigma')$ is related to the correlation function $\langle(r(\sigma)-r_\xi)\cdot(r(\sigma')-r_\xi)\rangle$ through the equation

$$g(\sigma, \sigma')=\frac{\zeta(\sigma)}{3kT}C(\sigma, \sigma') \quad (123)$$

where we have abbreviated $\langle(r(\sigma)-r_\xi)\cdot(r(\sigma')-r_\xi)\rangle$ by $C(\sigma, \sigma')$.

To prove the above relation, we show that $C(\sigma, \sigma')$ satisfies the same equations as does $g(\sigma, \sigma')$. From eq 105 and 107, we have

$$C(\sigma, \sigma')=\frac{1}{\xi^2}\int d\sigma_1 d\sigma_2$$

$$\times \langle(r(\sigma)-r(\sigma_1))\cdot(r(\sigma')-r(\sigma_2))\rangle\zeta(\sigma_1)\zeta(\sigma_2)$$

$$=\frac{1}{\xi^2}\int d\sigma_1 d\sigma_2$$

$$\times (\psi(\sigma, \sigma', \sigma_1)-\psi(\sigma; \sigma_2, \sigma_1))\zeta(\sigma_1)\zeta(\sigma_2) \quad (124)$$

Then by using eq 104 and 108, we obtain

$$\frac{\partial}{\partial \sigma}\frac{1}{b^2}\frac{\partial}{\partial \sigma}C(\sigma, \sigma')$$

$$=\frac{1}{\xi^2}\int d\sigma_1 d\sigma_2\left\{\frac{\partial}{\partial \sigma}\frac{1}{b^2}\frac{\partial}{\partial \sigma}\psi(\sigma; \sigma', \sigma_1)\right.$$

$$\left.-\frac{\partial}{\partial \sigma}\frac{1}{b^2}\frac{\partial}{\partial \sigma}\psi(\sigma; \sigma_2, \sigma_1)\right\}\zeta(\sigma_1)\zeta(\sigma_2)$$

$$=\frac{1}{\xi^2}\int d\sigma_1 d\sigma_2(-\delta(\sigma-\sigma')+\delta(\sigma-\sigma_2))\zeta(\sigma_1)\zeta(\sigma_2)$$

$$=-\delta(\sigma-\sigma')+\frac{\zeta(\sigma)}{\xi} \quad (125)$$

Further, it is readily seen that $C(\sigma, \sigma')$ satisfies the same boundary conditions as those for $g(\sigma, \sigma')$. Comparing eq 125 with eq 122, we obtain eq 123.

Now it is very easy to prove the sum rule. From eq 121 and 123 we obtain

$$\sum \tau_p = \int d\sigma g(\sigma\sigma)$$
$$= \frac{1}{3kT} \int d\sigma \zeta(\sigma)\langle(r(\sigma)-r_\xi)^2\rangle$$
$$= \frac{\xi}{3kT}\langle S^2\rangle_\zeta \tag{126}$$

In a similar manner, the sum rules of $\sum \tau_p^2$ and $\sum \tau_p^3$ are obtained, for example

$$\sum \tau_p^2 = \int d\sigma \, d\sigma' g(\sigma\sigma')g(\sigma'\sigma)$$
$$= \frac{1}{(3kT)^2} \int d\sigma \, d\sigma' \zeta(\sigma)\zeta(\sigma')$$
$$\times \{\langle(r(\sigma)-r_\xi)\cdot(r(\sigma')-r_\xi)\rangle\}^2 \tag{127}$$

DISCUSSION

In this paper, we have presented a method of calculating the relaxation spectrum of a branched polymer in case of the free draining limit. It is found that the calculation reduces to an eigenvalue problem defined in the network space of the polymer chain. The relaxation spectra of some typical branched polymers were calculated. In general, however, such a calculation will be difficult, although not impossible, for a polymer chain with general topological structure. Therefore it seems of importance to discuss some general properties of the relaxation spectrum which hold irrespective of the type of branching.

In the present paper, the following three points are clarified:

(i) For the short time region, the relaxation spectrum takes a universal form given by eq 30.

(ii) The longest relaxation time is closely related to the mean square radius of gyration and is estimated by eq 100.

(iii) The relaxation spectrum satisfies the inequality 28.

Unfortunately, we could not make any definite statement on the relation between the shape of the relaxation spectrum in the long time region and the topological structure of the branched polymer. It remains still open to question whether a branched polymer, or a permanent cross-linkage model in case of the entanglement problems, exhibits a box-type relaxation spectrum. However, from the observation of the calculated results made in the foregoing section, we presume the spectrum of such polymers cannot show any humps. This presumption is to some extent supported by the following theorem.

(iv) Let $H_b(\tau)$ and $H_1(\tau)$ be respectively the relaxation spectrum of the branched and linear polymers with the same molecular weight; then the following inequality holds for any time τ

$$\int_\tau^\infty H_b(\tau') \, d \ln \tau' \le \int_\tau^\infty H_1(\tau') \, d \ln \tau' \tag{128}$$

This theorem can be proved in the same manner as was used to show eq 28. If we assume that the above inequality is satisfied under the stronger condition

$$H_b(\tau) \le H_1(\tau) \tag{129}$$

we can conclude that $H_b(\tau)$ cannot have a hump, because $H_b(\tau)$ is equal to $H_1(\tau)$ for the short time region and eq 129 should hold for the whole time region.

In conclusion we may say that the permanent cross-linkage model will not be a good model for undiluted polymer solutions.

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