Theory of Entanglement Effects in Linear Viscoelastic Behavior of Polymer Solutions and Melts. I. Symmetry Considerations

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ABSTRACT: In this paper we assume polymer solutions and melts to behave as assemblies of random-flight chains of N statistical segments. When such an assembly is subjected to deformation—either continuously as in steady flow, or instantaneously as in stress relaxation—there will exist a probability $\mathcal{P}_{i,j;k}$ that masses i of a given molecule and j of any other molecule k will exert a force on each other through a point of entanglement. We assert that these probabilities should yield an $N \times N$ matrix **M** with elements $\mathfrak{M}_{i,j}$ that are the effective number of entanglement couplings between statistical segment i of the given molecule and statistical segments j from all other molecules. Since all molecules in the assembly are equivalent, we further assert that $\mathfrak{M}_{i,j} = \mathfrak{M}_{j,i}$, and, since both ends of any molecule are equivalent, that $\mathfrak{M}_{i,j} = \mathfrak{M}_{N+1-i,j}$. Introducing **M** into the Rouse development of the viscoelastic behavior of assemblies of random-flight chains predicts that only odd-order relaxation times are affected by chain entanglement. It is further shown that only relaxation times at the long-time end of the relaxation spectrum are altered by entanglements, and that for slight entanglement only the longest few odd-order relaxation times are affected.

Viscoelastic behavior of sufficiently dilute polymer solutions can be explained without introducing cooperative effects between polymer molecules. Various aspects of such behavior have been examined theoretically by Kramers,[1] Kirkwood and Riseman,[2] Rouse,[3] Bueche,[4] Zimm,[5] Nakada,[6] Pao,[7] Peterlin,[8] Isihara,[9] Blatz,[10] and DeWames, Hall, and Shen.[11] Much of this work has been recently reviewed by Stockmayer and Fixman.[12] Sufficiently long chainlike molecules in melts and sufficiently concentrated solutions do, however, require intermolecular cooperative motion in order to respond to stress. The viscoelastic behavior of such entangled polymer systems is not nearly so well understood.

Bueche[13] and Graessley[14] have formulated theories to explain Newtonian and non-Newtonian steady-state shear viscosity in terms of chain slipping. Williams, Landel, and Ferry[15,16] offered an argument based on qualitative considerations that the presence of entanglements affected only the longest several of the relaxation times as defined in the normal-coordinate analysis of Rouse,[3] but that the other aspect of the Rouse theory remained a valid description of linear viscoelastic behavior. Chompff and Duiser[17] extended these ideas by modifying the Rouse theory to include the effects of temporary cross-links.

In this paper we introduce the notion of a probability $\mathcal{P}_{i,j;k}$ that the segment i of a given molecule is entangled with (pulling against) segment j of a second molecule k. Given the matrix of these probabilities, many of the observed entanglement effects can be predicted.

The Model

The polymer system is assumed to behave as an assembly of linear, random-flight chains of $N + 1$ masses separated by N statistical segments. The masses are numbered 0 through N and the statistical segments 1 through N. For any chain of the assembly the (laboratory) coordinates of mass i relative to the center of mass are written as $\hat{x}_i$, $\hat{y}_i$, $\hat{z}_i$. Coordinates defining the state of a statistical segment i are x_i, y_i, and z_i. It follows that

$$\begin{aligned} x_i &= \hat{x}_i - \hat{x}_{i-1} \\ y_i &= \hat{y}_i - \hat{y}_{i-1} \\ z_i &= \hat{z}_i - \hat{z}_{i-1} \end{aligned} \tag{1}$$

The equilibrium distribution of each statistical segment, $w_i^0(x_i, y_i, z_i)$, is assumed to be Gaussian, that is

$$w_i^0(x_i, y_i, z_i) = (N^{3/2}\beta^3/\pi^{3/2}) \exp\{-N\beta^2(x_i^2 + y_i^2 + z_i^2)\} \tag{2}$$

where β is the parameter characterizing the distribution of end-to-end distances of the entire chain. But since the problem under consideration is a two-dimensional one, we need only consider the distributions

$$w_i^0(x_i, y_i) = (N\beta^2/\pi) \exp\{-N\beta^2(x_i^2 + y_i^2)\} \tag{3}$$

At equilibrium, the entire assembly of chains is characterized by the distribution

$$\Psi^0(x_1, y_1, x_2, y_2, \ldots, x_N, y_N) = \prod_{i=1}^{N} w_i^0(x_i, y_i) \tag{4}$$

When the assembly of chains is not at equilibrium (such as during flow or stress relaxation), it is characterized by a different distribution, $\Psi(x_1, y_1, x_2, y_2, \ldots, x_N, y_N)$. If there are no internal energy effects accompanying deformation, the stored (Helmholtz) free energy of the system, E, is given by

$$E = -kT \ln \Phi \tag{5}$$

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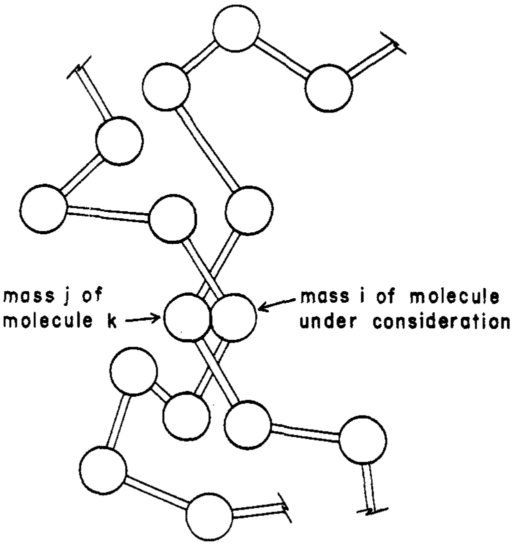

Figure 1. Interaction between mass i of a molecule under consideration and mass j of any other molecule k.

where

$$\Phi = \Psi/\Psi^0 \tag{6}$$

The x and y components of the driving force effecting a return of the components of statistical segment i back to Gaussian statistics are then given by

$$kT(\partial \ln \Phi/\partial x_i) \tag{7}$$

$$kT(\partial \ln \Phi/\partial y_i) \tag{8}$$

Forces impressed upon any chain by its surroundings (in this case by other polymer chains and solvent) will be classified as external forces. In theoretical treatments of chain dynamics of unentangled systems the only external forces considered are assumed to be analogous to hydrodynamic forces. That is, when a mass moves at a velocity different from that of the continuum, it will experience a hydrodynamic drag characterized by a friction coefficient f_0. Motion against such forces is totally dissipative and contributes only to the viscosity of the system. At entanglement points, however, pairs of polymer chains will be pulling against each other. Such forces represent energy storage and contribute to the elastic behavior of the system.

We will consider two molecules with centers of mass a distance r apart. Our attention will be focused on a given one of the pair, and the second one will be labeled molecule k. When the continuum in which the pair of molecules is imbedded is subjected to deformation—either continuously as in steady flow, or instantaneously as in stress relaxation—there will be a probability $\mathcal{P}_{i,j;k}$ that masses i of the given molecule and j of molecule k will exert a force on each other through a point of entanglement, as shown in Figure 1.

Consider all such pairs of molecules entangled at segments i and j. We will assume with Rouse[3] that the x component of the *mean* entanglement force on masses i due to entanglement with masses j will be proportional to

$$kT\left(\frac{\partial \ln \Phi}{\partial x_{j+1}} - \frac{\partial \ln \Phi}{\partial x_j}\right) \tag{9}$$

Since the mean velocity of masses j will be the continuum velocity, no corrections to the above are required for hydrodynamic effects.

Molecular Force Balance

As has been shown previously,[3] in the absence of entanglements a force balance on mass i of an average chain in a uniform flow field of rate-of-shear $\dot\gamma$ is written

$$f_0(\dot\gamma_i \hat{y}_i - \hat{x}_i) + kT\left(\frac{\partial \ln \Phi}{\partial x_{i+1}} - \frac{\partial \ln \Phi}{\partial x_i}\right) = 0 \tag{10}$$

$$-f_0\hat{y}_i + kT\left(\frac{\partial \ln \Phi}{\partial y_{i+1}} - \frac{\partial \ln \Phi}{\partial y_i}\right) = 0 \tag{11}$$

In considering entanglements we will still write a force balance on an average member of an assembly of chains. In addition, however, we will assume that the effects of entanglements on mass i due to interactions with all masses j will be given by a term of the form

$$kT\mathcal{M}_{i,j}\left(\frac{\partial \ln \Phi}{\partial x_{j+1}} - \frac{\partial \ln \Phi}{\partial x_j}\right) \tag{12}$$

In principle, we suggest that the "coupling coefficient," $\mathcal{M}_{i,j}$, could be determined by considering $\mathcal{P}_{i,j;k}$ (which can be evaluated from polymer concentration and chain statistics) and by properly accounting for the various ways entanglement forces are directed when the assembly of chains is deformed. Determining $\mathcal{M}_{i,j}$ is, however, beyond the scope of this work. For the present, therefore, we *postulate* eq 12 as the proper form for including effects on mass i by entanglement with all other mass j.

The complete molecular force balance in the presence of entanglement is thus obtained from eq 10 and 11 by adding the (postulated) contribution from the sum of entanglement forces from all segments j. The result is

$$f_0(\dot\gamma\hat{y}_i - \hat{x}_i) + kT\left(\frac{\partial \ln \Phi}{\partial x_{i+1}} - \frac{\partial \ln \Phi}{\partial x_i}\right) + kT\sum_{j=0}^{N}\mathcal{M}_{i,j}\left(\frac{\partial \ln \Phi}{\partial x_{j+1}} - \frac{\partial \ln \Phi}{\partial x_j}\right) = 0 \tag{13a}$$

and

$$-f_0\hat{y}_i + kT\left(\frac{\partial \ln \Phi}{\partial y_{i+1}} - \frac{\partial \ln \Phi}{\partial y_i}\right) + kT\sum_{j=0}^{N}\mathcal{M}_{i,j}\left(\frac{\partial \ln \Phi}{\partial y_{j+1}} - \frac{\partial \ln \Phi}{\partial y_j}\right) = 0 \tag{13b}$$

In order to eliminate the position coordinates of the masses in terms of the coordinates of the statistical segments, we take the difference between the equations for mass $i + 1$ and i. The result is

$$f_0(\dot\gamma y_i - \dot{x}_i) + kT\left(\frac{\partial \ln \Phi}{\partial x_{i-1}} - 2\frac{\partial \ln \Phi}{\partial x_i} + \frac{\partial \ln \Phi}{\partial x_{i+1}}\right) + kT\sum_{j=1}^{N}\mathcal{M}_{i,j}\frac{\partial \ln \Phi}{\partial x_j} = 0 \tag{14}$$

$$-f_0\dot{y}_i + kT\left(\frac{\partial \ln \Phi}{\partial y_{i-1}} - 2\frac{\partial \ln \Phi}{\partial y_i} + \frac{\partial \ln \Phi}{\partial y_{i+1}}\right) + kT\sum_{j=1}^{N}\mathcal{M}_{i,j}\frac{\partial \ln \Phi}{\partial x_j} = 0 \tag{15}$$

Although the above equations for coordinate i of a given molecule include coordinates j of interacting molecules, the derivatives $\partial \ln \Phi/\partial x_i$ and $\partial \ln \Phi/\partial y_i$ apply equally to all members of the assembly. Equations 13–15 thus describe the behavior of a single molecule.

In matrix form, the equations become

$$f_0(\dot{\gamma}\mathbf{y} - \dot{\mathbf{x}}) - kT(\mathbf{A} - \mathbf{M})\nabla_{\mathbf{x}} \ln \Phi = 0 \qquad (16a)$$

$$-f_0\dot{\mathbf{y}} - kT(\mathbf{A} - \mathbf{M})\nabla_{\mathbf{y}} \ln \Phi = 0 \qquad (16b)$$

where $\mathbf{y}$, $\dot{\mathbf{y}}$, and $\dot{\mathbf{x}}$ are column vectors with elements y_i, $\dot{y}_i$, and $\dot{x}_i$, $\mathbf{A}$ is the $N \times N$ matrix introduced by Rouse[8] and is given by

$$\mathbf{A} = \begin{bmatrix} 2 & -1 & 0 & 0 & 0 & \cdot & \cdot & \cdot \\ -1 & 2 & -1 & 0 & 0 & \cdot & \cdot & \cdot \\ 0 & -1 & 2 & -1 & 0 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \qquad (17)$$

and the elements of the column vectors $\nabla_{\mathbf{x}}$ and $\nabla_{\mathbf{y}}$ are the differential operators

$$\partial/\partial x_i \qquad (18a)$$

and

$$\partial/\partial y_i \qquad (18b)$$

The matrix $\mathbf{M}$ has elements

$$\mathcal{M}_{i,j} = -(\mathcal{N}_{i,j} - \mathcal{N}_{i-1,j} - \mathcal{N}_{i,j-1} + \mathcal{N}_{i-1,j-1}) \qquad (19a)$$

If $\mathcal{N}_{i,j}$ changes sufficiently slowly with i and j, which would be the case for sufficiently long chains, eq 19a can be written as

$$\mathcal{M}_{i,j} = -\frac{\partial^2\mathcal{N}_{i,j}}{\partial_i\partial_j} \qquad (19b)$$

From eq 14 and 15 we find that $\mathcal{M}_{i,j}$ can be interpreted as the *effective* number of entanglement couplings between statistical segment i of a given molecule and statistical segments j in all other molecules.

Since the $\mathcal{N}_{i,j}$ are (at present) unknown "coupling coefficients," it would seem that little can be deduced about the $\mathcal{M}_{i,j}$. But if the proposed linear coupling relationship is correct, the symmetry constraints placed upon $\mathcal{M}_{i,j}$ are severe and lead directly to conclusions about the effect of entanglement on the linear viscoelastic behavior of assemblies of monodisperse chains. Indeed, that constitutes the remaining development of this paper. Consider first eq 14 and 15 in which all $\mathcal{M}_{i,j} = 0$. Since both ends of the chain must be equivalent, these force-balance equations are, as they must be, invariant to an exchange of indices i and $N + 1 - i$. This feature must be preserved in the presence of entanglement, so it follows that

$$\mathcal{M}_{i,j} = \mathcal{M}_{N+1-i,j} \qquad (20a)$$

Furthermore, both ends of the chains with which the given chain is interacting are equivalent. It thus follows that

$$\mathcal{M}_{i,j} = \mathcal{M}_{i,N+1-j} \qquad (20b)$$

In addition to the above symmetry conditions, we argue that, since every molecule of the assembly is equivalent, the effective number of entanglements of segments j with segments i is the same as the effective number of entanglements of segments i with segments j. That is

$$\mathcal{M}_{i,j} = \mathcal{M}_{j,i} \qquad (21)$$

There is no loss of generality in considering i and j as continuous variables, even though we are only interested in values of $\mathcal{M}_{i,j}$ at integer values. The function $\mathcal{M}_{i,j}$ may thus be expanded in a two-dimensional Fourier series to give

$$\mathcal{M}_{i,j} = \sum_{q,r} C_{q,r} \sin\frac{iq\pi}{N} \sin\frac{jr\pi}{N} \qquad (22)$$

The symmetry conditions in eq 20 and 21 lead to $C_{q,r} = 0$ unless *both* q and r are odd integers. The dummy indices in eq 21 and in all following summations take on values from one to infinity unless stated otherwise.

Normal-Coordinate Analysis

Since both $\mathbf{A}$ and $\mathbf{M}$ are symmetric, eq 16 can be separated by the orthogonal transformations

$$\boldsymbol{\xi} = \mathbf{B}\mathbf{x}$$

$$\boldsymbol{\nu} = \mathbf{B}\mathbf{y} \qquad (23)$$

which gives

$$f_0(\dot{\gamma}\boldsymbol{\nu} - \dot{\boldsymbol{\xi}}) - kT\boldsymbol{\mu}\nabla_{\xi} \ln \Phi = 0 \qquad (24a)$$

$$-f_0\dot{\boldsymbol{\nu}} - kT\boldsymbol{\mu}\nabla_{\nu} \ln \Phi = 0 \qquad (24b)$$

where

$$\mathbf{B}(\mathbf{A} - \mathbf{M})\mathbf{B}^{-1} = \boldsymbol{\mu} \qquad (25)$$

$$\nabla_{\xi} = \mathbf{B}\nabla_{\mathbf{x}} \qquad (26a)$$

$$\nabla_{\nu} = \mathbf{B}\nabla_{\mathbf{y}} \qquad (26b)$$

The tensor properties of derivatives give column vector operators ∇_{ξ} and ∇_{ν} operating on $\ln \phi$ where ϕ is the distribution function in ξ–ν space. Since $\Phi(x_1, y_1, x_2, y_2, \ldots, x_N, y_N)$ is the ratio of Gaussian distributions and since the transformation of coordinates is orthogonal, it can be shown that $\phi(\xi_1, \nu_1, \xi_2, \nu_2, \ldots, \xi_N, \nu_N)$ is also the ratio of Gaussian distributions with the same dispersion parameter $N\beta^2$ used in eq 2–4.

When all $\mathcal{M}_{i,j} = 0$, the transformation is the same as that introduced by Rouse, and the eigenvalues are given by

$$\mu^0{}_p = 4 \sin^2 [p\pi/2(N + 1)] \qquad (27)$$

where the superscript used in eq 27 indicates the absence of entanglements. For sufficiently long chains,[17] estimated to be chains of more than 20 statistical segments,[18–20] the eigenvalues of physical significance are given by

$$\mu^0{}_p = p^2\pi^2/N^2 \qquad (28)$$

It has already been shown[18] that

$$\mathbf{A} = (N + 1)\mathbf{F}^{-1} \qquad (29a)$$

where $\mathbf{F}$ is the positive-definite $N \times N$ matrix which yields the radius of gyration in terms of the sum of squares of the same normal coordinates used in the Rouse treatment. Its elements are given by

$$\begin{aligned} F_{i,j} &= (N + 1 - i)j, \qquad i \geq j \\ &= (N + 1 - j)i, \qquad i \leq j \end{aligned} \qquad (30a)$$

For sufficiently long chains it is adequate to write

$$\mathbf{A} = N\mathbf{F}^{-1} \qquad (29b)$$

$$\begin{aligned} F_{i,j} &= (N - i)j, \qquad i \geq j \\ &= (N - j)i, \qquad i \leq j \end{aligned} \qquad (30b)$$

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(19) R. F. Hoffman and W. C. Forsman, *ibid.*, **50**, 2316 (1969).

(20) R. F. Hoffman and W. C. Forsman, *ibid.*, **52**, 2222 (1970).

and, for mathematical convenience, that i runs from 0 to N. We can thus replace the "unentangled" special case of eq 25, that is

$$\mathbf{B}^0\mathbf{A}(\mathbf{B}^0)^{-1} = \boldsymbol{\mu}^0 \tag{31}$$

by

$$\mathbf{B}^0\mathbf{F}(\mathbf{B}^0)^{-1} = \boldsymbol{\lambda}^0 \tag{32}$$

where

$$\mu^0{}_i = N(\lambda^0{}_i)^{-1} \tag{33}$$

If B_{ij} varies smoothly enough with i and j, the matrix problem of eq 32 can be replaced by an integral equation. Interpreting A_{ij} and B_{ij} as continuous functions of i and j (or any other dummy variables), the eigenvalue problem becomes

$$\int_0^N B^0{}_{i,k}F_{k,j}\mathrm{d}k = \lambda^0{}_iB^0{}_{i,j} \tag{34}$$

When the kernel is expanded in a Fourier series, it becomes

$$F_{k,j} = \frac{N^2}{\pi^2}\sum_P \frac{2}{P^2}\sin\frac{Pk\pi}{N}\sin\frac{Pj\pi}{N} \tag{35}$$

It therefore is convenient to write the elements of $\mathbf{B}^0$ in the form

$$B^0{}_{i,j} = \left(\frac{2}{N}\right)^{1/2}\sum_n D_{i,n}\sin\frac{nj\pi}{N} \tag{36}$$

where the coefficients $D_{i,n}$ are yet to be determined. Equation 34 can then be integrated to give

$$\frac{N^3}{\pi^2}\sum_n \frac{D_{i,n}}{n^2}\sin\frac{nj\pi}{N} = \lambda^0{}_i\sum_n D_{i,n}\sin\frac{nj\pi}{N} \tag{37}$$

The above equation has solutions only for the eigenvalues

$$\lambda^0{}_i = N^3/\pi^2i^2 \tag{38}$$

and the normalized eigenfunctions

$$B^0{}_{i,j} = (2/N)^{1/2}\sin\frac{ij\pi}{N} \tag{39}$$

or

$$D_{i,j} = \delta_{i,j}$$

where the $\delta_{i,j}$ are the Kronecker deltas.

Since eq 28 and 38 represent the physically significant eigenvalues in chain dynamics[3] and chain statistics,[18-20] we conclude that the associated eigenfunctions of eq 39 are adequate for the description of unentangled linear chain molecules.

After separating the equations describing the motion of the statistical segments by the normal-coordinate transformation described above, Rouse[3] solved for the viscoelastic behavior of assemblies of random-flight chains. He found that they acted as sets of Maxwell elements connected in parallel with equal spring constants given by

$$G_p = nkT \tag{40}$$

where n is the number of molecules per unit volume and kT is the Boltzmann constant times absolute temperature. Relaxation times τ_p are given by

$$\tau_p = \langle l^2\rangle f_0/6kT\mu^0{}_p \tag{41a}$$

$$= \langle l^2\rangle f_0\lambda^0{}_p/6(N+1)kT \tag{41b}$$

where $\langle l^2\rangle$ is the mean-square length of a statistical segment. Again, for sufficiently long chains, eq 28 applies, and the relaxation times of physical significance predicted by Rouse for unentangled assemblies are given by

$$\tau_p = N\langle l^2\rangle Nf_0/6\pi^2kTp^2 \tag{42}$$

Since $N\langle l^2\rangle$ is the mean-square end-to-end distance of the assembly of chains and Nf_0 is the frictional drag coefficient of one chain, eq 42 gives relaxation times independent of how the chain is subdivided into statistical segments.

The only additional treatment required to extend the Rouse theory to entangled systems is to solve for the eigenvalues λ_p or μ_p in the presence of entanglements. Since from this point on, the Rouse analysis is identical, we can write the general expressions

$$\tau_p = \langle l^2\rangle f_0/6kT\mu_p \tag{43a}$$

$$= \langle l^2\rangle f_0\lambda_p/6(N+1)kT \tag{43b}$$

To extend the treatment to entangled systems, we first assume that we can write

$$\mathbf{M} = (N/2)\,\mathbf{B}^0\mathbf{C}(\mathbf{B}^0)^{-1} \tag{44}$$

where, considering eq 22

$$\mathbf{C} = \begin{bmatrix} C_{1,1} & 0 & C_{1,3} & 0 & C_{1,5} & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & 0 & 0 & \cdot & \cdot & \cdot \\ C_{3,1} & 0 & C_{3,3} & 0 & C_{3,5} & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & 0 & 0 & \cdot & \cdot & \cdot \\ C_{5,1} & 0 & C_{5,3} & 0 & C_{5,5} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \tag{45}$$

Equation 44 implies that we must make one of two assumptions: either that the Fourier series of eq 22 is truncated at $r = q = N$ or that the treatment applies as $N \rightarrow \infty$. Either assumption would be adequate in this case.

By applying the Rouse transformation to eq 16a, b, we get

$$f_0(\dot{\gamma}\mathbf{v}^0 - \dot{\boldsymbol{\xi}}^0) - kT\left(\boldsymbol{\mu}^0 - \frac{N}{2}\mathbf{C}\right)\nabla_{\xi^0}\ln\phi = 0 \tag{46a}$$

$$-f_0\dot{\mathbf{v}}^0 - kT\left(\boldsymbol{\mu}^0 - \frac{N}{2}\mathbf{C}\right)\nabla_{\nu^0}\ln\phi = 0 \tag{46b}$$

Since all elements of $\mathbf{C}$ in even rows and columns are zero, all even-normal modes (as defined by Rouse) are separated by this transformation. Consequently all relaxation times associated with the even-normal modes are unaffected by entanglement. In addition, since $C_{i,j}$ are Fourier coefficients in the expansion of $\mathfrak{M}_{i,j}$ they will decrease rapidly with increasing i and j. Thus relaxation times associated with the normal modes of indices greater than some (as yet unknown) value are essentially unaffected by entanglement.

These predictions are indeed in agreement with experiment. It is well known that the transition zone is independent of molecular weight and entanglement.[16,21] This viscoelastic zone is therefore associated with Rouse indices greater than the highest harmonic contribution to the Fourier expansion of $\mathfrak{M}_{i,j}$. In addition, our laboratory recently published evidence that only odd-order normal modes are affected by chain entanglement.[21]

So far the treatment gives no indication of the effect of entanglement on the magnitude of the odd-normal modes (although intuition and experimental evidence would, of

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(21) R. I. Wolkowicz and W. C. Forsman, *Macromolecules*, **4**, 184 (1971).

course, indicate that relaxation times should increase). Such effects can best be illustrated by perturbation methods.

First-Order Perturbation

By applying the relationship between **A** and **F** given in eq 29b, we can write the reciprocal of eq 25 as

$$N^{-1}\mathbf{B}(\boldsymbol{\delta} - N^{-1}\mathbf{FM})^{-1}\mathbf{FB}^{-1} = \boldsymbol{\mu}^{-1} \tag{47}$$

where $\boldsymbol{\delta}$ has elements equal to the Kronecker delta. If the elements of **M** are sufficiently small, the term in parentheses can be expanded in a (matrix) Taylor series. If all terms beyond the second are assumed to be negligible, eq 47 becomes

$$\mathbf{B}(\boldsymbol{\delta} + N^{-1}\mathbf{FM})\mathbf{FB}^{-1} = N\boldsymbol{\mu}^{-1} \tag{48}$$

or, if by definition

$$\boldsymbol{\mu}^{-1} = N^{-1}\boldsymbol{\lambda} \tag{49}$$

$$\mathbf{B}(\boldsymbol{\delta} + N^{-1}\mathbf{FM})\mathbf{FB}^{-1} = \boldsymbol{\lambda} \tag{50}$$

If B_{ij} varies smoothly with the indices, the summations in the eigenvalue problem of eq 50 can be adequately approximated by the integral equation

$$\int B_{ik}F_{kj}\mathrm{d}k = \lambda_i B_{ij} - N^{-1}\int B_{ik}F_{kl}\mathcal{M}_{lm}F_{mj}\mathrm{d}k\mathrm{d}l\mathrm{d}m \tag{51}$$

As before, we let

$$B_{ik} = \left(\frac{2}{N}\right)^{1/2}\sum_n D_{i,n}\sin\frac{kn\pi}{N}$$

When $\mathcal{M}_{l,m}$ and $F_{k,j}$ are written in their Fourier series forms (eq 22 and 35) the integrations in eq 51 can be performed in closed form with the result

$$\frac{N^3}{\pi^2}\sum_n \frac{D_{i,n}}{n^2}\sin\frac{nj\pi}{N} = \lambda\sum_n D_{i,n}\sin\frac{jn\pi}{N} - \frac{N^6}{2\pi^4}\sum_{n,s}\frac{D_{i,n}C_{n,s}}{n^2s^2}\sin\frac{sj\pi}{N} \tag{52}$$

If eq 52 is multiplied by sin $(mj\pi/N)$ and integrated over j, the result is

$$\left(\frac{N^3}{\pi^2m^2} - \lambda\right)D_{i,m} + \frac{N^6}{2\pi^4}\sum_n\frac{D_{i,n}C_{n,m}}{n^2m^2} = 0 \tag{53}$$

for $m = 1, 2, \ldots$ or

$$(\lambda^0_m - \lambda)D_{i,m} + \lambda^0_m\sum_n \epsilon_{n,m}D_{i,n} = 0 \tag{54}$$

for $m = 1, 2, \ldots,$ where

$$\epsilon_{n,m} = \frac{N^3C_{n,m}}{2\pi^2n^2} \tag{55}$$

The secular determinant of eq 54 is

$$\begin{vmatrix} \lambda^0_1(1 + \epsilon_{1,1}) - \lambda & \lambda^0_1\epsilon_{2,1} & \lambda^0_1\epsilon_{3,1} & \cdot\ \cdot \\ \lambda^0_2\epsilon_{1,2} & \lambda^0_2(1 + \epsilon_{2,2}) - \lambda & \lambda^0_2\epsilon_{3,2} & \cdot\ \cdot \\ \lambda^0_3\epsilon_{1,3} & \lambda^0_3\epsilon_{2,3} & \lambda^0_3(1 + \epsilon_{3,3}) - \lambda & \cdot\ \cdot \\ \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot & \cdot\ \cdot \end{vmatrix} = 0 \tag{56}$$

In the absence of all entanglements all $\epsilon_{n,m} = 0$, and the solution to the above set of equations is, of course

$$\lambda = \lambda^0_1, \lambda^0_2, \lambda^0_3, \ldots$$

To the first order in $\epsilon_{i,j}$ we can ignore the off-diagonal terms and the solution becomes

$$\lambda_1 = \lambda^0_i(1 + \epsilon_{1,1})$$

$$\lambda_2 = \lambda^0_2$$

$$\lambda_3 = \lambda^0_3(1 + \epsilon_{3,3})$$

or

$$\lambda_n = \lambda^0_n\left(1 + \frac{N^3C_{n,n}}{2\pi^2n^2}\right) \tag{57}$$

The Fourier coefficients $C_{n,n}$ will decrease with increasing n. The n^2 factor in eq 57 will drive the perturbation term rapidly to zero with increasing n. We thus conclude that only the first several odd-order relaxation times will be affected by entanglements.

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