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(23) Substituting $V_g/m_0 = Ad_0$ into equations[11] $V_c/m_0 = 14\sigma$ and $V_c/m_0 = 4.4\sigma^{3.5}$ for the EC and HC series, respectively, one obtains, log σ = log A - 1.042 and log σ = -0.184 + 0.286 log A, which should be compared to Boyer et al.'s result,[5] log σ = 0.38 + 0.22 log A. It appears, therefore, that the latter expression would apply at best only to HC polymers.

Linear Viscoelasticity in Gaussian Networks

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ABSTRACT: The relaxation spectrum at long times has been calculated for tree-like networks of Gaussian strands in which all strands have the same length and all junctions have the same functionality F. The phantom network approximation has been used, so entanglement effects are not included. As in an earlier analysis of the equilibrium elasticity of networks, the calculations were performed in two steps. The spectrum for an ensemble of arbitrarily large sample networks with peripheral junctions anchored at their most probable distribution of locations was obtained, then the contribution associated with elements far removed from the peripheral junctions was extracted. The resulting spectrum is continuous and becomes narrower with increasing functionality. The maximum relaxation time is $\tau_0/(1 - 2(F-1)^{1/2}/F)$ in which τ_0 is the primary relaxation time of unattached strands. Thus, even in the most extreme case of trifunctional junctions ($F = 3$), the longest relaxation time is smaller than $20\tau_0$, indicating the need to consider additional structural features, such as dangling strands and entanglements, to account for the much broader relaxation spectra of real networks.

Recently we proposed a model for dealing with equilibrium elasticity in Gaussian networks which uses the properties of small sample networks.[1,2] These micronetworks consist of Gaussian strands which are joined by mobile junctions. They are anchored at the periphery by other junctions which move affinely with macroscopic deformations. The micronetworks have no internal loops, consistent with the locally tree-like connectivity of most real networks. They are free to assume any configuration, regardless of the state of their environment, so effects such as entanglement or association are not included.

The free energy of deformation for an ensemble of micronetworks was found to consist of two terms, one proportional to the number of strands joining two mobile junctions (internal strands), the other proportional to the number of strands joining a mobile junction and a fixed junction (peripheral strands). The free energy of deformation for macroscopic networks, in which all junctions are mobile, was assumed to be associated with the term in the micronetwork expression applying to internal strands, with the following result for volume-preserving deformations.

$$\Delta A = (S - J)kT\left[\frac{\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3}{2}\right] \qquad (1)$$

The quantities S and J are the number of elastically active strands and the number of junctions in the network; α_x, α_y, and α_z are the extension ratios along the principal axes of deformation.

In this article we apply the same model to the calculation of linear viscoelastic behavior in networks. The relaxation spectrum $H(\tau)$ is calculated for micronetwork ensembles by the procedure of Zimm[3] for the case of no hydrodynamic interaction ($h = 0$). The spectrum associated with portions of the network which are remote from the fixed points is then extracted and applied to macroscopic networks. The equilibrium and relaxation problems are related since each depends on the eigenvalues of a matrix defined by the structure of the network. However, equilibrium elasticity depends only on the number of eigenvalues, while relaxation behavior also depends on their magnitudes. Thus ΔA depends only on the total number of strands and junctions, while $H(\tau)$ also depends on strand length distribution and the distribution of junction functionalities. Also, the separation of the contribution of fixed junctions to relaxation behavior turns out to be less straightforward than that in equilibrium elasticity because the effects of fixed junctions on $H(\tau)$ extend well into the micronetwork interior.

We consider here only the simplest possible structure with tree-like local connectivity: all strands have the same contour length, and all junctions have the same functionality. Interactions between the network and its surroundings are characterized merely by a frictional coefficient. Attributes of real networks such as dangling structures are not considered. Eventually we hope to extend the calculations to deal with dangling structures which, in combination with entanglement effects, appear to be mainly responsible for the long relaxation times of lightly cross-linked networks.[4,5] Since long time processes are the principal interest we will omit intra-strand relaxations entirely.

Background

Several years ago Chompff and co-workers published a series of papers on relaxation in tetrafunctional net-

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works.[6-9] The network strands were represented by sequences of frictional beads and linear springs. The junctions were mobile while the network connectivity was mesh-like, involving a two-dimensional cubic arrangement which contained numerous local loops. It was shown that at short times $H(\tau) \propto \tau^{-1/2}$, associated with relaxation within the strands. At long times $H(\tau) \propto \tau^{-1}$, associated with cooperative relaxation through the junctions. We will call the former strand relaxation and the latter network relaxation. Our main interest here is in the long-time end of the spectrum, so for simplicity we omit entirely the resistances along the strands, localizing them at the junctions. Thus we ignore the strand modes and focus on the network modes, and in fact only the lowest of even these modes.

If the junction functionality is F and the monomeric frictional coefficient is ζ_0, the junctions each have a frictional coefficient $\zeta = F n\zeta_0/2$ for network strands with n monomer units. The connectivity pattern is tree-like, as distinct from the locally looped networks of Chompff. Doi[10] has dealt with relaxations in tree-like molecules, arriving at results similar to those of Chompff and coworkers although he did not describe his calculations in detail. Rubin and Zwanzig[11] have treated the related problem of vibrational spectra for tree-like arrays of mass points connected by linear springs.

In bead-spring models the distribution of configurations for the subchains which join the frictional sites is taken to be Gaussian. The subchains are therefore mechanically equivalent to linear springs with the spring constant $K = 3kT/\langle r^2\rangle_0$, $\langle r^2\rangle_0$ being the mean-square end-to-end distance of free subchains.[3] In our analysis, where the long-time relaxations are emphasized, each network strand is in effect a subchain.

In the Zimm calculation each bead is subject to a force balance, such that

$$\mathbf{F}_{\text{drag}} + \mathbf{F}_{\text{spring}} + \mathbf{F}_{\text{osmotic}} = 0 \tag{2}$$

In matrix notation, with $\mathbf{x}$ and $\partial/\partial\mathbf{x}$ as column vectors for the x components of the N frictional beads of the molecule, and with all beads having the same frictional coefficient ζ,

$$-\zeta \frac{\mathrm{d}}{\mathrm{d}t}\mathbf{x} - K\mathbf{A}\cdot\mathbf{x} - kT\frac{\partial \ln \psi}{\partial \mathbf{x}} = 0 \tag{3}$$

The systematic velocity of the medium is here taken to be zero (such as would be the case for all times greater than zero in a stress relaxation experiment); ψ is the distribution function for the bead positions. The terms in the matrix $\mathbf{A}$ depend on the connections among the beads; $-K(\mathbf{A}\cdot\mathbf{x})_i$ is the sum of x component spring forces acting on bead i. Similar equations apply to the y and z components of the beads. The relaxation times for a collection of such

$$G(t) = \nu kT \sum_{i=1}^{N} \exp\left[-\frac{2K}{\zeta}\lambda_i t\right] \tag{4}$$

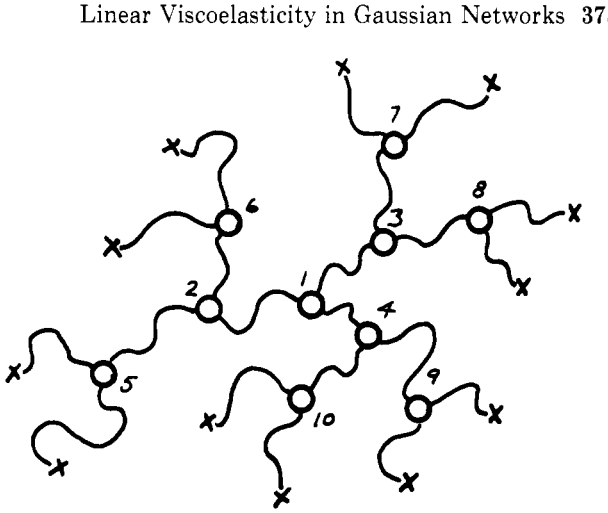

Figure 1. Trifunctional third order micronetwork.

in which ν is the number of molecules per unit volume and the λ_i are the eigenvalues of the connectivity matrix $\mathbf{A}$.

Calculations for Micronetworks

The calculation for micronetworks proceeds in the manner described above, the force balances being applied in this case to frictional beads at the mobile junctions. Figure 1 is a sketch of a third order, trifunctional micronetwork built around a central junction. There are ten mobile junctions, each with frictional coefficient $\zeta = 3n\zeta_0/2$, and there are 12 fixed junctions. Thus $N = 10$ with the mobile junctions labeled 1, 2, ..., 10 outward from the central junction. Row i in the connectivity matrix corresponds to mobile junction i. The matrix rows are constructed by writing +3 in the diagonal position (the total number of strands leading away from that junction), −1 in any column j of that row when one of the strands leads to the mobile junction labeled j, and 0 otherwise. Thus, for the example above, we get eq 5. The eigenvalues are

$$\mathbf{A} = \begin{vmatrix} 3 & -1 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 3 & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 3 & 0 & 0 & 0 & -1 & -1 & 0 & 0 \\ -1 & 0 & 0 & 3 & 0 & 0 & 0 & 0 & -1 & -1 \\ 0 & -1 & 0 & 0 & 3 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 3 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 3 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 3 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 3 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 3 \end{vmatrix} \tag{5}$$

solutions of the characteristic equation for $\mathbf{A}$, eq 6, which

$$\mathrm{Det}(\mathbf{A} - \lambda) = 0 \tag{6}$$

for the example is given in eq 7. The characteristic equation can be obtained by successive partitioning of the determinant, using the identity[12]

$$|\mathbf{M}| = \begin{vmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{vmatrix} = |\mathbf{D}| \cdot |\mathbf{A} - \mathbf{B}\cdot\mathbf{D}^{-1}\cdot\mathbf{C}| \tag{8}$$

Thus, with the partitioning indicated by dashed lines in eq 7,

$$\mathrm{Det}(\mathbf{A} - \lambda) = \left|\begin{array}{cccc|cccccc} 3-\lambda & -1 & -1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 3-\lambda & 0 & 0 & -1 & -1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 3-\lambda & 0 & 0 & 0 & -1 & -1 & 0 & 0 \\ -1 & 0 & 0 & 3-\lambda & 0 & 0 & 0 & 0 & -1 & -1 \\ \hline 0 & -1 & 0 & 0 & 3-\lambda & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 3-\lambda & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 3-\lambda & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 3-\lambda & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 3-\lambda & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 3-\lambda \end{array}\right| \tag{7}$$

$$\mathrm{Det}(\mathbf{A}-\lambda)=\begin{vmatrix} 3-\lambda & 0 & 0 & 0 & 0 & 0 \\ 0 & 3-\lambda & 0 & 0 & 0 & 0 \\ 0 & 0 & 3-\lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & 3-\lambda & 0 & 0 \\ 0 & 0 & 0 & 0 & 3-\lambda & 0 \\ 0 & 0 & 0 & 0 & 0 & 3-\lambda \end{vmatrix} \cdot$$

$$\begin{vmatrix} 3-\lambda & -1 & -1 & -1 \\ -1 & 3-\lambda-\dfrac{2}{3-\lambda} & 0 & 0 \\ -1 & 0 & 3-\lambda-\dfrac{2}{3-\lambda} & 0 \\ -1 & 0 & 0 & 3-\lambda-\dfrac{2}{3-\lambda} \end{vmatrix} \quad (9)$$

With further partitioning of the second determinant, the right side of eq 9 becomes

$$(3-\lambda)^6 \cdot \begin{vmatrix} 3-\lambda-\dfrac{2}{3-\lambda} & 0 & 0 \\ 0 & 3-\lambda-\dfrac{2}{3-\lambda} & 0 \\ 0 & 0 & 3-\lambda-\dfrac{2}{3-\lambda} \end{vmatrix} \cdot$$

$$\left| 3-\lambda-\frac{3}{3-\lambda-[2/(3-\lambda)]} \right| \quad (10)$$

or

$$(3-\lambda)^6\left(3-\lambda-\frac{2}{3-\lambda}\right)^3\left(3-\lambda-\frac{3}{3-\lambda-[3/(3-\lambda)]}\right) \quad (11)$$

The characteristic equation is therefore

$$(3-\lambda)^4\cdot((3-\lambda)^2-2)^2\cdot((3-\lambda)^2-5)=0 \quad (12)$$

and the ten roots are

$$\lambda = 3, 3, 3, 3, 3+2^{1/2}, 3+2^{1/2}, 3-2^{1/2}, 3-2^{1/2}, 3+5^{1/2}, 3-5^{1/2}$$

The generalization of the partitioning procedure to regular micronetworks of arbitrary order J and junction functionality F is straightforward. Let $C_m(F,\lambda)$ be a continued fraction of the form

$$C_m(F,\lambda) = F-\lambda-\cfrac{F-1}{F-\lambda-\cfrac{F-1}{F-\lambda-\cfrac{F-1}{F-\lambda-\cdots}}} \quad (13)$$

such that

$$C_1(F,\lambda) = F-\lambda$$
$$C_2(F,\lambda) = F-\lambda-\frac{F-1}{F-\lambda}$$
$$C_3(F,\lambda) = F-\lambda-\cfrac{F-1}{F-\lambda-\cfrac{F-1}{F-\lambda}}$$
$$\text{etc.} \quad (14)$$

Successive partitioning of the determinant for J-order F-functional micronetworks leads to the following characteristic equation

$$C_1^{F(F-1)^{J-2}}\cdot C_2^{F(F-1)^{J-3}}\cdot C_3^{F(F-1)^{J-4}}\cdots C_{J-1}^{F}\cdot\left[C_J-\frac{1}{(F-1)C_{J-2}}\right]=0 \quad (15)$$

With the substitution

$$z+\frac{1}{z}=\frac{F-\lambda}{(F-1)^{1/2}} \quad (16)$$

the continued fractions can be written

$$C_m=\frac{(F-1)^{1/2}}{z}\frac{S_m(z)}{S_{m-1}(z)} \quad (17)$$

in which

$$S_m(z)=\sum_{i=0}^{m}z^{2i}=\frac{1-z^{2m+2}}{1-z^2} \quad (18)$$

Thus, the characteristic equation is

$$\left[\frac{(F-1)^{1/2}}{z}\right]^{1+[F/(F-2)][(F-1)^{J-1}-1]}\left(\prod_{m=1}^{m=J-2}S_m^{F(F-2)(F-1)^{J-2-m}}\right)\cdot\left[S_J-\frac{z^2}{F-1}S_{J-2}\right](S_{J-1})^{F-1}=0 \quad (19)$$

The roots of eq 19 are thus the roots of S_m ($m = 1, 2, \ldots, J-1$) and the roots of $S_J-[z^2/(F-1)]S_{J-2}$. The roots of S_m are known[7]

$$z_m(r)=\exp\left(\frac{i\pi r}{m+1}\right)$$
$$r = 1, 2, \ldots, m \quad (20)$$

and therefore

$$\frac{F-\lambda}{(F-1)^{1/2}}=z_m(r)+\frac{1}{z_m(r)}=2\cos\frac{\pi r}{m+1}$$
$$r = 1, 2, \ldots, m \quad (21)$$

so

$$\lambda_m(r)=\left(1-\frac{2(F-1)^{1/2}}{F}\cos\frac{\pi r}{m+1}\right)F$$
$$r = 1, 2, \ldots, m \quad (22)$$

Finally, the relaxation modulus of the micronetwork ensemble is

$$G(t)=G_e+\nu kT\left[\sum_{r=1}^{J}\exp\left[-\frac{t}{\tau_J'(r)}\right]+(F-1)\sum_{r=1}^{J-1}\exp\left[-\frac{t}{\tau_{J-1}(r)}\right]+F(F-2)\sum_{m=1}^{J-2}(F-1)^{J-2-m}\sum_{r=1}^{m}\exp\left[-\frac{t}{\tau_m(r)}\right]\right] \quad (23)$$

in which ν in the number of micronetworks per unit volume, G_e is the equilibrium shear modulus of the micronetwork ensemble, $\tau_m(r)$ indicates the relaxation times associated with S_m:

$$\tau_m(r)=\frac{\tau_0}{1-\dfrac{2(F-1)^{1/2}}{F}\cos\dfrac{\pi r}{m+1}}$$
$$r = 1, 2, \ldots, m \quad (24)$$

the $\tau_J'(r)$ are derived from the solutions of $S_J-[z^2/(F-1)]S_{J-2}=0$, and

$$\tau_0 = \frac{\zeta}{2KF} = \frac{n\zeta_0\langle r^2\rangle_0}{12kT} \tag{25}$$

For large order micronetworks the term in eq 23 containing the double sum dominates. Thus, with negligible error, we can write (for $J \gg 1$):

$$G(t) = G_e + \nu kT\frac{F(F-2)}{(F-1)}\sum_{m=1}^{J-2}(F-1)^{J-1-m}\left[\sum_{r=1}^{m}\exp\left[-\frac{t}{\tau_m(r)}\right]\right] \tag{26}$$

Relaxation Spectra in Macroscopic Networks

The number of j-order junctions in a regular J-order F-functional micronetwork (counting outward from the center) is $F(F-1)^{j-2}$ $(2 \le j \le J)$. Thus, the number of mobile junctions connected directly to fixed junctions is $F(F-1)^{J-2}$, the number with one intervening mobile junction is $F(F-1)^{J-3}$, ..., and finally the number with m intervening mobile junctions is $F(F-1)^{J-1-m}$ $(m = 1, ..., J-1)$. Therefore, $G(t)$ in large micronetworks (eq 26) is given by a sum over all m of the number of mobile junctions which are m strands removed from fixed junctions, multiplied by a contribution which depends on m, that is, the number of intervening mobile junctions to a fixed point. In macroscopic networks all junctions are equivalent and far removed from fixed points. We therefore take as the spectrum for macroscopic networks the limiting contribution to the micronetwork spectrum associated with junctions far removed from the nearest fixed point:

$$\tau(r) = \lim_{m\to\infty}\left[\frac{\tau_0}{1-\frac{2(F-1)^{1/2}}{F}\cos\frac{\pi r}{m+1}}, \quad r = 1, 2, ..., m\right] \tag{27}$$

which assumes the continuous form

$$\tau(\xi) = \frac{\tau_0}{1-\frac{2(F-1)^{1/2}}{F}\cos\pi\xi}, \qquad 0 < \xi < 1 \tag{28}$$

Accordingly, the network relaxation times of the macroscopic network are distributed continuously over the range from $\tau_{min} = \tau_0/(1 + [2(F-1)^{1/2}/F])$ to $\tau_{max} = \tau_0/(1 - [2(F-1)^{1/2}/F])$ with the density obtainable from eq 28.

The relaxation spectrum can now be calculated. Solving eq 28 for ξ we find

$$\xi = \frac{1}{\pi}\cos^{-1}\left[\alpha\left(1-\frac{\tau_0}{\tau}\right)\right] \tag{29}$$

so

$$d\xi = -\frac{1}{\pi}\left[\frac{1}{1-\alpha^2\left(1-\frac{\tau_0}{\tau}\right)^2}\right]^{1/2}\frac{\alpha\tau_0}{\tau^2}\,d\tau \tag{30}$$

in which

$$\alpha = F/2(F-1)^{1/2} \tag{31}$$

Now $H(\tau)$ is defined such that

$$d\xi = -\frac{H(\tau)\,d\ln\tau}{NkT} \tag{32}$$

in which N is the number of junctions per unit volume in the macroscopic network. Therefore

$$H(\tau) = NkT\frac{F}{2\pi(F-1)^{1/2}}\frac{\tau_0/\tau}{\left[1-\frac{F^2}{4(F-1)}(1-\tau_0/\tau)^2\right]^{1/2}}$$

$$\tau_{min} < \tau < \tau_{max} \tag{33}$$

and the stress relaxation modulus of the macroscopic network is

$$G(t) = G_e + NkT\int_0^1 \exp-\left[\frac{t}{\tau_0}\left(1-\frac{2(F-1)^{1/2}}{F}\cos\pi\xi\right)\right]d\xi \tag{34}$$

or

$$G(t) = G_e + NkTe^{-t/\tau_0}I_0\left[\frac{2(F-1)^{1/2}t}{F\tau_0}\right] \tag{35}$$

in which $I_0(\,)$ is the modified Bessel function of order zero. The equilibrium modulus G_e is $(NkT/2)(F-2)$ according to results given elsewhere.[1,2]

In principle the value of τ_0 for such regular networks can be estimated from viscosity measurements on the uncross-linked polymer. The viscosity of linear chains with molecular weight equal to the strand molecular weight M_s is given by the Rouse expression

$$\eta_s = \frac{\zeta_0 n\langle r^2\rangle_0 N_a\rho}{36M_s} \tag{36}$$

in which N_a is Avogadro's number and ρ is the polymer density. When this is used to eliminate ζ_0 from eq 25 the result is

$$\tau_0 = \frac{3\eta_s}{\nu kT} = \frac{3\eta_s M_s}{\rho RT} \tag{37}$$

Of course this estimate omits entanglement and dangling strand contributions and thus drastically underestimates the relaxation time for most real networks.

The breadth of the network spectrum can be characterized by the ratio $\langle\tau^2\rangle/\langle\tau\rangle^2$. With

$$\langle\tau\rangle = \int_0^1 \frac{\tau_0}{1-\frac{1}{\alpha}\cos\pi\xi}\,d\xi = \frac{\alpha\tau_0}{(\alpha^2-1)^{1/2}} \tag{38}$$

and

$$\langle\tau^2\rangle = \int_0^1 \frac{{\tau_0}^2}{\left(1-\frac{1}{\alpha}\cos\pi\xi\right)^2}\,d\xi = \frac{\alpha^3{\tau_0}^2}{(\alpha^2-1)^{3/2}} \tag{39}$$

we obtain

$$\frac{\langle\tau^2\rangle}{\langle\tau\rangle^2} = \frac{\alpha}{(\alpha^2-1)^{1/2}} = \frac{F}{F-2} \tag{40}$$

Thus the network spectrum becomes narrower as the functionality of the junctions increases. This can be seen in Figure 2 in which the relaxation spectrum calculated from eq 33 is shown for different network functionalities. Again it must be emphasized that the results will be seriously in error and the spectrum spread over a much wider

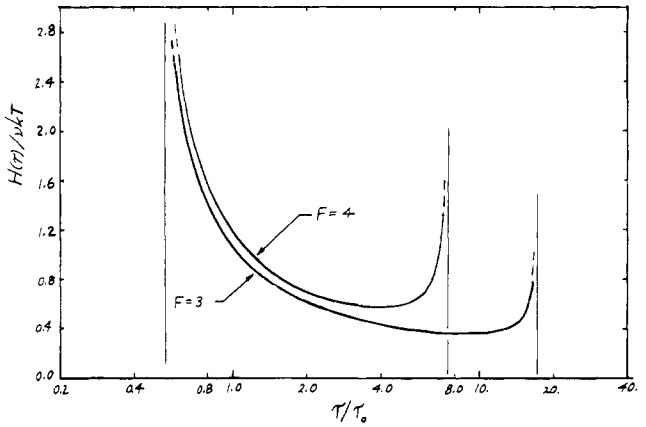

Figure 2. Relaxation spectra calculated from eq 33 for trifunctional and tetrafunctional networks.

range of times when dangling strand and entanglement contributions are important.

The micronetwork ensemble for $F = 2$ is simply a collection of linear chains with end points fixed. One can easily show that for $F = 2$ the relaxation times in eq 27, for m still finite, are

$$\tau_m(r) = \frac{\tau_0/2}{\sin^2 \dfrac{\pi r}{2(m+1)}}$$

$$r = 1, 2, ..., m \qquad (41)$$

which, as expected, is the familiar expression for Rouse relaxation times.

It is interesting, but perhaps only fortuitous, that $\langle\tau^2\rangle/\langle\tau\rangle^2 = 2$ for tetrafunctional junctions, which is very close to the value for the terminal spectrum in noncrosslinked but highly entangled chains, deduced from the values of plateau modulus G_N^0 and steady state compliance J_e^0 at high molecular weights[13]

$$G_N^0 J_e^0 = \langle\tau^2\rangle/\langle\tau\rangle^2 = 2\sim3 \qquad (42)$$

In their treatment of vibrational spectra for trees of mass points and springs Rubin and Zwanzig[11] obtain the same set of eigenvalues as ours (eq 22) although by a somewhat different method. The spectrum they derive differs of course from a relaxation spectrum. However, the major difference is that they stop short of separating out for particular attention the contributions associated with elements far removed from fixed points. When we do this we obtain a continuous spectrum in the limit (eq 28), while their spectrum, retaining the contributions of all elements, is discontinuous (as is the unseparated spectrum implicit in our eq 23). Such a separation is necessary when applying the results to macroscopic networks because of the unrepresentative behavior of elements near fixed points. The separation procedure we have used seems reasonable from a physical standpoint, but we are unable to offer a more precise justification.

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