

Frequency dependent energetics of a polymer chain represented by the Orwoll—Stockmayer hopping model

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The analogue of acoustic absorption in the simple hopping model of Orwoll and Stockmayer is treated and the features emerging from the model discussed. The results are shown to be at variance with the experimental evidence and it seems unlikely that simple modifications on this or any other hopping model will produce the high frequency relaxational behaviour of dilute polymer solutions. Indirect support is therefore given to the idea that the motion of a polymer in solution, at least up to a frequency in the MHz region, is best described by the solution of a realistic diffusion equation in which the solvent is treated as a continuous medium.

INTRODUCTION

The dynamical properties of polymers at low frequencies are adequately accounted for by the Rouse-Zimm model. At higher frequencies deviations from the model occur, the explanation of which necessitates a more explicit treatment of the local conformational changes in the polymer molecule.

Theoretical approaches to this problem may be divided into two categories. First, attempts to solve a diffusion equation which includes an intermonomer potential energy term; secondly, hopping models — attempts to represent the motion of the polymer as a series of discrete local transitions between conformational minima. The two methods are related to different physical ideas about the way a polymer moves in solution. The diffusion equation arises when the solvent is represented as a continuous medium interacting dynamically with the polymer only through a friction constant. Hopping would describe the situation where monomers rotate only when they can jump into an adjacent vacancy which has arisen in the solvent. Many well-known theories of liquid behaviour are based on such an idea.

Since it is very difficult to decide on *a priori* grounds which of the two pictures agrees with the real situation, it is desirable to work out the observable consequences of each and to compare these with experiments. A simple hopping model which includes the essential features was introduced by Orwoll and Stockmayer¹. Here we attempt to calculate the relaxation of the energy stored in a chain which moves according to this model. The energy in the chain is unambiguously related to the statistical mechanics of the chain motion in a way that other experimentally measurable quantities, such as the net electric dipole moment, are not. Experimentally, a quantity closely related to the energy in the chain is thought to make an important contribution to the ultrasonic absorption signal. The observed signal in such experiments follows a single Debye-type relaxation at a frequency in the MHz region. The calculations show, however, that the analogue of the energetic part of the ultrasonic relaxation in the hopping model follows the Rouse relaxation spectrum, as does the relaxation of the displacement of the particles calculated in the original paper of Orwoll and Stockmayer.

Acoustic analogue of the Orwoll and Stockmayer model for a one-dimensional linear chain with correlations

Let a one-dimensional linear chain comprise $N + 1$ beads which are indexed serially along the chain from 0 to N . Assuming constant bond lengths, the configuration of the chain is specified by the set of N scalars $\{\sigma_1, \sigma_2, \dots, \sigma_N\}$ where the 'bond directions' σ_i can take on only values of $+1$ or -1 depending on whether bead $i + 1$ is to the right or left of bead i . [If b is the bond length, $\sigma_i = b^{-1}(x_i - x_{i-1})$].

The chain configuration is made to vary in time by allowing beads to move one at a time and the restriction is made that bead i can move only if bonds i and $i + 1$ point in opposite directions, i.e. if $\sigma_i = -\sigma_{i+1}$. When bead i hops, the bond directions σ_i and σ_{i+1} change to $-\sigma_i$ and $-\sigma_{i+1}$, respectively.

As in the case of a linear Ising chain², the Hamiltonian of the system will be given by

$$\mathcal{H} = -E \sum_i \sigma_i \sigma_{i+1} \quad (1)$$

where we have introduced correlations between adjacent bonds by assigning an energy E for each pair of consecutive bonds which point in opposite directions and an energy $-E$ for each pair of adjacent bonds which point in the same direction. At equilibrium, the probability $p_{eq}(\sigma_1, \sigma_2, \dots, \sigma_N)$ that the chain has the configuration $\{\sigma_1, \sigma_2, \dots, \sigma_i, \sigma_{i+1}, \dots, \sigma_N\}$ is

proportional to the Boltzmann factor. Moreover, if $\omega_i(\sigma_i, \sigma_{i+1})$ denotes the probability per unit time that bead i flips, then the principle of microscopic reversibility requires:

$$\omega_i(\sigma_i, \sigma_{i+1})p_{eq}(\sigma_1, \sigma_2, \dots, \sigma_i, \sigma_{i+1}, \dots, \sigma_N) = \omega_i(-\sigma_i, -\sigma_{i+1})p_{eq}(\sigma_1, \sigma_2, \dots, -\sigma_i, -\sigma_{i+1}, \dots, \sigma_N), \quad (2)$$

Therefore $\omega_i(\sigma_i, \sigma_{i+1})$ is proportional to

$$\exp\left\{\frac{E}{kT}(\sigma_{i-1}\sigma_{i+1} + \sigma_i\sigma_{i+2})\right\}$$

Noting that even powers of any σ_i equal one, series expansion of the exponential gives:

$$\omega_i(\sigma_i, \sigma_{i+1}) = \frac{\alpha}{1-\beta^2}(1 + \beta\sigma_{i-1}\sigma_{i+1})(1 + \beta\sigma_i\sigma_{i+2}) \quad (3)$$

and

$$\omega_i(-\sigma_i, -\sigma_{i+1}) = \omega_i(\sigma_{i+1}, \sigma_i) = \frac{\alpha}{1-\beta^2}(1 + \beta\sigma_{i-1}\sigma_i)(1 + \beta\sigma_{i+1}\sigma_{i+2}) \quad (4)$$

where α is a proportionality constant and $\beta = \tanh(E/kT)$. Since the transition probability is a property independent of the restrictions of equilibrium, equations (3) and (4) can be used for non-equilibrium situations.

Let $p(\{\sigma^N\}, t)$ denote the probability that the chain has the configuration $\{\sigma_1, \sigma_2, \dots, \sigma_i, \sigma_{i+1}, \dots, \sigma_N\}$ at time t . Then, the master equation for this model is:

$$\frac{dp(\{\sigma^N\}, t)}{dt} = -\sum_i \left\{ \omega_i(\sigma_i, \sigma_{i+1})p(\{\sigma^N\}, t) - \omega_i(\sigma_{i+1}, \sigma_i)p(\hat{T}_i\{\sigma^N\}, t) \right\} \quad (5)$$

where $\hat{T}_i\{\sigma^N\}$ is the resulting configuration after bead i has flipped, i.e.:

$$\hat{T}_i\{\sigma^N\} = \{\sigma_1, \sigma_2, \dots, \sigma_{i-1}, \sigma_{i+1}, \sigma_i, \sigma_{i+2}, \dots, \sigma_N\} \quad (6)$$

Multiplication of equation (5) by σ_j and summation over all 2^n possible configurations gives the differential equations for the average value of the bond directions:

$$\begin{aligned} \frac{dq_i}{dt} = & -\frac{\alpha}{1-\beta^2} \{ 2q_i - (1+\beta)(q_{i-1} + q_{i+1}) + \beta(q_{i-2} + q_{i+2}) - \beta\langle\sigma_{i-2}\sigma_{i-1}\sigma_i\rangle + \\ & 2\beta\langle\sigma_{i-1}\sigma_i\sigma_{i+1}\rangle - \beta\langle\sigma_i\sigma_{i+1}\sigma_{i+2}\rangle + \beta^2\langle\sigma_{i-2}\sigma_{i-1}\sigma_{i+1}\rangle + \\ & \beta^2\langle\sigma_{i-1}\sigma_{i+1}\sigma_{i+2}\rangle - \beta^2\langle\sigma_{i-2}\sigma_i\sigma_{i+1}\rangle - \beta^2\langle\sigma_{i-1}\sigma_i\sigma_{i+2}\rangle \} \end{aligned} \quad (7)$$

where the brackets $\langle \rangle$ denote ensemble average and $q_i = \langle \sigma_i \rangle$. Equation (7) is the same as equation (32) in Orwoll and Stockmayer's paper (with $a=0$) and therefore their subsequent analysis applies.

To obtain the two bond correlation functions, which describe whatever tendency on the average the pair of bonds σ_j and σ_l may have, to be correlated in direction at a particular instant (and hence the time dependence of the energy of the system) we perform multiplication of equation (5) by $\sigma_j\sigma_l$ and summation over all possible configurations. That is:

$$\frac{dr_{j,l}}{dt} = -\sum_{i,j,l} \{ \sigma_j\sigma_l\omega_i(\sigma_i, \sigma_{i+1})p(\{\sigma^N\}, t) - \sigma_j\sigma_l\omega_i(\sigma_{i+1}, \sigma_i)p(\hat{T}_i\{\sigma^N\}, t) \} \quad (8)$$

where $r_{j,l} = \langle \sigma_j\sigma_l \rangle$. Clearly $r_{i,i} = 1$.

Noting that the only non-vanishing terms in the summation are for $i=j, j-1, l$ and $l-1$ and assuming translational invariance (i.e. $r_h \equiv r_{j,l}$ where $h=l-j$) equation (8) can be rewritten as follows:

$$\frac{dr_1}{dt} = \frac{2\alpha}{1-\beta^2} \{ -r_1 + r_2 + \beta(1-r_3 + \langle\sigma_0\sigma_1\sigma_2\sigma_3\rangle - \langle\sigma_0\sigma_1\sigma_2\sigma_2\rangle) + \beta^2(\langle\sigma_0\sigma_2\sigma_3\sigma_3\rangle - \langle\sigma_0\sigma_1\sigma_3\sigma_3\rangle) \} \quad (9a)$$

and $h \geq 2$

$$\begin{aligned} \frac{dr_h}{dt} = & \frac{2\alpha}{1-\beta^2} \{ -2r_h + (1+\beta)(r_{h+1} + r_{h-1}) - \beta(r_{h+2} + r_{h-2} - \langle\sigma_0\sigma_1\sigma_2\sigma_{h+2}\rangle) + 2\langle\sigma_0\sigma_1\sigma_2\sigma_{h+1}\rangle \\ & - \langle\sigma_0\sigma_1\sigma_2\sigma_h\rangle + \beta^2(\langle\sigma_0\sigma_2\sigma_3\sigma_{h+2}\rangle + \langle\sigma_0\sigma_1\sigma_3\sigma_{h+1}\rangle - \langle\sigma_0\sigma_1\sigma_3\sigma_{h+2}\rangle - \langle\sigma_0\sigma_2\sigma_3\sigma_{h+1}\rangle) \} \end{aligned} \quad (9b)$$

The evaluation of the fourth order correlations cannot be made without approximation. Marsh³ has given an expression for the general 'n-spin' correlation function for an Ising chain in equilibrium with an external field. Assuming that the field is the same at each spin we set $S = \langle \sigma_i \rangle_{eq} = \langle \sigma \rangle_{eq}$ and $R^2 = 1 - S^2$. For the two and four spin correlations, Marsh's expression then reduces to:

$$\langle \sigma_i \sigma_{i+l} \rangle_{eq} = S^2 + R^2 \beta^l \tag{10a}$$

and

$$\langle \sigma_i \sigma_{i+l} \sigma_{i+l_1+l_2+l_3} \rangle_{eq} = S^4 + S^2 R^2 (\beta^{l_1} + \beta^{l_2} + \beta^{l_3} - \beta^{l_1+l_2} - \beta^{l_2+l_3} + \beta^{l_1+l_2+l_3}) + R^4 \beta^{l_1+l_2} \tag{10b}$$

If $S < 1$ so that terms in S^2 and S^4 are negligible and $R^2 \simeq 1$, then:

$$\langle \sigma_i \sigma_{i+l} \rangle_{eq} \simeq \beta^l$$

and

$$\langle \sigma_i \sigma_{i+l} \sigma_{i+l_1+l_2+l_3} \rangle_{eq} \simeq \langle \sigma_i \sigma_{i+l_1+l_2+l_3} \rangle_{eq} \tag{11}$$

This approximation is equivalent to the assumption $\langle \sigma_i \sigma_{i+l} \rangle_{eq} \simeq \langle \sigma_i \sigma_{i+l} \rangle_{eq}^l$, since we also have $\langle \sigma_i \sigma_{i+1} \rangle_{eq} \simeq \beta$ in this case. In fact, for zero-field equilibrium, the result is exact, namely:

$$\begin{aligned} \langle \sigma_i \rangle_{eq} & \\ \langle \sigma_i \sigma_{i+1} \rangle_{eq} &= \beta && \text{(zero-field equilibrium)} \\ \langle \sigma_i \sigma_{i+1} \rangle_{eq} &= \beta^l = \langle \sigma_i \sigma_{i+1} \rangle_{eq}^l && \tag{12} \end{aligned}$$

A justification of the application of these formulae as approximations in non-equilibrium situations has been attempted by Orwoll and Stockmayer¹. We restrict their use to the reduction of the four 'spin' functions to two 'spin' functions, thereby hoping to minimize the effect of the error introduced by the approximation.

Accordingly equations (9a) and (9b) reduce to:

$$\frac{dr_1}{dt} = -\frac{2\alpha}{1-\beta^2} \{ (1+\beta+\beta^2)r_1 - (1+\beta+\beta^2)r_2 - \beta(1-r_3) \} \tag{13a}$$

and ($h \geq 2$):

$$\frac{dr_h}{dt} = -\frac{2\alpha}{1-\beta^2} \{ 2(1+\beta+\beta^2)r_h - (1+2\beta+\beta^2)(r_{h+1} + r_{h-1}) + \beta(r_{h+2} + r_{h-2}) \} \tag{13b}$$

Equations (13a) and (13b) can be rewritten as a single matrix equation as follows:

$$\frac{d\vec{r}}{dt} = \{ (1+\beta^2)\underline{L}_0 + \beta\underline{L}_1 \} \vec{r} + \beta \vec{p}_0 \tag{14}$$

where

$$\vec{r} = \begin{pmatrix} r_1 \\ r_2 \\ \cdot \\ \cdot \\ \cdot \\ r_{N-1} \end{pmatrix} \quad \vec{p}_0 = \begin{pmatrix} 1 \\ -1 \\ 0 \\ \cdot \\ \cdot \\ 0 \end{pmatrix}$$

$$\underline{L}_0 = \begin{pmatrix} -1 & 1 & 0 & 0 & 0 & \dots & 0 & 0 & 0 & 0 \\ 1 & -2 & 1 & 0 & 0 & \dots & 0 & 0 & 0 & 0 \\ 0 & 1 & -2 & 1 & 0 & \dots & 0 & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & 0 & \dots & 0 & 1 & -2 & 1 \\ 0 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & 1 & -2 \end{pmatrix}$$

$$\underline{L}_1 = \begin{pmatrix} -1 & 1 & -1 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 2 & -2 & 2 & -1 & 0 & 0 & 0 & \dots & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 2 & -2 & 2 & -1 & 0 & 0 & \dots & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 2 & -2 & 2 & -1 & 0 & \dots & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & 0 & -1 & 2 & -2 & 2 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & -1 & 2 & -2 & 2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & 0 & 0 & 0 & -1 & 2 & -2 & 0 \end{pmatrix}$$

$$\tau = \frac{2\alpha}{1 - \beta^2 t} \tag{15}$$

the order of the matrices and vectors being $N - 1$.

The equilibrium solution of equation (14) is $r_h = \beta^h$. In the particular case, where $r_h(0) = \beta_0^h$ and we neglect terms of order β_0^2 [i.e. $r_1(0) = \beta_0$ and $r_h(0) = 0$ for $h \geq 2$], and the bonds in the chain are not correlated at $t = \infty$ (that is, $\beta = 0$), it is possible to find an analytical solution of equation (14). Such a solution, as may readily be verified, is:

$$r_h(\tau) = \beta_0 \{ I_{h-1}(2\tau) - I_h(2\tau) \} e^{-2\tau} \quad (h \geq 1) \tag{16}$$

where the I_h are Bessel functions of imaginary argument, given by:

$$I_h(x) = i^{-h} J_h(ix) \tag{17}$$

Although this is clearly not the most interesting case, it shows the sort of mathematics involved in the problem and resembles the case treated by Glauber². To get a solution for the general problem, we will use perturbation theory. Assume we subject our system to a periodic temperature perturbation (for instance through the passage of an ultrasonic wave). The net result will be a deviation from equilibrium. That is, we put:

$$\beta = \beta_{Av} (1 + \delta e^{i\omega\tau}), \tag{18}$$

$$\vec{r} = \vec{r}_{Av} + (\delta \beta_{Av} e^{i\omega\tau}) \vec{\eta}, \tag{19}$$

where $\vec{\eta}$ is the response function, ω the frequency of the perturbation, β_{Av} the equilibrium value of the correlation, δ is a measure of the intensity of the perturbation and \vec{r}_{Av} is the $(N - 1)$ dimensional vector whose n th component is β_{Av}^n .

Substitution of equations (18) and (19) in equation (14) and linearization of the resulting equation in $\delta \beta_{Av}$ (which is a very good approximation) leads to:

$$i\omega \vec{\eta} = \{ (1 + \beta_{Av}^2) \underline{L}_0 + \beta_{Av} \underline{L}_1 \} \vec{\eta} + \{ \underline{L}_1 + 2\beta_{Av} \underline{L}_0 \} \vec{r}_{Av} + \vec{p}_0 \tag{20}$$

The first few equations for η_1, η_2 etc. are irregular and the matrices are unsymmetrical. Specifically, η_1 is to be determined, since it is essentially the relaxational specific heat and this is the quantity related to the ultrasonic absorption measurements. Clearly, the solution to this problem is mathematically more difficult than the one for the average value of the bond directions given by Orwoll and Stockmayer.

The eigenvalues and eigenfunctions of \underline{L}_0 can be readily obtained. They are given by:

$$\omega_k = 2(1 - \cos k), \quad (21)$$

and $\vec{\xi}_k$, the $(N-1)$ dimensional vector whose n th component is:

$$\xi_{k,n} = C e^{ik/2} \cos k(n - \frac{1}{2}) \quad (22)$$

C being a normalization constant. So far we have only considered the case of a finite chain but the extension to an infinite one represents no problem. The range of k values and the constant C depend on whether the chain is finite or infinite. In the former case

$$k = \frac{2n+1}{2N-1} \pi \quad (n=0, 1, 2, \dots, N-2) \quad (23)$$

$$C_1 = \frac{2}{(2N-1)^2} \quad (24)$$

Whereas in the latter k becomes a continuous variable in the interval $[0, \pi]$ and:

$$C_{inf} = \frac{2}{(2\pi)^2} \quad (25)$$

The eigenvectors $\vec{\xi}_k$ form a complete orthonormal set and hence we can expand $\vec{\eta}$ in terms of them:

$$\vec{\eta} = \sum_k a_k \vec{\xi}_k, \quad (26)$$

for the finite chain and

$$\vec{\eta}_{inf} = \int_0^\pi A(k) \vec{\xi}_k dk \quad (27)$$

for the infinite one. In what follows we will consider the case of a finite chain, bearing in mind that the extension to the infinite chain involves only the replacement of summations by integrals and of C_1 by C_{inf} . We will also assume N to be very large to avoid treating the end-effects, but this represents no loss of generality and simplifies the mathematical treatment. Substitution of equations (26) in (20) and multiplication of the resulting equation by $\vec{\xi}_k^*$, gives:

$$a_k = \beta_{Av} \sum_k \left\{ \frac{\vec{\xi}_k^* \cdot \underline{L}_1 \vec{\xi}_k}{i\omega + (1 + \beta_{Av}^2)\omega_k} \right\} a_k + \frac{\vec{\xi}_k^* \cdot \{(\underline{L}_1 + 2\beta_{Av}\underline{L}_0)\vec{r}_{Av} + \vec{\rho}_0\}}{i\omega + (1 + \beta_{Av}^2)\omega_k} \quad (28)$$

where $\vec{\xi}_k$ is the $(N-1)$ dimensional vector whose n th component is $\xi_{k,n}$ and we have made use of the fact that $\underline{L}_0 \vec{\xi}_k = -\omega_k \vec{\xi}_k$ and $\vec{\xi}_k^* \cdot \vec{\xi}_k = \delta_{k,k}$. Performing the matrix operations, we obtain:

$$a_k = C_1 e^{-ik/2} \left\{ \frac{(1 - \beta_{Av} - \beta_{Av}^2 + \beta_{Av}^3) \cos\left(\frac{k'}{2}\right) + \left(\cos\frac{3k'}{2} - \beta_{Av} \cos\frac{k'}{2}\right) \left(\frac{2\beta_{Av} - 2\beta_{Av}^3 + \beta_{Av} - 1}{1 + \beta_{Av}^2 - 2\beta_{Av} \cos k'}\right) - 2C_1 \beta_{Av} \sin\frac{k'}{2} \sum_k a_k e^{ik/2} \cos\frac{k}{2}}{2\omega + 2(1 + 2\beta_{Av} + \beta_{Av}^2)(1 - \cos k') - 2\beta_{Av}(1 - \cos 2k')} \right\} \quad (29)$$

Equation (29) has the form of a Fredholm's integral equation of the second kind with a separable kernel:

$$\varphi = f(x) + \lambda F(x) \int_a^b G(y) \varphi(y) dy \quad (30)$$

where

$$\varphi(x) = a_x \quad (31)$$

$$f(x) = C_1 e^{-ix/2} \left\{ \frac{(1 - \beta_{Av} - \beta_{Av}^2 + \beta_{Av}^3) \cos \frac{x}{2} + \left(\cos^3 \frac{x}{2} - \beta_{Av} \cos \frac{x}{2} \right) \left(\frac{2\beta_{Av} - 2\beta_{Av}^3 + \beta_{Av}^4 - 1}{1 + \beta_{Av}^2 - 2\beta_{Av} \cos x} \right)}{i\omega + 2(1 + 2\beta_{Av} + \beta_{Av}^2)(1 - \cos x) - 2\beta_{Av}(1 - \cos 2x)} \right\} \quad (32)$$

$$\lambda = \beta_{Av} \quad (33)$$

$$F(x) = \frac{2C_1^2 \sin \frac{x}{2} \sin x e^{-ix/2}}{i\omega + 2(1 + 2\beta_{Av} + \beta_{Av}^2)(1 - \cos x) - 2\beta_{Av}(1 - \cos 2x)} \quad (34)$$

$$G(y) = e^{iy/2} \cos(y/2) \quad (35)$$

The solution of (30) is⁴:

$$\varphi(x) = f(x) + \frac{\lambda F(x) \int_a^b G(y) f(y) dy}{1 - \lambda \int_a^b F(x) G(x) dx} \quad (36)$$

This expression would in principle give us the desired result for η_1 after substitution in equation (26). However, we note that $\eta_1(\omega)$ is given by (see equations 26 and 22):

$$\eta_1(\omega) = C_1 \sum_k a_k e^{ik/2} \cos \frac{k}{2} \quad (37)$$

and this fact makes it unnecessary to use equation (36). From equation (29), after multiplication by $C_1 e^{ik/2} \cos k'/2$ and summation over k' , we obtain:

$$\eta_1(\omega) = \frac{\sum_{k'} \left\{ \frac{X(k')}{i\omega + Y(k')} \right\}}{\frac{1}{C_1^2} + \beta_{Av} \sum_{k'} \left\{ \frac{Z(k')}{i\omega + Y(k')} \right\}} \quad (38)$$

where:

$$X(k) = (1 - \beta_{Av} - \beta_{Av}^2 + \beta_{Av}^3) \cos^2 \frac{k}{2} + \left(\cos^3 \frac{k}{2} - \beta_{Av} \cos \frac{k}{2} \right) \left(\frac{2\beta_{Av} - 2\beta_{Av}^3 + \beta_{Av}^4 - 1}{1 + \beta_{Av}^2 - 2\beta_{Av} \cos k} \right) \quad (39)$$

$$Y(k) = 2(1 + 2\beta_{Av} + \beta_{Av}^2)(1 - \cos k) - 2\beta_{Av}(1 - \cos 2k) \quad (40)$$

$$Z(k) = \sin^2 k \quad (41)$$

Apart from a proportionality constant (which we will call K_1) the ultrasonic absorption α/f^2 will be governed⁵ by $-\eta_1''(\omega)/\omega$ where η_1'' is the imaginary component of η_1 . That is:

$$\frac{\alpha}{f^2(\omega)} = -K_1 \frac{\eta_1''(\omega)}{\omega}$$

$$= K_1 \left[\frac{\left\{ \sum_k \frac{X(k)}{\omega^2 + Y^2(k)} \right\} \left\{ \frac{1}{C_1^2} + \beta_{Av} \sum_k \frac{Z(k)Y(k)}{\omega^2 + Y^2(k)} \right\}}{\left\{ \frac{1}{\rho_1^2} + \beta_{Av} \sum_k \frac{Z(k)Y(k)}{\omega^2 + Y^2(k)} \right\}^2 + \beta_{Av}^2 \omega^2 \left\{ \sum_k \frac{Z(k)}{\omega^2 + Y^2(k)} \right\}^2} - \frac{\beta_{Av} \left\{ \sum_k \frac{X(k)Y(k)}{\omega^2 + Y^2(k)} \right\} \left\{ \sum_k \frac{Z(k)}{\omega^2 + Y^2(k)} \right\}}{\left\{ \frac{1}{C_1^2} + \beta_{Av} \sum_k \frac{Z(k)Y(k)}{\omega^2 + Y^2(k)} \right\}^2 + \beta_{Av}^2 \omega^2 \left\{ \sum_k \frac{Z(k)}{\omega^2 + Y^2(k)} \right\}^2} \right] \quad (42)$$

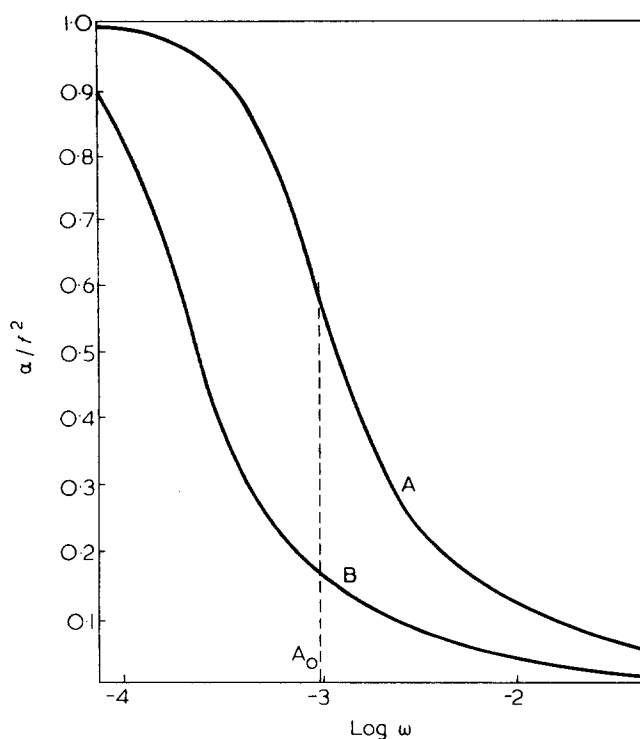


Figure 1 Effect of the value of the correlation on the acoustic absorption for a fixed chain length ($N = 51$). A; $\beta_{Av} = 0$; B, $\beta_{Av} = 0.5$. Both curves have been normalized for $\omega = 0$. The frequency units are arbitrary $A_0 = \log \omega_0$, where ω_0 is the frequency corresponding to the first Rouse mode for the case $\beta_{Av} = 0$

RESULTS AND DISCUSSION

For an infinite random chain, we obtain the following expression for the acoustic absorption:

$$\frac{\alpha}{f^2}(\omega) = K_{1inf} \int_0^{\pi} \frac{\sin^2 k dk}{\mu(1 - \cos k)^2 + \omega^2} \quad (\beta_{Av} = 0) \quad (43)$$

It is clear that $\alpha/f^2 \rightarrow \infty$ as $\omega \rightarrow 0$ in this case, which means that the main contribution to the acoustic absorption comes from the slowest modes and thus a Rouse-like behaviour is obtained.

Computer calculations of α/f^2 as given by (42) have been carried out for different chain lengths, (i.e. different molecular weight samples) and different values for the bond correlations. The results show an increase in the amplitude of the acoustic absorption with increasing molecular weight and also, for a fixed chain length, an increase in this amplitude with increasing bond correlations. Again, the main contribution to the acoustic absorption comes from the slowest modes and for the case $\beta_{Av} = 0$ the same Rouse-like behaviour is obtained. However, as the value of the correlation is increased, the relaxation is pushed to a lower frequency. This effect can be seen in Figure 1, where we have plotted the acoustic absorption α/f^2 as a function of frequency for a chain having $N = 51$ and $\beta_{Av} = 0$ and $\beta_{Av} = 0.5$, respectively.

Acoustic absorption experiments on dilute polystyrene solutions⁶ have shown the existence of an almost ideal Debye-type relaxation in the lower MHz region which is molecular weight independent (at least for molecular weights above some critical value). For molecular weights of the order of 10 000, this relaxation takes place at a frequency about two decades higher than the observed Rouse-like viscoelastic relaxation in the same system. We therefore find that the results of the present model, where no such high frequency behaviour is obtained, are not able to explain the experimental facts.

CONCLUSIONS

The analogue of the ultrasonic energy absorption response function in the simple hopping model does not show high frequency behaviour of the type found experimentally. The relaxation is in fact dominated by a Rouse-like spectrum as are the viscosity analogues in the same model, which are related to $\langle \sigma_i \rangle$. A more distinct high frequency feature can be produced by allowing a spectrum of hops of blocks of increasing size and gradually diminishing probability to take place. There is no simple physical idea underlying such a device in the way that the notion that a vacancy in the solvent leads to the idea of monomeric hops. Even if such a spectrum of hops is introduced, difficulties in producing the experimental

features of the viscoelastic and ultrasonic relaxation curves are still found. These difficulties are similar to those discussed by Pugh and Jones⁷. The flattening of the $1/\tau$ vs. k curve which results from introducing hops involving blocks of different sizes is similar to that produced by introducing a linear internal viscosity term into the Langevin equation which is the starting point of the Rouse model. Recent work⁸⁻¹⁰ has shown that the qualitative features observed experimentally in the relaxation behaviour of polymers are reproduced much more naturally in the solutions of diffusion equations with intermonomer rotational barrier type potentials. The results of the present work may therefore be taken as providing further indirect confirmation that the motion of a polymer in solution, at least up to a frequency $\sim 10^7$ or 10^8 Hz is best treated from the point of view of a realistic diffusion equation.

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