Internal viscosity–normal mode description of ultrasonic absorption in dilute polymer solutions

D. Pugh and D. A. Jones

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK

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A normal mode model of ultrasonic absorption in dilute polymer solutions is constructed by including internal viscosity and stiffness terms in the polymer equations of motion. The normal mode Smoluchowski equation is solved and the relaxing specific heat calculated by averaging over two different energy absorption terms: a bending force term of the type used by Harris and Hearst and an energy term resulting from a change in the end to end distance of the polymer. The results are then compared with some recent ultrasonic absorption measurements of Cochran, Dunbar, North and Pethrick on dilute polystyrene–toluene solutions. We find that both specific heat terms provide an explanation of the shape, position and molecular weight independence of the single relaxation for large molecular weights, but are unable to describe the molecular weight dependence observed by Cochran *et al.* when the molecular weight goes below 10 000. There is also some difficulty in obtaining exact numerical agreement between the calculated and observed absorption amplitudes.

INTRODUCTION

Recent acoustic absorption experiments by Cochran, Dunbar, North and Pethrick[1] on dilute polystyrene–toluene solutions have shown the existence of an almost ideal Debye-type relaxation in the low MHz range which is independent of the molecular weight of the polymer (at least for molecular weights above some critical value). Similar relaxations have also been observed in dielectric, nuclear magnetic, and resonance fluorescence experiments.

Because of the molecular weight independence of this relaxation, the most popular explanation is in terms of a 'local mode', i.e. a non-cooperative localized movement of some small segment of the backbone. The most likely mechanism for this local mode motion is generally considered to be the crankshaft model of Shatzki[2], where four backbone carbon atoms rotate as a single unit and leave the remainder of the molecule completely undisturbed. The difficulties involved in such a crankshaft model have been discussed by Jones and Pugh[3].

Recently however Pugh and MacInnes[4] have shown that an explanation in terms of cooperative modes is still possible by including in the equation of motion an internal viscosity term similar to the one used by Peterlin[5] to obtain a finite value for the limiting high frequency intrinsic viscosity. The introduction of this term results in a modification of the relaxation spectrum so that it now contains both low frequency molecular weight dependent modes and also modes associated with a molecular weight independent peak in the relaxation time spectrum. The ability of these two contrasting theories to provide a qualitative description of the molecular weight independent high frequency relaxation has been discussed recently by MacInnes and North[6].

The significance of the peak in the relaxation time spectrum will depend on the contribution made by each mode to the particular quantity being observed. In this paper we present a quantitative treatment of this problem for the ultrasonic absorption experiment.

Model

Our starting point is the familiar Rouse–Zimm[7,8] bead and spring model of the polymer chain. We replace the molecule by a set of $N-1$ identical segments joining N identical beads. Each segment contains sufficient monomer units so that the equilibrium separation of the ends of each segment is given by a Gaussian distribution. The segments then act as 'entropy springs' and lead to a force on the jth bead of the form:

$$\mathbf{F}_{\text{entropy}} = -\epsilon_1(-\mathbf{R}_{j-1} + 2\mathbf{R}_j - \mathbf{R}_{j+1}) \tag{1}$$

where $\epsilon_1 = 3kT/a^2$ and a^2 is the mean square end to end distance of a Gaussian segment.

In a real polymer the junctions between the segments are not perfectly free joints, the potential energy barriers for internal rotation about the carbon–carbon bonds require a finite time to surmount and this leads to an internal viscosity in the molecule, which we represent by a term proportional to the rate of change of curvature of the chain, i.e.:

$$\mathbf{F}_{IV} = -\rho_{IV}\frac{\mathrm{d}}{\mathrm{d}t}\,(-\mathbf{R}_{j-1} + 2\mathbf{R}_j - \mathbf{R}_{j+1}) \tag{2}$$

where ρ_{IV} is the internal viscosity coefficient. This differs slightly from the expression used by Peterlin[5] because of the absence of the term to account for the overall rotational motion of the polymer, but is similar to the expression used by Edwards and Freed[9], and Pugh and MacInnes[4].

The cause of the relaxation in the acoustic absorption experiment is the inability of the energy absorption to remain in phase with the perturbing sound wave. To provide a mechanism for this energy absorption we introduce two additional terms into the equations of motion. The first is a bending force term used by Harris and Hearst[10]. This introduces a degree of stiffness into the polymer by requiring that the potential energy must be proportional to the square of the curvature of the chain. In a bead and spring

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model this implies a force on the jth bead of the form:

$$\mathbf{F}_{BF} = -\sigma(\mathbf{R}_{j-2} - 4\mathbf{R}_{j-1} + 6\mathbf{R}_{j-1}$$
$$4\mathbf{R}_{j+1} + \mathbf{R}_{j+2}) \quad (3)$$

where σ is the bending force constant. The term provides a very good explanation of the shape of the relaxation but is unable to provide quantitative agreement with experiment, and so we also include another term in the equation

$$\mathbf{F}_{ES} = \epsilon_2(-\mathbf{R}_{j-1} + 2\mathbf{R}_j - \mathbf{R}_{j+1}) \quad (4)$$

where ϵ_2 is a constant which is independent of temperature. This produces an energy contribution when the end to end distance of the chain is changed.

The Langevin equation for the jth bead has the form:

$$m\frac{\mathrm{d}}{\mathrm{d}t}\dot{\mathbf{R}}_j = -\xi\dot{\mathbf{R}}_j + \mathbf{F} + \vec{\eta}(t) \quad (5)$$

where m is the mass of a bead, ξ the friction coefficient, $\vec{\eta}(t)$ the fluctuating force and $\mathbf{F}$ is the intramolecular force on the bead, which is just the sum of the forces previously mentioned:

$$\mathbf{F} = \mathbf{F}_{\text{entropy}} + \mathbf{F}_{IV} + \mathbf{F}_{BF} + \mathbf{F}_{ES} \quad (6)$$

In terms of the normal modes $\mathbf{K}_n$ defined by:

$$\mathbf{K}_n = \frac{1}{(N)^{1/2}}\sum_{j=1}^{N}\mathbf{R}_j\exp\left(\frac{-2\pi i}{N}nj\right) \quad (7)$$

the equation is:

$$m\frac{\mathrm{d}}{\mathrm{d}t}\dot{\mathbf{K}}_n = -\xi'\dot{\mathbf{K}}_n + f(k_n)\mathbf{K}_n + \mathbf{A}_n(t) \quad (8)$$

where

$$\xi' = \xi + 2\rho_{IV}(1 - \cos k_n); \qquad k_n = \frac{2\pi n}{N}$$

$$f(k_n) = 2\epsilon(\cos k_n - 1) - 4\sigma(\cos k_n - 1)^2$$

with

$$\epsilon = \epsilon_1 - \epsilon_2$$

and

$$\mathbf{A}_n(t) = \frac{1}{(N)^{1/2}}\sum_{j=1}^{N}\vec{\eta}(t)\exp\left(\frac{-2\pi i}{N}nj\right)$$

From equation (8) we can now write a normal mode Smoluchowski equation of the form:

$$\frac{\partial W_n}{\partial t} = \nabla\cdot\left\{\frac{kT}{\xi'}\nabla W_n - \frac{f(k_n)}{\xi'}\mathbf{K}_n W_n\right\} \quad (9)$$

where $W_n = W_n(\mathbf{K}_{n,t})$ and the divergence and gradient are taken with respect to the coordinates of $\mathbf{K}_n$. We note that ξ' is also temperature dependent but since it multiplies every term on the right hand side its variation will not produce a first order contribution. The distribution function for the polymer will then be given by:

$$W(\mathbf{K}_1, \mathbf{K}_2, \ldots\ldots \mathbf{K}_n, t) \equiv \Pi_n W_n(\mathbf{K}_n, t) \quad (10)$$

The adiabatic passage of the sound wave will cause a small sinusoidal variation in the temperature and hence a perturbation to equation (9). To include this temperature effect we write:

$$T = T_1 + \Delta T\exp(i\omega t) \quad (11)$$

where ω is the angular frequency of the sound wave.

If the Cartesian coordinates of $\mathbf{K}_n$ are p, q and u and we define dimensionless coordinates r, s and v by:

$$r = (b_3/b_1)^{1/2}p; \quad s = (b_3/b_1)^{1/2}q; \quad v = (b_3/b_1)^{1/2}u$$

where

$$b_1 = kT/\xi' \text{ and}$$

$$b_3 = \frac{\epsilon(1 - \cos k_n) + 2\sigma(1 - \cos k_n)^2}{\xi'}$$

and also a dimensionless time variable $\upsilon = b_3 t$, then substitution of equation (11) into equation (9) gives:

$$\frac{\partial W_n}{\partial \upsilon} = \nabla^2 W_n + 2LW_n + \frac{\Delta T}{T_1}\mathrm{e}^{i\bar{\omega}\upsilon}\left\{\nabla^2 W_n + 2\beta LW_n\right\} \quad (12)$$

where

$$LW_n = 3W_n + \frac{r\partial W_n}{\partial r} + \frac{s\partial W_n}{\partial s} + \frac{v\partial W_n}{\partial v}$$

$$\beta = \left[1 + \frac{2\sigma(1 - \cos k_n) - \epsilon_2}{\epsilon_1}\right]^{-1}$$

and

$$\bar{\omega} = \frac{\omega}{b_3}$$

Calculation of specific heat

To solve equation (12) we first define a new function $P(r,s,v:\upsilon)$ as follows

$$W(r,s,v:\upsilon) = \exp[-\tfrac{1}{2}(r^2 + s^2 + v^2)]\,P(r,s,v,:\upsilon) \quad (13)$$

This ensures that the unperturbed spatial operator in equation (12) is now in self-adjoint form. We then assume that P can be written as the sum of the equilibrium distribution P_0 and a correction term P_1, linear in $\Delta T/T_1$ and having a time dependence $\exp(i\bar{\omega}\upsilon)$. i.e.

$$P(r,s,v:\upsilon) = P_0(r,s,v) + \frac{\Delta T}{T_1}\exp(i\bar{\omega}\upsilon)P_1(r,s,v) \quad (14)$$

An expression for P_1 is easily found by expanding in the eigenfunctions of the unperturbed operator; we find:

$$P_1(r, s, v) = \sum_{l,m,n=0}^{\infty} a_{l,m,n}\phi_l(r)\phi_m(s)\phi_n(v) \qquad (15)$$

where the ϕs are Hermite functions and

$$a_{l,m,n} = \frac{1-\beta}{i\bar{\omega} + \lambda_{l,m,n}} \left\{ \delta_{l-2,0,0} + \delta_{0,m-2,0} + \delta_{0,0,n-2} \right\} \qquad (16)$$

with

$$\lambda_{l,m,n} = 2(l + m + n)$$

To calculate the specific heat contribution from the rotational degrees of freedom we have to calculate the average energy stored in the chain. The energy contribution arising from a change in the end to end separation of the chain is just

$$-\tfrac{1}{2}\epsilon_2 \sum_j |\mathbf{R}_{j+1} - \mathbf{R}_j|^2 \qquad (17)$$

while the expression for the bending force energy is:

$$\tfrac{1}{2}\sigma \sum_j |-\mathbf{R}_{j-1} + 2\mathbf{R}_j - \mathbf{R}_{j+1}|^2 \qquad (18)$$

In normal mode form these become:

$$-\epsilon_2 \sum_n (1 - \cos k_n)\langle \mathbf{K}_n \cdot \mathbf{K}_n^* \rangle \qquad (19)$$

and

$$2\sigma \sum_n (1 - \cos k_n)^2 \langle \mathbf{K}_n \cdot \mathbf{K}_n^* \rangle \qquad (20)$$

respectively. The average of $|\mathbf{K}_n|^2$ is easily found from equations (15) and (16) to be:

$$\langle \mathbf{K}_n \cdot \mathbf{K}_n^* \rangle = \frac{3}{2}\frac{b_1}{b_3}\left[1 + \frac{\Delta T}{T_1} e^{i\omega t}\left(\frac{1-\beta}{1 + i\omega\tau_n'}\right)\right] \qquad (21)$$

where $\tau_n' = 1/4b_3$. When this equation is used to calculate the average spring energy we find two contributions, the first is just the normal equilibrium quadratic potential energy term and reduces to the usual $3NkT/2$ (provided $\sigma = \epsilon_1 = 0$). The second term represents the change in the stored energy caused by the temperature perturbation as the sound wave passes. If we divide this change in energy by the change in temperature, $\Delta T e^{i\omega t}$, then we define a 'rotational' specific heat C_{rot}^{ω}:

$$C_{\text{rot}}^{\omega}(ES) = \sum_{n=1}^{N} \frac{C_{ES}(n)}{1 + i\omega\tau_n'} \qquad (22)$$

where

$$C_{ES}(n) = \frac{3}{2} k\epsilon_2 \frac{[\epsilon_2 - 2\sigma(1 - \cos k_n)]}{[\epsilon_1 + 2\sigma(1 - \cos k_n) - \epsilon_2]^2}$$

The corresponding specific heat for the bending force energy is:

$$C_{\text{rot}}^{\omega}(BF) = \sum_{n=1}^{N} \frac{C_{BF}(n)}{1 + i\omega\tau_n'} \qquad (23)$$

where

$$C_{BF}(n) = \frac{3}{2} k \frac{2\sigma(1 - \cos k_n)[2\sigma(1 - \cos k_n) - \epsilon_2]}{[\epsilon_1 + 2\sigma(1 - \cos k_n)]^2}$$

Before using these results to calculate the ultrasonic absorption we have to evaluate the frequency dependence of the viscosity for this model. This is done in the next section.

Calculation of viscosity

We consider the polymer to be in a velocity field $\mathbf{v}_{0j}$ given by $\mathbf{v}_{0j} = (gy_j, 0, 0)$ where the velocity gradient $g = g_0 e^{i\omega t}$. According to Yamakawa[11] the expression for the intrinsic viscosity is then:

$$[\eta] = -\frac{N_A}{m\eta_0 g} \sum_j \langle F_{xj} Y_j \rangle \qquad (24)$$

where η_0 is the viscosity of the solvent and $-\mathbf{F}_j$ is the frictional force exerted on the jth bead by the fluid,

$$-\mathbf{F}_j = -\xi(\mathbf{v}_j - \mathbf{v}_{0j}) \qquad (25)$$

An alternate expression for this force is:

$$-\mathbf{F}_j = \nabla_j U + kT\nabla_j \ln W \qquad (26)$$

where $\nabla_j U$ represents the sum of the intramolecular forces and the second term represents the fluctuating Brownian force. This will integrate out of the final expression for the viscosity so we neglect it from here on. The intramolecular force is given by equation (6), and so the expression for the viscosity, in normal mode form, becomes:

$$[\eta] = \frac{2N_A}{M\eta_0 g} \sum_{n=1}^{N} \langle p_n q_n \rangle (1 - \cos k_n)[\epsilon - 2\sigma(1 - \cos k_n) - \rho_{IV} f(k_n)/\xi'] \qquad (27)$$

where we have used the Langevin equation to eliminate a term in $\dot{p}_n$.

To calculate $\langle p_n q_n \rangle$ we rewrite equation (9) in the form of a continuity equation:

$$\frac{\partial W_n}{\partial t} = -\nabla_n \cdot \mathbf{J}_n \qquad (28)$$

$$\text{where } \mathbf{J}_n = [f(k_n)\mathbf{K}_n W_n - kT\nabla_n W_n]/\xi' \qquad (29)$$

In the presence of a velocity field $\mathbf{v}_{0j}$ this expression needs to be modified by the addition of the term $\mathbf{v}_{0j}W$, in normal mode space this is simply $gq_n W_n\mathbf{i}$, and so the diffusion equation becomes

$$\frac{\partial W_n}{\partial t} = -gq_n\frac{\partial W_n}{\partial p_n} - \frac{f(k_n)}{\xi'}\nabla\cdot(\mathbf{K}_n W_n) + \frac{kT}{\xi'}\nabla^2 W_n \qquad (30)$$

The equation is now identical to Yamakawa's[11] equation (33, 26) so we can use his result to find:

$$\langle p_n q_n\rangle = \frac{kTg}{f(k_n)}\,\frac{\tau_n'}{1 + i\omega\tau_n'} \qquad (31)$$

where the τ_n' is the same as defined in equation (21). The expression for the intrinsic viscosity now becomes:

$$[\eta] = \frac{RT}{m\eta_0}\sum_{n=1}^{N}\frac{\tau_n}{1 + i\omega\tau_n'} \qquad (32)$$

The result differs from the expressions given by Cerf[12] and Peterlin[5] and from that of MacInnes[13].

The form of τ_n' differs from the modified relaxation times of these authors because of the inclusion of the energy terms in the diffusion equation. If only the internal viscosity term is retained the τ_n' become identical with those of MacInnes[13].

However, formula (32) has the unmodified τ_n as the multiplicative factor in the numerator whereas MacInnes has τ_n'. In ref 13 two derivations of the viscosity formula are given. The first employs Kirkwood's[14] theory of the friction coefficient, but the integrals identified as internal friction constants are not, in fact, analogous to the type of expression associated with friction constants by Kirkwood.

The second derivation, from a correlation function, is equivalent to the treatment given here (based on that of Yamakawa[11]) but the internal viscosity force has implicitly been omitted in the expression equivalent to the right hand side of equation (26).

The fundamental difference between the present treatment and the Cerf–Peterlin scheme is that we do not include a non-relaxing contribution associated with rigidity of the whole molecule. Since it is assumed to be non-relaxing its omission is not important in the study of high frequency relaxation phenomena. A rigorous treatment of such a term requires a much more explicit analysis of the effect of the intramolecular potentials.

Ultrasonic absorption

We begin by calculating the contribution to the absorption from the rotational degrees of freedom. The displacement of the medium from its equilibrium position during the passage of the sound wave can be represented by an expression of the form:

$$\chi = \chi_0\exp[i\omega(t - x/U)]\exp(-\alpha x) \qquad (33)$$

where U is the velocity of the wave and α the absorption coefficient. If we define a complex velocity U^* this can be written:

$$\chi = \chi_0\exp[i\omega(t - x/U^*)] \qquad (34)$$

where

$$\frac{1}{U^*} = \frac{1}{U} - \frac{i\alpha}{\omega} \qquad (35)$$

In the low frequency limit when no relaxation is present the velocity U_0 is given by:

$$U_0^2 = \frac{\gamma}{\rho\beta_T} \qquad (36)$$

where ρ is the density, β_T the isothermal compressibility and γ the ratio of specific heat at constant pressure to specific heat at constant volume. Combining (35) and (36) gives:

$$\frac{U_0^2}{U^*} = \left(\frac{U_0}{U} - \frac{i\alpha U_0}{\omega}\right)^2 = \frac{\gamma}{\gamma_\omega} \qquad (37)$$

where γ_ω is the effective heat capacity ratio for a sound wave of frequency ω, i.e. $\gamma_\omega = C_p^\omega/C_v^\omega$. The specific heats will have contributions from both the solvent and the dissolved polymer, hence we write:

$$C_p^\omega = C_p^L + C_p^\omega(\text{poly}) \qquad (38)$$

where C_p^L is the specific heat of the solvent, which we take to be independent of frequency, and C_p^ω (poly) is the specific heat contribution from the polymer, which of course is strongly dependent on frequency. In fact:

$$C_p^\omega(\text{poly}) = C_{p\infty} + \sum_n \frac{C_i(n)}{1 + i\omega\tau_n'} \qquad (39)$$

where the second term represents the contribution from the rotational degrees of freedom and $C_i(n)$ stands for either the bending force form of this specific heat given by equation (23) or the energy spring form of equation (22). $C_{p\infty}$ represents the non-relaxing contribution form all the other degrees of freedom. The corresponding expressions for C_v are obvious. If we define A and B by:

$$A = \sum_{n=1}^{N}\frac{C_i(n)}{1 + \omega^2\tau_n'^2}$$

$$B = \sum_{n=1}\frac{C_i(n)\omega\tau_n'}{1 + \omega^2\tau_n'^2} \qquad (40)$$

then

$$\frac{\gamma}{\gamma_\omega} = \frac{C_p}{C_v}\left(\frac{C_v^L + C_{v\infty} + A - iB}{C_p^L + C_{p\infty} + A - iB}\right) \qquad (41)$$

where C_p and C_v are the low frequency specific heats.

The expression for α is found by equating the imaginary parts of equations (41) and (37) and assuming that the solvent contribution to the specific heat is far larger than the polymer contribution. We also make the usual approximation that the velocity dispersion is small (i.e. $U \approx U_0$). This gives:

$$\left(\frac{\alpha}{f^2}\right)_{\text{rot}} = \frac{2\pi^2}{U_0}\left(\frac{\gamma^L - 1}{C_p^L}\right)\sum_{n=1}^{N}\frac{C_i(n)\tau_n'}{1 + \omega^2\tau_n'^2} \tag{42}$$

where

$$\gamma^L = C_p^L/C_v^L \text{ and } f = \omega/2\pi$$

We now turn our attention to the classical viscous absorption. For a fluid with shear viscosity η_s and bulk viscosity η_v this is simply:

$$\frac{\alpha}{f^2} = \frac{2\pi^2}{\rho U_0^3}\left(\frac{4}{3}\eta_s + \eta_v\right) \tag{43}$$

(For polymer solutions however see the recent paper by Metia and Freed[15].)

The normal classical expression also includes a term resulting from the thermal conductivity of the medium but this is negligible in our case. We consider the contributions from the toluene and polystyrene separately.

Toluene. This contribution is non-relaxing. The ratio of bulk to volume viscosity is tabulated in Nozdrev[16]. At 30°C we have $\eta_v/\eta_s = 15.5$; ρ, U_0 and η_s are given by Cochran *et al.* to be: $\rho = 0.86$ g/cm^3; $U_0 = 1.3 \times 10^3$ m/sec and $\eta_s = 0.520$ cp, which gives

$$\alpha/f^2 = 91.5 \times 10^{-15} \text{ sec}^2/\text{m} \tag{44}$$

Polystyrene. There are no experimental figures for the ratio of bulk to shear viscosity in polystyrene so we follow the example of Cochran *et al.*[1] and take $\eta_v/\eta_s = 5/3$. Using the values for the constants given above we find:

$$\frac{\alpha}{f^2} = 31.3\, nkT \sum_{n=1}^{N}\frac{\tau_n}{1 + \omega^2\tau_n'^2} \times 10^{-15} \text{ sec}^2/\text{m} \tag{45}$$

Before we can use this expression we have to estimate the values of the parameters ϵ_1, ξ and ρ_{IV}. The ratio ξ/ϵ_1 can be found by fitting to the zero frequency viscosity data. This gives:

$$\xi/\epsilon_1 = 1.6 \times 10^{-9} \text{ sec}$$

which agrees well with rough estimates of ξ and ϵ_1 using the expressions: $\epsilon_1 = 3kT/a^2$; $\xi = 6\pi\eta_s a$ provided we take 'a' to be approximately 10 Å, which corresponds to 10 monomer units in the subchain. (We take the monomer length for polystyrene to be about 3 Å.) To estimate ρ_{IV} we look at the expression for τ_n' given by equation (21). This can be written as the sum of two parts:

$$\tau_n' = \xi/[4\epsilon(1 - \cos k_n) + 8\sigma(1 - \cos k_n)^2] + \rho_{IV}/[2\epsilon + 4\sigma(1 - \cos k_n)] \tag{46}$$

The first is the normal Rouse mode expression for the relaxation times, (modified by the bending force constant σ) while the second corresponds to a molecular weight independent relaxation with relaxation time τ, given by $\tau = \rho_{IV}/2\epsilon$. (We ignore the dependence on molecular weight introduced by the bending force term in a first approximation). Taking this molecular weight independent relaxation to occur at 20 MHz gives:

$$\tau = \frac{\rho_{IV}}{2\epsilon} = 8.0 \times 10^{-9} \text{ sec}$$

We are now in a position to calculate the shape of the absorption curve for the two different energy terms, and we discuss the results of these calculations in the next section.

RESULTS AND DISCUSSION

The argument for the molecular weight independent relaxation goes as follows: if there is a value of n, equal to n_0, for which

$$2\rho_{IV}\left[1 - \cos\left(\frac{n\pi}{Z}\right)\right] \gg \xi \tag{47}$$

then, for n greater than n_0, τ_n' has a constant value given by;

$$\tau_n' \approx \frac{\rho_{IV}}{2\epsilon}\left\{1 - \frac{2\sigma}{\epsilon}\left[1 - \cos\left(\frac{n\pi}{Z}\right)\right]\right\} \tag{48}$$

(Note that we are considering a ring polymer with cyclic boundary conditions, hence we must put $N = 2Z$, where Z is now the number of beads in the polymer). The contribution to the ultrasonic absorption from all the modes having n greater than n_0 will then produce a single molecular weight independent Debye type relaxation, while the modes for which n is less than n_0 will produce a molecular weight dependent Rouse-like contribution which will appear similar to the absorption due to the viscous relaxation.

We can see this contrasting behaviour quite clearly in *Figures 3* and *4* which show the calculated acoustic absorption for a 100 000 molecular weight sample of polystyrene in toluene. The concentration is 2.5% w/v and we are using the energy spring form of the specific heat given by equation (22). *Figure 1* shows f_n' *versus n*. The Rouse spectrum f_n, is shown for comparison. For small n values the spectrum follows the Rouse curve, while above $n = 30$ the condition of equation (47) is met and f_n' is constant at 20 MHz. *Figure 2* shows the contribution to $(\alpha/f^2)_{\text{rot}}$ from the first 30 modes. We see a broad relaxation starting at the first Rouse mode which looks very similar to the viscous contribution to the relaxation shown in *Figure 3*. The contribution from the remaining 70 modes is shown in *Figure 4*, and clearly fits a single Debye relaxation at 20 MHz. The total acoustic absorption is shown in *Figure 5*.

A similar set of results is obtained for the 20 000 *MW* sample. In this case f_n' reaches a constant value at $n = 6$ instead of $n = 30$. The rotational contribution from the first 6 modes again displays a Rouse-like spectrum with an amplitude very much dependent on molecular weight while the contribution from modes 7 to 20 produces a single Debye-type relaxation which remains independent of the change in molecular weight, the relaxation again occurring at 20 MHz with an amplitude of approximately 40×10^{-15} sec^2/m, as in *Figure 4*. The independence of this contribution to a

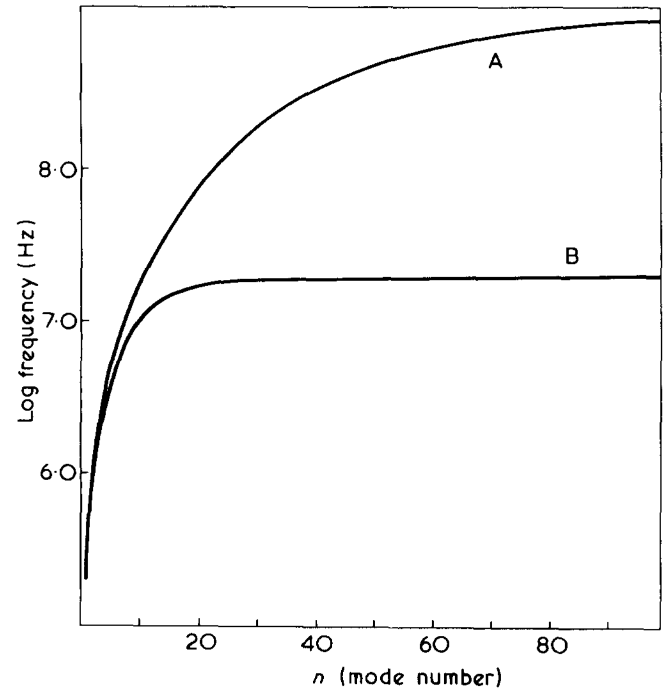

Figure 1 Relaxation frequencies f_n' and f_n *versus* mode number n for the 100 000 molecular weight sample. A, f_n; B, f_n'. $Z = 100$

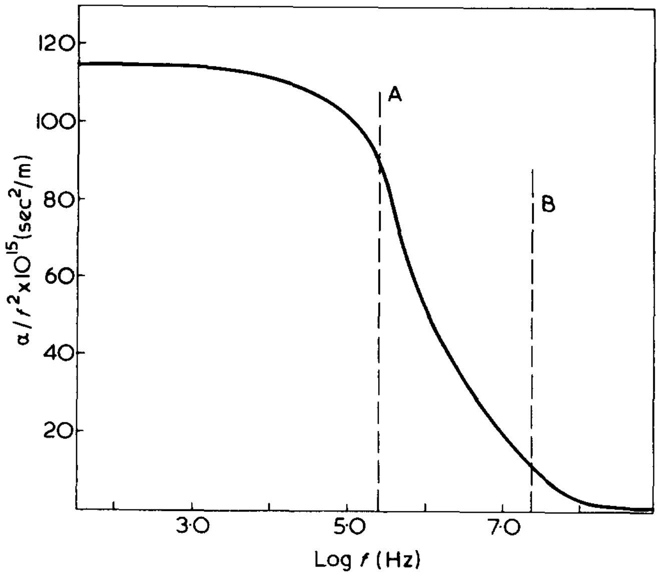

Figure 2 $(\alpha/f^2)_{rot}$ *versus* frequency. The energy spring form of the specific heat has been used and only the first 30 modes are included in the summation. *MW* = 100 000. A, 1st Rouse mode; B, acoustic mode

change in molecular weight is the main prediction of the internal viscosity – normal mode description.

For molecular weights below 10 000 the results of Cochran *et al.*[1] indicate that the absorption starts to become molecular weight dependent, with the absorption frequency increasing and amplitude decreasing as the molecular weight is lowered. The model described here is unable to account for these results. From equation (46) we can see that, for very small Z, f_n' will have a constant value of $\rho_{IV}/2\epsilon$ irrespective of the value of n, so the relaxation will continue to occur at 20 MHz. There is a slight molecular weight effect below 10 000 but not in the right direction. For the 4000 *MW* sample the amplitude increases from 40 $\times 10^{-15}$ to 60 $\times 10^{-15}$ sec^2/m, in direct contrast to the experimental results.

The magnitude of the total acoustic absorption leads to another problem. To obtain agreement with experiment for the Debye-type contribution to the absorption we have to take the ratio of ϵ_2 to ϵ_1 equal to 0.72. This leads to a low frequency rotational contribution from the first few modes of about 115 (*Figure 2*), and hence a total low frequency acoustic absorption of about 270 (*Figure 5*), which is much larger than the experimentally observed value. To produce better agreement with experiment we need a specific heat term which reduces this contribution, and the one calculated from the Harris–Hearst bending force term does this. Equation (23) shows that $C_{BF}(n)$ is strongly mode dependent and tends to zero as n becomes small. This means that the contribution from the Rouse-like part of the spectrum will be negligible and only the single relaxation will survive. The amplitude of the rotational contribution to the absorption will now be governed by the parameter σ, and in fact we find that the amplitude has a maximum value when $\sigma = \epsilon_1$. Using this value of σ for the 100 000 *MW* sample results in an amplitude of 1.0×10^{-15} sec^2/m, which is now much too low (by a factor of 40). The only way we can increase the amplitude is to increase the number of degrees of freedom, i.e. Z. But even if we take Z to the maxi-

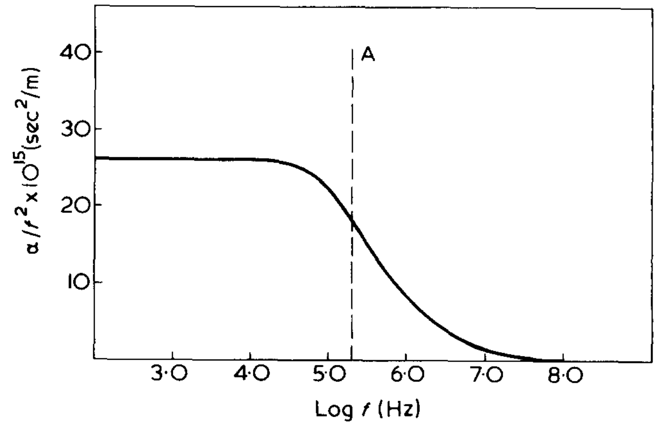

Figure 3 Classical viscous absorption *versus* frequency. *MW* = 100 000

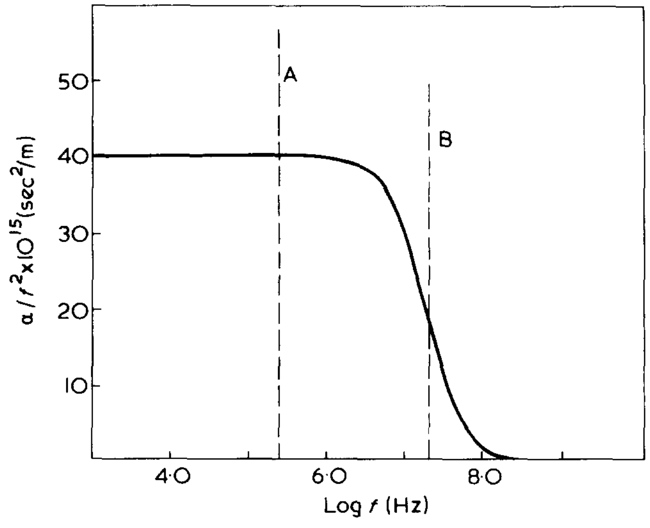

Figure 4 $(\alpha/f^2)_{rot}$ *versus* frequency. The energy spring form of specific heat has been used and the summation taken over modes 31 to 100. *MW* = 100 000. A, 1st Rouse mode; B, acoustic mode

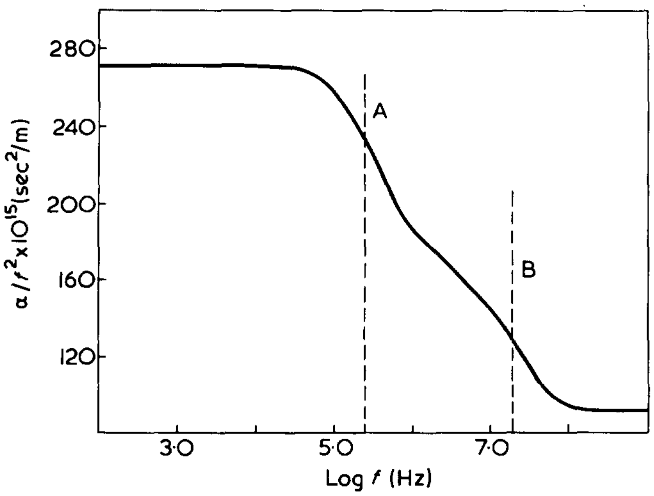

Figure 5 Total calculated acoustic absorption *versus* frequency for the 100 000 *MW* sample of Cochran *et al.* A, 1st Rouse mode; B, acoustic mode

mum possible value of 1000, which corresponds to each monomer being a 'Gaussian unit', we are still appreciably below the experimentally observed value. The other difficulty with this particular form of the specific heat is that it is also unable to explain the decrease in amplitude when the molecular weight goes below 10 000.

CONCLUSIONS

We have described a quantitative calculation of ultrasonic absorption in dilute polystyrene–toluene solutions based on the cooperative mode interpretation of Pugh and MacInnes[4]. By including an internal viscosity term in the polymer equations of motion we have been able to describe the observed Debye-type relaxation in terms of a flattening of the relaxation time spectrum. This model provides a good explanation of the observed effects for large molecular weights but is unable to explain the molecular weight dependence observed by Cochran *et al.*[1] as the molecular weight goes below 10 000. There is also a difficulty due to a loss in the number of degrees of freedom when the polymer chain is divided into Gaussian subunits.

We therefore conclude that the modified Gaussian chain model cannot provide a really adequate treatment of the observed ultrasonic behaviour. Further progress towards the explanation of the phenomenon will probably involve models which take more explicit account of the intermolecular rotational potentials[17,18].

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