

# Correlation Function Approach to the Dielectric Behaviour of Amorphous Polymers

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The equilibrium and dynamic aspects of the dielectric behaviour of polymer systems are considered in macroscopic terms and molecular terms. The role of dipole moment correlations is considered for a model polyether series. It is suggested that studies of certain copolymers reveal that the reorientation term  $\langle \mu_k(0) \cdot \mu_k(t) \rangle$  for a reference dipole in a polymer chain is not given by a simple exponential dependence upon time. A method is given for the evaluation of the macroscopic decay function from experimental dispersion and absorption data, and this is applied to the  $\alpha$  relaxation in amorphous polyethyl acrylate.

The dielectric relaxation of flexible polymer chains in the bulk amorphous state or in solution may be considered to arise from two types of chain motion. The first type involves the long-range motions of whole polymer chains and such behaviour has been studied by Stockmayer and Baur<sup>1, 2</sup> and by Stockmayer,<sup>3</sup> who have, e.g. interpreted the lower frequency relaxation process in liquid polypropylene oxides in terms of a modified Rouse-Zimm normal mode theory for chain motions. The second type of relaxation involves the motions of fairly short chain sequences (the "perpendicular dipole" case of Stockmayer<sup>3</sup>), and in solid amorphous polymers give rise to two relaxation regions,<sup>4</sup> normally termed the  $\alpha$  and  $\beta$  processes. The  $\alpha$  process, which is associated with the glass transition of bulk polymer, is observed in both liquid and solid states. The  $\beta$  process, which occurs in solid amorphous polymers is not yet fully understood, but it is significant that the  $\alpha$  and  $\beta$  processes coalesce at high temperatures for a number of polymers,<sup>5-8</sup> indicating a strong connection in their origins even when they are well resolved on the log frequency axis.

The theories of the  $\alpha$  and  $\beta$  relaxations have been considered by many authors (for a review, see ref. (4)). However, since it is necessary to consider both dipole correlations along a chain and a detailed model for chain motions,<sup>9, 10</sup> it appears difficult to give a physical assessment for the detailed relaxations obtained by some of these treatments. It is the aim of the present paper to emphasize that the dielectric relaxation behaviour may be expressed in terms of a macroscopic decay function  $\phi(t)$ . This decay function may in turn be related to a molecular correlation function  $\Gamma(t)$ , where  $\Gamma(t)$  involves the time-dependent dipole moment correlations along a chain. In this way the role of correlations may be assessed in a more obvious manner.

## THEORY

The complex dielectric constant  $\epsilon^*$  may be expressed in terms of the superposition relation<sup>4, 11-13</sup>

$$\frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \int_0^\infty \left( -\frac{d\phi(t)}{dt} \right) \exp -i\omega t \, dt = \mathcal{L} \left( -\frac{d\phi(t)}{dt} \right). \quad (1)$$

$\epsilon_0$  and  $\epsilon_\infty$  are the limiting low- and high-frequency dielectric constants respectively,  $\phi(t)$  is the macroscopic decay function for a parallel plate sample, obtained on removal of a steady macroscopic electric field  $E$ . Eqn (1) means that if we know  $\phi(t)$  over its entire range, then  $(\epsilon^*(\omega) - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty)$  is also known.\* It is important to note that the converse is true, and we show (appendix) that

$$\phi(t) = \frac{2}{\pi} \int_0^\infty \left( \frac{\epsilon_0 - \epsilon'(\omega)}{\epsilon_0 - \epsilon_\infty} \right) \sin \omega t \frac{d\omega}{\omega}, \quad (2a)$$

$$\phi(t) = \frac{2}{\pi} \int_0^\infty \left( \frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_\infty} \right) \cos \omega t \frac{d\omega}{\omega}. \quad (2b)$$

Eqn (2b) has been given previously by Le Roy.<sup>14</sup> Thus, if we know  $\epsilon''(\omega)$  over the entire relaxation range, the decay function follows immediately from eqn (2b).

The relationship between the static dielectric constant and the constituent dipole moments of a polymer medium has been given previously<sup>4, 15</sup> in terms of the Fröhlich theory for dielectric media.<sup>18</sup> In order to make our presentation fairly complete, a brief derivation will be given, using the correlation function notation and a different starting relation from that used previously.<sup>4</sup> The static dielectric constant expression is (see ref. (18), p. 181):

$$(\epsilon_0 - \epsilon_\infty) = \left\{ \frac{4\pi}{3kT} \frac{3\epsilon_0(2\epsilon_0 + \epsilon_\infty)}{(2\epsilon_0 + 1)^2} \right\} \frac{\langle \mathbf{M}(0) \cdot \mathbf{M}(0) \rangle}{V}. \quad (3)$$

$\mathbf{M}(0)$  is the instantaneous dipole moment of a macroscopic sphere in the medium, of volume  $V$ , and  $\langle \mathbf{M}(0) \cdot \mathbf{M}(0) \rangle$  is the mean square dipole moment evaluated in the absence of an applied electric field. If the volume  $V$  contains  $N$  polymer chains and the instantaneous dipole moment of the chain  $i$  is  $\mathbf{P}_i(0)$  where  $\mathbf{P}_i(0)$  is the vector sum of the elementary dipole moments  $\mu_{ji}(0)$  in the chain,<sup>†</sup> then in the absence of orientation correlations between different polymer chains,

$$\langle \mathbf{M}(0) \cdot \mathbf{M}(0) \rangle = \sum_{i=1}^N \left\{ \sum_{j=1}^{n_{ri}} \sum_{j'=1}^{n_{ri}} \langle \mu_{ji}(0) \cdot \mu_{j'i}(0) \rangle \right\}. \quad (4)$$

$n_r$  is the number of elementary dipoles in chain  $i$ ,  $\mu_{ji}(0)$  and  $\mu_{j'i}(0)$  are two elementary dipoles in the same chain  $i$ .

If we restrict consideration to polymers containing only one type of dipolar group then  $\mu_{ji} = \mu_{j'i} = \mu$  say, and eqn (4) becomes

$$\langle \mathbf{M}(0) \cdot \mathbf{M}(0) \rangle = \sum_{i=1}^N \left\{ n_{ri} \mu^2 + 2 \sum_{j=2}^{n_{ri}} \sum_{j'=1}^{j-1} \langle \mu_{ji}(0) \cdot \mu_{j'i}(0) \rangle \right\}. \quad (5)$$

For flexible polymer chains  $\langle \mu_{ji}(0) \cdot \mu_{j'i}(0) \rangle$  will decrease as the separation of the dipoles  $j$  and  $j'$  along the chain is increased. Thus, for the special case of flexible polymer chains and high average molecular weight polymers, eqn (5) is approximated by

$$\frac{\langle \mathbf{M}(0) \cdot \mathbf{M}(0) \rangle}{V} = c_r \left\{ \mu^2 + \sum_{\substack{k' \\ k' \neq k}} \langle \mu_k(0) \cdot \mu_{k'}(0) \rangle \right\}. \quad (6)$$

\* Eqn (1) may be regarded as a one sided Fourier transform of  $(-d\phi(t)/dt)$ , or as a pure imaginary Laplace transformation of  $(-d\phi(t)/dt)$ .

† Note that  $\mu_{ji}$  is a "liquid" dipole moment and is related<sup>18</sup> to the vacuum dipole moment by

$$\mu_{ji} = (\mu_{ji})_{\text{vac}} \frac{(\epsilon_\infty + 2)(2\epsilon_0 + 1)}{3(2\epsilon_0 + \epsilon_\infty)}.$$

$c_r$  is the number of dipole units per unit volume,  $\mu_{k'}(0)$  is the instantaneous dipole moment of a dipole  $k'$  contained in the same chain as the reference dipole  $k$ . The summation extends over the  $k'$  dipoles and the terms will only be significant for near neighbour correlations with the  $k$  dipole for this special case of flexible polymer chains. A combination of eqn (3) and (5) or (6) gives the desired relation between  $\epsilon_0$  and the dipoles present in the polymer medium. The correlation terms  $\langle \mu_k(0) \cdot \mu_{k'}(0) \rangle$  form a necessary part of the  $\epsilon_0$  expression and it is these terms which distinguish a polymer medium from a simple, non-associated, small-molecule medium.

The molecular theory for the complex dielectric constant of polymer media is made complicated by the effects of induced moments and internal field factors.<sup>19-22</sup> We consider a macroscopic spherical sample in the polymer medium, then the time dependent quantity  $\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle$  is given by

$$\begin{aligned} \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle &= \sum_{i=1}^N \left\{ \sum_{j=1}^{n_{r_i}} \sum_{j'=1}^{n_{r_i}} \langle \mu_{ji}(0) \cdot \mu_{j'i}(t) \rangle \right\} \\ &= \sum_{i=1}^N \left\{ \sum_{j=1}^{n_{r_i}} \langle \mu_{ji}(0) \cdot \mu_{ji}(t) \rangle + 2 \sum_{j=2}^{n_{r_i}} \sum_{j'=1}^{j-1} \langle \mu_{ji}(0) \cdot \mu_{j'i}(t) \rangle \right\}. \end{aligned} \quad (7)$$

Since  $\langle \mu_{ji}(0) \cdot \mu_{j'i}(t) \rangle$  will decrease in magnitude with increasing separation of the dipoles for flexible polymer chains, then for polymers of high average molecular weight, having flexible chains, eqn (7) is approximated by

$$\frac{\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle}{V} = c_r \left\{ \langle \mu_k(0) \cdot \mu_k(t) \rangle + \sum_{k' \neq k} \langle \mu_k(0) \cdot \mu_{k'}(t) \rangle \right\}. \quad (8)$$

As before, the dipoles  $k$  and  $k'$  belong to the same polymer chain.  $\langle \mu_k(0) \cdot \mu_k(t) \rangle / \mu^2$  is the average decay function for the reference dipole  $k$ . The dipoles  $k$  and  $k'$  are physically linked by the chain bonds and there will be a number of initial relative orientations of the two dipoles.  $\langle \mu_k(0) \cdot \mu_{k'}(t) \rangle / \mu^2$  is obtained as the weighted sum of the decay functions for given initial relative orientations, where the weighting factors are the equilibrium probabilities of these relative orientations. We see that  $\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle / V$  involves only short-range orientation terms. We normalize eqn (8) by writing a molecular correlation function  $\Gamma(t)$  as

$$\Gamma(t) = \frac{\langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle}{\langle \mathbf{M}(0) \cdot \mathbf{M}(0) \rangle} = \frac{\langle \mu_k(0) \cdot \mu_k(t) \rangle + \sum_{k'} \langle \mu_k(0) \cdot \mu_{k'}(t) \rangle}{\{\mu^2 + \sum_{k'} \langle \mu_k(0) \cdot \mu_{k'}(0) \rangle\}} = \frac{g(t)}{g(0)}. \quad (9)$$

Here  $g(t)$  has the significance of a dynamic  $g$  factor and  $g(0)$  is the equilibrium factor similar to that of Kirkwood.<sup>23</sup>

We now have the problem of relating  $\Gamma(t)$  to the complex dielectric constant. The theory for non-associated liquids<sup>19-25</sup> gives relations of the form

$$\left( \frac{\epsilon^*(\omega) - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} \right) p(\omega) = \mathcal{L} \left[ -\frac{d\Gamma_0(t)}{dt} \right]. \quad (10)$$

The dipole moment correlation function  $\Gamma_0(t) = \langle \mu(0) \cdot \mu(t) \rangle / \langle \mu(0) \cdot \mu(0) \rangle$ .  $p(\omega)$  depends upon internal field considerations and for the Onsager model of a dielectric, several forms for  $p(\omega)$  have been proposed. Cole<sup>20</sup>  $p(\omega) = 3\epsilon_0 / (2\epsilon_0 + \epsilon^*)$ , Klug and others<sup>22</sup> and Fatuzzo and Mason<sup>21b</sup>  $p(\omega) = \epsilon_0(2\epsilon^* + \epsilon_\infty) / [\epsilon^*(2\epsilon_0 + \epsilon_\infty)]$ , Scaife<sup>24</sup>  $p(\omega) = \epsilon_0(2\epsilon_1^* + \epsilon_\infty)(2\epsilon^* + 1) / [\epsilon^*(2\epsilon_1^* + 1)(2\epsilon_0 + \epsilon_\infty)]$ , (where  $\epsilon_1^*$  is the complex conjugate of  $\epsilon^*$ ), Collie, Hasted and Ritson<sup>25</sup>  $p(\omega) = \epsilon_0(2\epsilon^* + 1) / [\epsilon^*(2\epsilon_0 + 1)]$ . Clearly the  $\Gamma_0(t)$  derived from eqn (10) will depend upon the form taken for  $p(\omega)$ , but for only

moderately polar media, the functions from ref. (22) and (21b) may be approximated by  $p(\omega) \doteq 1$ .

For the polymer case, if we introduce  $\varepsilon_\infty$  into the Kubo approach of Fatuzzo and Mason<sup>21a</sup> according to the Fröhlich model (ref. (18), p. 46) of a cavity having a dielectric constant  $\varepsilon_\infty$ , then if we write  $G = (3\varepsilon^*/2\varepsilon^* + \varepsilon_\infty)E$ , we obtain

$$\left( \frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} \right) p(\omega) = \mathcal{L} \left[ -\frac{d\Gamma(t)}{dt} \right], \quad (11)$$

where  $p(\omega) = \varepsilon_0(2\varepsilon^* + \varepsilon_\infty)/[\varepsilon^*(2\varepsilon_0 + \varepsilon_\infty)]$  and  $\Gamma(t)$  is given by eqn (9). This equation reduces to that derived by Klug and others<sup>22</sup> and by Fatuzzo and Mason<sup>21b</sup> if correlations of dipole orientations are absent, i.e.,  $\Gamma(t) = \Gamma_0(t)$ .

Thus, from eqn (11), dielectric relaxation in polymer media arises from the "auto-correlation term"  $\langle \mu_k(0) \cdot \mu_k(t) \rangle$  and the higher correlation terms  $\langle \mu_k(0) \cdot \mu_{k'}(t) \rangle$ . For a flexible polymer chain, the higher terms become progressively less important as the dipole separation is increased along the chain.

### DISCUSSION

It has not been necessary to specify the details of chain conformation or of chain dynamics in arriving at eqn (3), (5) and (6) and eqn (7-9) and (11). Thus, these equations may be regarded as a restatement of the general problem, where the role of

TABLE 1.—VALUES OF THE COEFFICIENTS OF  $(n-m)/n$  FOR  $p = 2, 3, 4$  AND 5 FOR  $\cos \alpha = \frac{1}{3}$  AND FOR CHOSEN VALUES OF  $\eta = \langle \cos \phi \rangle$

$p = 2$					
$\eta$	$C_{(n-1)/n}$	$C_{(n-2)/n}$	$C_{(n-3)/n}$	$C_{(n-4)/n}$	
-0.50	-1.00	+0.250	+0.062	-0.109	
-0.25	-0.639	+0.084	+0.013	-0.009	
0	-0.222	-0.025	-0.003	0.000	
+0.25	+0.250	+0.016	-0.007	+0.005	
+0.50	+0.778	+0.300	+0.113	+0.040	
+0.75	+1.361	+0.926	+0.630	+0.428	
$p = 3$					
$\eta$	$C_{(n-1)/n}$	$C_{(n-2)/n}$	$C_{(n-3)/n}$		
-0.50	-0.50	+0.062	+0.024		
-0.25	-0.183	+0.013	0.000		
0	-0.074	-0.003	0.000		
+0.25	-0.187	-0.007	-0.004		
+0.50	-0.537	+0.113	-0.038		
+0.75	-1.137	+0.630	-0.361		
$p = 4$					
$\eta$	$C_{(n-1)/n}$	$C_{(n-2)/n}$	$\eta$	$C_{(n-1)/n}$	$C_{(n-2)/n}$
-0.50	0.250	-0.109	-0.50	+0.380	+0.066
-0.25	0.084	-0.009	-0.25	+0.081	+0.001
0	-0.025	0.000	0	-0.008	0.000
+0.25	+0.016	+0.005	+0.25	-0.043	-0.002
+0.50	+0.300	+0.042	+0.50	-0.219	+0.014
+0.75	+0.926	+0.428	-0.75	-0.775	+0.291

orientation correlations may possibly be assessed in a more obvious manner. The details of the equilibrium correlations have received much attention.<sup>4, 26-30</sup> It is, however, of interest to see in a model case the extent to which the higher correlations

in eqn (6) decrease in magnitude with increasing separation of dipoles along the chain. Read<sup>31</sup> derived a general expression for the mean square dipole moment for the polyether series  $[(CH_2)_{p-1}-O]_n$ , where  $p = 2, 3 \dots$ . He considered the model in which (i) correlations of internal rotation states were absent, (ii) all three bond systems had, on average, the same internal rotation characteristics, (iii) all valence angles were the same, and (iv)  $\langle \sin \phi \rangle = 0$ , where  $\phi$  is the internal rotation angle,  $\phi = 0$  for the trans state of a three bond system. Although this model may not be strictly obeyed for the polyethers,<sup>29</sup> Read's theory makes it possible to evaluate the correlation terms in such a model chain using the minimum of internal rotation parameters. Read's eqn (3) may be written as

$$\begin{aligned} \langle P(0) \cdot P(0) \rangle = & n\mu^2 + 2(n-1)k^2[2\bar{A}^p - \bar{A}^{p+1} - \bar{A}^{p-1}]_{33} + \\ & 2(n-2)k^2[2\bar{A}^{2p} - \bar{A}^{2p+1} - \bar{A}^{2p-1}]_{33} + \dots + \\ & 2k^2[2\bar{A}^{(n-1)p} - \bar{A}^{(n-1)p+1} - \bar{A}^{(n-1)p-1}]_{33}; \end{aligned} \quad (12)$$

$\mu$  is the C—O—C group dipole moment,  $k$  is the C—O bond dipole moment,  $\bar{A}$  is the average coordinate transformation matrix as defined in ref (31). The subscript 33 denotes the 33 element of the appropriate matrix. The  $2(n-1)$  terms and the  $2(n-2)$  terms correspond to the correlations between a reference dipole and both its next nearest neighbour group dipoles, and both its next plus one nearest group dipoles, respectively along the chain. Remembering<sup>31</sup> that  $\mu^2 = 2k^2(1 - \cos \alpha)$ , where  $\cos \alpha = \frac{1}{3}$  for tetrahedral valence angles, then

$$\begin{aligned} \langle P(0) \cdot P(0) \rangle = & n\mu^2 \left\{ 1 + \left( \frac{n-1}{n} \right) \frac{[2\bar{A}^p - \bar{A}^{p+1} - \bar{A}^{p-1}]_{33}}{(1 - \cos \alpha)} + \right. \\ & \left( \frac{n-2}{n} \right) \frac{[2\bar{A}^{2p} - \bar{A}^{2p+1} - \bar{A}^{2p-1}]_{33}}{(1 - \cos \alpha)} + \dots + \\ & \left. \frac{1}{n} \frac{[2\bar{A}^{(n-1)p} - \bar{A}^{(n-1)p+1} - \bar{A}^{(n-1)p-1}]_{33}}{(1 - \cos \alpha)} \right\}. \end{aligned} \quad (13)$$

We have estimated the coefficients of  $(n-m)/n$  in the above series for  $p = 2, 3, 4$  and 5 for different values of  $\eta = \langle \cos \phi \rangle$ . For  $\eta = 0$  the dipolar correlations arise only due to the valence angle restriction. For  $\eta > 0$  the trans conformation is preferred, while for  $-0.5 < \eta < 0$  the gauche conformation is preferred. The results are shown in table 1.

Considering first  $\eta = 0$ , then for  $p = 2$  the first nearest neighbours contribute  $-0.222$ , the second nearest neighbours  $-0.025$ , and the third and fourth nearest neighbours make a very small contribution. For  $\eta = 0$  and  $p = 3$  only the nearest neighbours make a significant contribution, and for  $\eta = 0$ , and  $p = 4$  and 5 the nearest neighbours make only a small contribution to  $\langle P^2 \rangle$ . For  $\eta \neq 0$ , the correlation terms generally decrease in magnitude with increasing dipole separation, but for  $\eta \rightarrow 0.75$  or  $\eta \rightarrow 0.5$ , the correlations extend over very long sequences of the chain. Thus, we conclude for the model system that correlations decrease rapidly in magnitude with increasing dipole separation if  $-0.25 < \eta < 0.5$ , but for less flexible chains the correlations are significant over long intervening chain sequences.

If we now consider the dynamic case (eqn (8), (9), (11), the magnitudes of the higher correlation terms will be given by their equilibrium values  $\langle \mu_k(0) \cdot \mu_k(0) \rangle$  which for our model case (table 1) decrease markedly for flexible polymer chains as the separation of the dipoles is increased. Thus, if we write  $\gamma_{kk}(t) = \langle \mu_k(0) \cdot \mu_k(t) \rangle$  then we would expect the dielectric relaxation behaviour of flexible polymers to have contributions from  $\gamma_{kk}(t)$ , from the next nearest neighbour dipoles  $\gamma_{k,k\pm 1}(t)$ , then the

successively higher terms would be of decreasing magnitude, and possibly small magnitude compared with  $\gamma_{kk}(t)$  and  $\gamma_{k,k\pm 1}(t)$ . One case is of special interest. If it were possible to separate the dipoles sufficiently, then the relaxation behaviour would essentially be given by the factor  $\gamma_{kk}(t)$ . The question to be answered by such studies is whether the broad distribution of relaxation times observed in ordinary polymers for the  $\alpha$  process is a direct result of higher correlation terms, or is it due to some other factor. Leffingwell and Bueche<sup>32</sup> made a systematic study of styrene+2-chloro-styrene copolymers and found that the shape of the  $\alpha$  relaxation was essentially independent of the polar component in the range studied (8-33 % v/v). The loss curves had a half-width near 2.3 decades of frequency, which is typical for amorphous homopolymers.<sup>4</sup> Mikhailov and Krasner<sup>33</sup> found that the  $\alpha$  relaxation in both styrene+methyl acrylate copolymers and styrene+methyl vinyl ketone copolymers had the broad characteristic shape found in ordinary homopolymers. In both these studies<sup>32, 33</sup> the copolymers comprise one polar and one weakly polar component. We would suggest that the results of both studies at low concentrations of the polar component reflect the behaviour of  $\gamma_{kk}(t)$ , and since the loss curves are of the same shape as those observed in homopolymers, it suggests that the time dependence of the various  $\gamma_{kk}(t)$  are not very different from  $\gamma_{kk}(t)$ . Since the  $\gamma_{kk}(t)$  in these copolymers appears to be far removed from a simple exponential decay, it is suggested that the motion of a reference dipole in a polymer chain is governed by the mechanical motion of the chain segments and the immediate environment of the dipole. There is no reason to expect that such motions would lead to a simple exponential decay for  $\gamma_{kk}(t)$  and we suggest that the characteristic loss curve obtained in these copolymers at low polar concentrations is closely related to the actual mechanical motions of the chain segment to which the dipole is attached.

We may evaluate the macroscopic decay function  $\phi(t)$  directly from experimental results using eqn (2) above. Experimentally it is often found that the  $\alpha$  and  $\beta$  processes in amorphous polymers are well separated on the  $\log f$  scale. It follows that  $\phi(t)$  may be written as the sum of two decay terms,

$$\phi(t) = \frac{2}{\pi} \frac{1}{(\epsilon_0 - \epsilon_\infty)} [I_\alpha(t) + I_\beta(t)], \quad (14)$$

where  $I_\alpha(t)$  is the integral  $\int \epsilon'' \cos \omega t (d\omega/\omega)$  taken over the entire  $\alpha$  process and  $I_\beta(t)$  is the same integral taken over the entire  $\beta$  process. Now  $I_\alpha(0) = (\epsilon_0 - \epsilon_\infty)_\alpha \frac{1}{2}\pi$  and  $I_\beta(0) = (\epsilon_0 - \epsilon_\infty)_\beta \frac{1}{2}\pi$ , where  $(\epsilon_0 - \epsilon_\infty)_i$  are the magnitudes of the  $\alpha$  and  $\beta$  processes respectively. Thus, eqn (14) may be written as

$$\phi(t) = \frac{(\epsilon_0 - \epsilon_\infty)_\alpha}{(\epsilon_0 - \epsilon_\infty)} \phi_\alpha(t) + \frac{(\epsilon_0 - \epsilon_\infty)_\beta}{(\epsilon_0 - \epsilon_\infty)} \phi_\beta(t). \quad (15)$$

The shape of the plot  $(\epsilon''(\omega)/\epsilon''_{\max})$  against  $\log(\omega/\omega_{\max})$  is often essentially independent of temperature and pressure for  $\alpha$  relaxations.<sup>4, 34</sup> This means that the "master plot"  $(\epsilon''(\omega)/\epsilon''_{\max})$  against  $\log(\omega/\omega_{\max})$  is a convenient method to bring together a large amount of experimental data, and we may obtain the temperature and pressure "reduced" decay function  $\phi_\alpha(t/\langle\tau\rangle)$  as

$$\phi_\alpha\left(\frac{t}{\langle\tau\rangle}\right) = \frac{\left[ \int_{-\infty}^{\infty} \left( \frac{\epsilon''}{\epsilon''_{\max}} \right) \cos \left\{ \left( \frac{\omega}{\omega_{\max}} \right) \left( \frac{t}{\langle\tau\rangle} \right) \right\} d \log \left( \frac{\omega}{\omega_{\max}} \right) \right]_\alpha}{\left[ \int_{-\infty}^{\infty} \left( \frac{\epsilon''}{\epsilon''_{\max}} \right) d \log \left( \frac{\omega}{\omega_{\max}} \right) \right]_\alpha}, \quad (16)$$

where we define  $\omega_{\max}\langle\tau\rangle = 1$ .



Fig. 1 shows the plot of  $(\epsilon''/\epsilon''_{\max})$  against  $\log(\omega/\omega_{\max})$  for the  $\alpha$  relaxation in polyethyl acrylate at 20.3°C, and four applied pressures. The measurements were made using a three terminal high-pressure cell, a General Radio 1615-A bridge ( $10^2$ - $10^5$  Hz) and a Scheiber Bridge ( $10^{-2}$ - $10^2$  Hz). The transformation of the frequency-dependent data was carried out by hand, and fig. 2 shows  $\phi_\alpha(t/\langle\tau\rangle)$  plotted against  $\log(t/\langle\tau\rangle)$ . The decay function covers a very wide reduced time scale as required by the breadth of the loss factor curve.

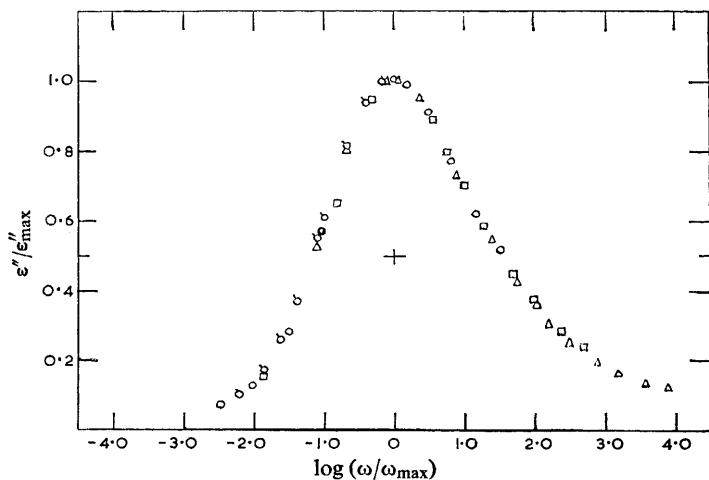


FIG. 1.— $\epsilon''/\epsilon''_{\max}$  against  $\log(\omega/\omega_{\max})$  for polyethyl acrylate at 20.3°C.  $\circ$ ,  $5.5 \times 10^7$ ,  $\circ$ ,  $1.11 \times 10^8$ ,  $\square$ ,  $1.57 \times 10^8$  and  $\triangle$ ,  $2.05 \times 10^8$  N m $^{-2}$ .

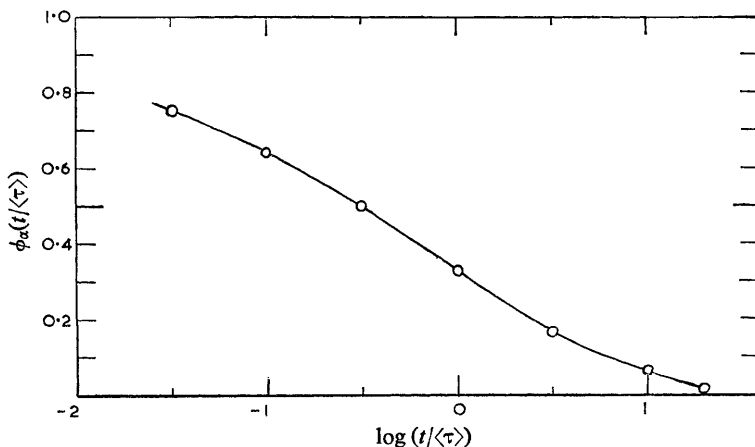


FIG. 2.— $\phi_\alpha(t/\langle\tau\rangle)$  against  $\log(t/\langle\tau\rangle)$  for polyethyl acrylate at 20.3°C.

Having shown that  $\phi_\alpha(t/\langle\tau\rangle)$  may be obtained from experimental results for  $(\epsilon''/\epsilon''_{\max})_\alpha$ , the next step would be to obtain a molecular theory for chain motions which would correspond to the form shown in fig. 2. For the present work we note that  $\phi_\alpha(t)$  conforms with the empirical relation<sup>36</sup>

$$\phi_\alpha(t) = \exp -(t/\tau_0)^{\bar{\beta}}, \quad 0 < \bar{\beta} \leq 1. \quad (17)$$

The plot of  $\log [-\log \phi_\alpha(t/\langle\tau\rangle)]$  against  $\log(t/\langle\tau\rangle)$  for the results shown in fig. 2 is

linear and we deduce  $\bar{\beta} = 0.38$  and  $\log(\langle\tau\rangle/\tau_0) = 0.12$ . It is evident from fig. 2 that the larger part of the decay occurs for  $\log(t/\langle\tau\rangle) < 1$ , and this gives the  $(\varepsilon''/\varepsilon''_{\max})_{\alpha}$  plot of fig. 1 its asymmetric shape.

We have not carried through the corresponding calculation of  $\Gamma(t)$  using eqn (11), but to a rough approximation we have  $p(\omega) \approx 1$ , in which case  $\Gamma_{\alpha}(t)$  would not be greatly different from the  $\phi_{\alpha}(t)$  shown in fig. 2 for polyethyl acrylate.

### CONCLUSIONS

The relationship between  $\varepsilon^*(\omega)$  and the macroscopic decay function  $\phi(t)$  has been considered, and a method is outlined for the determination of  $\phi(t)$  from experimental  $\varepsilon^*(\omega)$  data. The role of dipole correlations is considered for the equilibrium and dynamic behaviour of amorphous polymers. The magnitude of the equilibrium correlation terms has been deduced for a model polyether series, and it is shown that the correlations decrease in magnitude with increasing separation of dipoles for flexible polymer chains. It is suggested that the  $\alpha$  relaxation in certain amorphous copolymers gives a measure of the  $\gamma_{kk}(t)$  term, and further, that the time dependence of the  $\gamma_{kk'}(t)$  terms will be approximately the same as the  $\gamma_{kk}(t)$  term for the relaxation in amorphous polymers. The macroscopic decay function  $\phi_{\alpha}(t)$  was deduced from experimental  $\varepsilon''$  data for polyethyl acrylate at 20.3°C, and conforms with the empirical decay function  $\phi_{\alpha}(t) = \exp -(t/\tau_0)^{\bar{\beta}}$ , where  $\bar{\beta} = 0.38$ .

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### APPENDIX

We wish to obtain eqn (2) of the text. Writing  $f(t) = [d\phi(t)/dt]$  it follows from the principle of causality (see ref. (17), p. 151) that  $f(t) = 0$  for  $t < 0$ . Writing  $f(t) = f_e(t) + f_o(t)$ , where  $f_e(t)$  and  $f_o(t)$  are even and odd functions of time respectively, then  $f_e(t) = f_o(t) = \frac{1}{2}f(t)$  for  $t > 0$ , and  $f_e(t) = -f_o(t)$  for  $t < 0$ . Equating the real and imaginary parts of eqn (1), then

$$\frac{\varepsilon'(\omega) - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} = - \int_0^{\infty} 2f_e(t) \cos \omega t \, dt = - \int_{-\infty}^{\infty} f_e(t) \cos \omega t \, dt, \quad (\text{A},1)$$

$$\frac{\varepsilon''(\omega)}{\varepsilon_0 - \varepsilon_{\infty}} = - \int_0^{\infty} 2f_o(t) \sin \omega t \, dt = - \int_{-\infty}^{\infty} f_o(t) \sin \omega t \, dt. \quad (\text{A},2)$$

Eqn (A,1) and (A,2) may be inverted, giving

$$2f_e(t) = -\frac{2}{\pi} \int_0^{\infty} \left( \frac{\varepsilon'(\omega) - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} \right) \cos \omega t \, d\omega, \quad (\text{A},3)$$

or

$$f(t) = -\frac{2}{\pi} \int_0^{\infty} \left( \frac{\varepsilon'(\omega) - \varepsilon_{\infty}}{\varepsilon_0 - \varepsilon_{\infty}} \right) \cos \omega t \, d\omega; \quad t > 0. \quad (\text{A},4)$$

In a similar manner,

$$f(t) = -\frac{2}{\pi} \int_0^{\infty} \frac{\varepsilon''(\omega)}{(\varepsilon_0 - \varepsilon_{\infty})} \sin \omega t \, d\omega; \quad t > 0. \quad (\text{A},5)$$



Since

$$\phi(t) - 1 = \int_0^t f(t) dt,$$

it follows from eqn (A,4) and (A,5) that

$$\phi(t) = \frac{2}{\pi} \int_0^\infty \left( \frac{\varepsilon_0 - \varepsilon'(\omega)}{\varepsilon_0 - \varepsilon_\infty} \right) \sin \omega t \frac{d\omega}{\omega}; \quad t > 0 \quad (\text{A,6})$$

$$\phi(t) = \frac{2}{\pi} \int_0^\infty \left( \frac{\varepsilon''(\omega)}{\varepsilon_0 - \varepsilon_\infty} \right) \cos \omega t \frac{d\omega}{\omega}; \quad t > 0. \quad (\text{A,7})$$

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