Non-Symmetrical Dielectric Relaxation Behaviour Arising from a Simple Empirical Decay Function

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The empirical dielectric decay function $\gamma(t) = \exp -(t/\tau_0)^{\beta}$ may be transformed analytically to give the frequency dependent complex dielectric constant if β is chosen to be 0.50. The resulting dielectric constant and dielectric loss curves are non-symmetrical about the logarithm of the frequency of maximum loss, and are intermediate between the Cole-Cole and Davidson-Cole empirical relations. Using a short extrapolation procedure, good agreement is obtained between the empirical representation and the experimental curves for the α relaxation in polyethyl acrylate. It is suggested that the present representation would have a general application to the α relaxations in other polymers. The Hamon approximation, with a small applied correction, is valid for the present function with $\beta = 0.50$ in the range $\log(\omega\tau_0) > -0.5$, but cannot be used at lower frequencies.

The dielectric dispersions and absorptions of many systems do not correspond to a single relaxation time expression. Where the behaviour is symmetrical about the logarithm of the frequency of maximum loss, the empirical equations of Cole and Cole,[1] and Fuoss and Kirkwood [2] often give an adequate fit to the experimental behaviour. In many cases the behaviour is not symmetrical about the logarithm of the frequency of maximum loss, and the Davidson-Cole empirical relation [3, 4] gives a good fit to the experimental data. The details of the " skewed arc " representation have been reviewed by Davidson.[5] In the course of our studies on the primary (α) relaxation of amorphous polymers the non-symmetrical behaviour has become evident, and does not appear to be adequately fitted to a Davidson-Cole distribution. It is the aim of the present paper to examine a simple empirical form for the dielectric decay function which leads to non-symmetrical behaviour of the type observed in polymers.

THEORY

The complex dielectric constant ε^* is related to the normalized decay function $\gamma(t)$ by the equation [6]

$$\frac{\varepsilon^*-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} = \mathscr{L}\left[-\frac{d\gamma(t)}{dt}\right]. \tag{1}$$

$\mathscr{L}$ indicates the Laplace transform,† $[-d\gamma(t)/dt]$ is the normalized transient decay current obtained when a steady electric field is removed from a sample. ε_0 and ε_∞ are the limiting low and high frequency dielectric constants of the given medium. If the decay function $\gamma(t)$ is given by the relation $\gamma(t) = \exp(-t/\tau)$, where τ is a macroscopic time constant, then eqn (1) yields the single relaxation time expression

$$(\varepsilon^*-\varepsilon_\infty)/(\varepsilon_0-\varepsilon_\infty) = (1+j\omega\tau)^{-1}.$$

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† $\mathscr{L}[F(t)] = \int_0^\infty \exp(-j\omega t)F(t)dt$.

We consider the empirical decay function

$$\gamma(t) = \exp -(t/\tau_0)^{\beta}, \tag{2}$$

$0 < \beta \leqslant 1$, and τ_0 is some effective relaxation time. Insertion of (2) into (1) gives

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \mathscr{L}\left[\frac{\beta}{\tau_0}\left(\frac{t}{\tau_0}\right)^{-(1-\beta)} \exp -\left(\frac{t}{\tau_0}\right)^{\beta}\right]. \tag{3}$$

The evaluation of eqn. (3) by analytical means appears complicated. However, if we choose the particular value $\beta = 0.50$, the transform is readily evaluated. For this special case, eqn (3) becomes

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \tfrac{1}{2}\left(\frac{\pi}{\tau_0}\right)^{\frac{1}{2}} \mathscr{L}\left[\frac{1}{(\pi t)^{\frac{1}{2}}} \cdot \exp -2k(t)^{\frac{1}{2}}\right] \tag{4}$$

where $2k = (\tau_0)^{-\frac{1}{2}}$. The Laplace transform is now in a standard form,[7] giving

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \tfrac{1}{2}\left(\frac{\pi}{\tau_0}\right)^{\frac{1}{2}} \cdot \frac{1}{(j\omega)^{\frac{1}{2}}} \exp \frac{k^2}{j\omega} \cdot \operatorname{erfc} \frac{k}{(j\omega)^{\frac{1}{2}}}. \tag{5}$$

Since $(j)^{\frac{1}{2}} = (1/\sqrt{2})(1+j)$, eqn (5) becomes

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = (\pi)^{\frac{1}{2}} \frac{(1-j)}{\rho} w(z). \tag{6}$$

$\rho = (8\omega\tau_0)^{\frac{1}{2}}$; $z = (1+j)/\rho$ and $w(z) = \exp(-z^2) \cdot \operatorname{erfc}(-jz)$. The values of $w(z)$ have been tabulated (ref. (7), p. 325), so $(\varepsilon^* - \varepsilon_0)/(\varepsilon_0 - \varepsilon_\infty)$ may be determined as a function of $\omega\tau_0$ for $\beta = 0.50$.

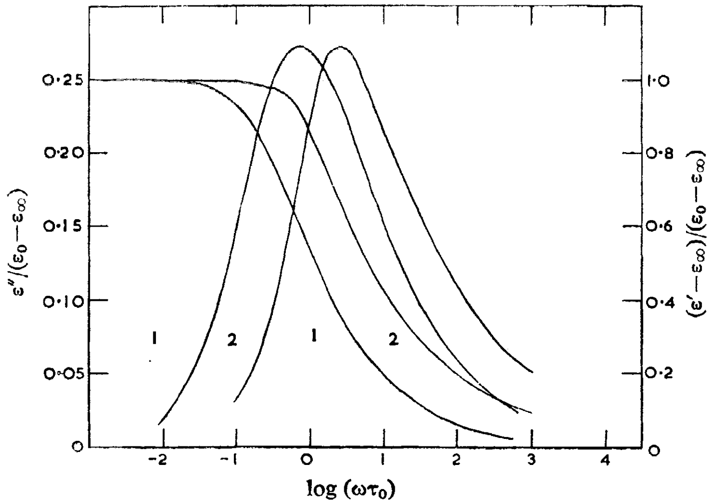

FIG. 1.—$(\varepsilon' - \varepsilon_\infty)/(\varepsilon_0 - \varepsilon_\infty)$ and $\varepsilon''/(\varepsilon_0 - \varepsilon_\infty)$ against log $(\omega\tau_0)$ for the present function with $\beta = 0.50$ (curves 1), and Davidson-Cole function with $\sigma = 0.322$ (curves 2).

DISCUSSION

Fig. 1 shows the plots of $(\varepsilon' - \varepsilon_\infty)/(\varepsilon_0 - \varepsilon_\infty)$ and $\varepsilon''/(\varepsilon_0 - \varepsilon_\infty)$ against log $(\omega\tau_0)$, for $\beta = 0.50$, as determined by eqn (6). Also shown in fig. 1 are the corresponding plots for the Davidson-Cole empirical relation with the parameter ($\sigma = 0.322$)

chosen to give the same $\varepsilon''_{\max}/(\varepsilon_0-\varepsilon_\infty)$ as the present representation with $\beta = 0.50$. These plots have the same general appearance, but differ significantly in detail, as is shown by table 1. The τ_0 values are different for the two functions, and so are their shapes, for although the half-widths of the loss factor curves are similar, their assymmetries, as measured by Δ (low)/Δ (high), are quite different. This comparison is extended to fig. 2, where the Argand plot shows a difference in shape, especially at high frequencies.

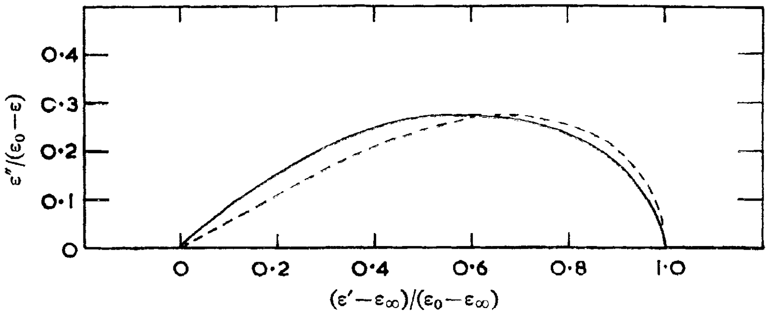

FIG. 2.—$\varepsilon''/(\varepsilon_0-\varepsilon_\infty)$ against $(\varepsilon'-\varepsilon_\infty)/(\varepsilon_0-\varepsilon_\infty)$ for the present function with $\beta = 0.50$ (solid line), and Davidson-Cole function with $\sigma = 0.322$ (dashed line).

In order to compare the function with experimental data it is desirable to have values for the function for which $\beta \neq 0.50$. The case where $\beta = 0.50$ has been evaluated exactly, and the case where $\beta = 1$ is also known, as this corresponds to the single relaxation time function. Using this information a short extrapolation has given the relaxation curves for $\beta \neq 0.5$.

TABLE 1.—A COMPARISON OF THE DAVIDSON-COLE FUNCTION AND THE PRESENT FUNCTION (EQN (6)) FOR $\varepsilon''_{\max}/(\varepsilon_0-\varepsilon_\infty) = 0.272$

	$\log(\omega_{\max}\tau_0)$	total half width (decade)	Δ(low)	Δ(high)	$\Delta_{(\text{low})}/\Delta_{(\text{high})}$
Davidson-Cole	0.40	2.02	0.70	1.32	0.53
present function	−0.15	2.12	0.90	1.22	0.74

Δ(low) and Δ(high) correspond to $|\log(\omega_i/\omega_{\max})|$, where ω_i are the angular frequencies corresponding to $(\varepsilon''/\varepsilon''_{\max}) = 0.50$.

The dielectric relaxation in amorphous polyethyl acrylate (PEA) has been studied in the frequency range 10^{-2}-10^5 Hz using a General Radio 1615-A bridge and a Scheiber bridge.[8] The measurements were performed at 3 pressures at 10.3°C using techniques similar to those described earlier.[9] Fig. 3 shows the experimental data plotted in normalized form, for which $\varepsilon''_{\max}/(\varepsilon_0-\varepsilon_\infty) = 0.21$. Accordingly a value of $\beta = 0.38$ has been chosen for the present function, for which $\varepsilon''_{\max}/(\varepsilon_0-\varepsilon_\infty)$ is also 0.21. Similarly, a value of $\sigma = 0.217$ has been chosen for the Davidson-Cole function, so that $\varepsilon''_{\max}/(\varepsilon_0-\varepsilon_\infty) = 0.21$. All the information has been plotted in normalized form, and the agreement between the experimental data and the present function is reasonable, whereas the Davidson-Cole curve is more skewed. If an attempt is made to fit the α process for polypropylene oxide,[10] polyethylene terephthalate [11] and polyvinylacetate,[12] a reasonable fit is also obtained, and therefore the function may be of use for polymers.

Our main conclusion is that if $\gamma(t) = \exp -(t/\tau_0)^\beta$ is an approximately correct decay function, then it would be desirable to construct a molecular theory, giving a non-exponential decay of this form. A distribution of relaxation times has *not* been introduced, though this decay function would correspond to a particular distribution.

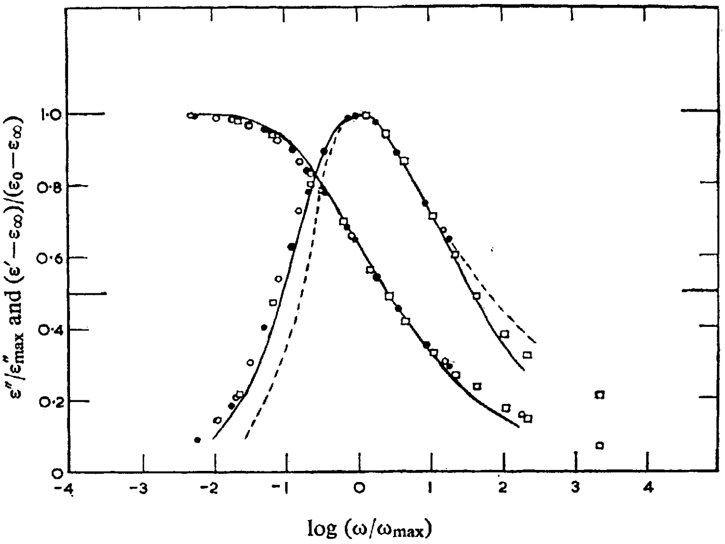

FIG. 3.—$\varepsilon''/\varepsilon''_{max}$ against log (ω/ω_{max}) for (i) present function with $\beta = 0.38$ (solid line); (ii) Davidson-Cole function with $\sigma = 0.217$ (dashed line); (iii) PEA at different applied pressures at 10.3°C. ○, 1.01×10^5 N m^{-2} (1 atm); ●, 4.20×10^7 N m^{-2} (4.16×10^2 atm); □, 8.27×10^7 N m^{-2} (8.20×10^2 atm).

We may compare the forms of $\phi(t) = -\mathrm{d}\gamma(t)/\mathrm{d}t$ for the present function, the Davidson-Cole function [13] and the Cole-Cole function.[14] These are given by eqn (7*a*), (7*b*) and (7*c*) respectively:

$$\phi(t) = \frac{\beta}{\tau_0}\left(\frac{t}{\tau_0}\right)^{-(1-\beta)} \exp-\left(\frac{t}{\tau_0}\right)^{\beta}, \tag{7a}$$

$$\phi(t) = \frac{1}{\tau\Gamma(\sigma)}\left(\frac{t}{\tau}\right)^{-(1-\sigma)} \exp\left(-\frac{t}{\tau}\right), \tag{7b}$$

$$\left.\begin{aligned}\phi(t) &= \frac{n}{\tau\Gamma(1+n)}\left(\frac{t}{\tau}\right)^{-(1-n)}; \quad \text{for } \left(\frac{t}{\tau}\right)\ll 1\\ &= \frac{n}{\tau\Gamma(1-n)}\left(\frac{t}{\tau}\right)^{-(1+n)}; \quad \text{for } \left(\frac{t}{\tau}\right)\gg 1\end{aligned}\right\} \tag{7c}$$

For short times ($t/\tau \ll 1$) which correspond to high frequencies, these three functions have the same dependence upon time, for chosen parameters, apart from a small numerical difference. However, as we proceed from the high frequency side of the loss peak, down to the low frequency side, the Davidson-Cole function falls away much more rapidly than does the Cole-Cole function, due to the exponential factor in $\phi(t)$. Our present function falls away less rapidly than does the Davidson-Cole function and the Cole-Cole function, in the low frequency region. This is because $\exp-(t/\tau_0)^\beta$ is a slower function of time than $\exp(-t/\tau)$, provided that $0<\beta\leqslant 1$.

Finally, since we know $\gamma(t)$ and $\varepsilon^*(\omega)$ for $\beta = 0.50$, we may investigate the accuracy of the Hamon approximation,[15], i.e.,

$$\varepsilon''(\omega) = \phi(t)\omega^{-1}, \tag{8a}$$

$$\omega t = 0.1 \times 2\pi. \tag{8b}$$

These equations have been used extensively [16, 17] for transforming data obtained as a function of time, to the corresponding frequency dependent data.

When $\beta = 0.50$, then from eqn (7a),

$$\phi(t) = \frac{1}{2(t\tau_0)^{\frac{1}{2}}} \exp -\left(\frac{t}{\tau_0}\right)^{\frac{1}{2}}. \tag{9}$$

Substituting eqn (9) into (8a) gives (10a); and (10b) is equivalent to (8b):

$$\varepsilon''(\omega) = (1/1.256)\alpha \exp(-\alpha), \tag{10a}$$

$$\omega\tau_0 = 0.1 \times 2\pi/\alpha^2, \tag{10b}$$

where $\alpha = (t/\tau_0)^{\frac{1}{2}}$.

The loss factor curve has been evaluated using eqn (10), in the following manner. Particular values of (t/τ_0) were chosen, and the corresponding values of ε'' and $\omega\tau_0$ were then determined using (10a) and (10b) respectively. The result is compared with the true values, calculated by taking the imaginary part of eqn (6), and this is presented as the plot of $\varepsilon''(\text{Hamon})/\varepsilon''(\text{true})$ in fig. 4. The agreement for log $(\omega/\omega_{\max}) \geqslant 0.5$ is good, but for log $(\omega/\omega_{\max}) < 0.5$ there is a discrepancy which rises to a maximum of 10 % at about log $(\omega/\omega_{\max}) = -0.5$. Below this frequency, the ratio $\varepsilon''(\text{Hamon})/\varepsilon''(\text{true})$ decreases to about 0.7 at log $(\omega/\omega_{\max}) = -1.4$.

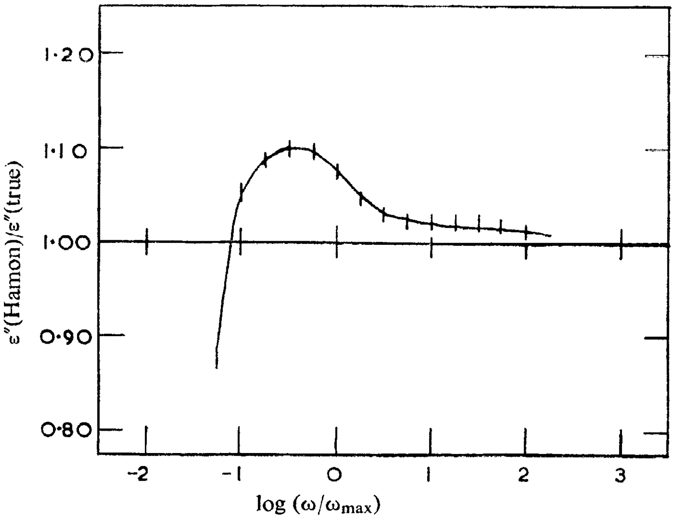

FIG. 4.—ε''(Hamon)/(ε''(true) against log $(\omega/\omega_{\max})$ for the present function with $\beta = 0.50$.

A similar pattern of behaviour has been observed [18] when the Hamon approximation has been applied to the Cole-Cole distribution function. For $0.3 \leqslant n \leqslant 0.5$ the Cole-Cole, $\varepsilon''(\text{Hamon})/\varepsilon''(\text{true})$ behaves in a similar manner to our function for $(\omega\tau_0) > 1$, i.e., the high frequency region, while at low frequencies $(\omega\tau_0 < 1)$ the ratio departs from unity as does our function (fig. 4). Thus, we conclude that the Hamon approximation may be used with good accuracy in the region $\omega\tau_0 > 1$, for experimental results which conform to our function (eqn. 7(*a*)) with $\beta = 0.5$. The approximation may be used with good accuracy, if the correction is applied from fig. 4, for results in the region $-0.5 < \log(\omega\tau_0) < 0$, but cannot be applied to transient data which would transform to loss data below $\log(\omega\tau_0) = -0.5$.

CONCLUSIONS

The empirical decay function $\gamma(t) = \exp -(t/\tau_0)^\beta$ may be transformed analytically into the complex dielectric constant if we choose $\beta = 0.5$. The resulting dispersion and absorption curves are non-symmetrical about the logarithm of the frequency of maximum loss and the behaviour lies between that obtained from the Cole-Cole and the Davidson-Cole empirical relations. The present decay function with $\beta = 0.38$ gives a reasonably satisfactory representation of the α relaxation in polyethyl acrylate at 10.3°C, and it is suggested that the α relaxation in other amorphous polymers could be fitted to the present function for suitably chosen distribution parameters. The accuracy of the Hamon approximation has been investigated for $\beta = 0.5$ and is applicable to the frequency range $\log(\omega\tau_0) > -0.5$, but fails at lower frequencies.

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