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A CRITICAL EXAMINATION OF THE DIELECTRIC RELAXATION THEORIES ABOUT NON-DEBYE RESPONSE

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ABSTRACT

The objective of this article is to review the characteristics of the α,β and $\alpha\beta$- dispersion data of polymers and to discuss the physical ideas underlying those existing dielectric relaxation theories and assess their success and rationality as applied to the loss data observed in polymers. Some of the complicated problem peculiar dielectrics such as internal field calculation, relations between macroscopic and microscopic parameters of bulk materials, have been briefly described. It is concluded that the present theories do not offer a satisfactory interpretation of the experimental observations and hence a much more acceptable model of cooperative molecular relaxation should be derived from the first principles is strongly required.

INTRODUCTION

The dielectric response of solids and liquids has been an active topic of research for over half a century by chemists, physicists and electrical engineers for a number of reasons: Chemists have been trying to obtain information about the molecular structure, interactions and dynamics of the subtances under study; physicists have been looking at the fundamental processes existing in materials, electrical engineers seeking for improved insulating materials. From the works of these rather separate schools there is a great amount of experimental data regarding the polarization or relaxation behavior of materials. Existing data covers a wide range of frequencies from 10^{-3} to 10^{13} Hz., and of temperatures from cryogenic to high temperature. This may offer an excellent opportunity to compare the existing dielectric relaxation theories with these data. Such attemps have been made in a number of articles and books (McCrum et al., 1967; Hill et al., 1969; Böttcher et al. 1978; Jonscher, 1983). It has been shown that the frequency response data, (which is obtained from measurement of real permittivity $\in'$ (w) and loss factor

$\epsilon''(w)$ as a function of radian frequency w under constant temperature where the complex permittivity $\epsilon(w) = \epsilon'(w) - i\,\epsilon''(w)$, of a very wide range of materials obey a certain types of emprically derived dispersion functions (Fuoss and Kirkwood, 1941; Cole and Cole, 1951; Davidson and Cole, 1951; Havriliak and Negami; 1966). For example, for polar molecules observed behaviour is summarized well (Cole and Cole, 1951; Davidson and Cole, 1951; Buckley and Maryott 1958; Davidson, 1961) by the Cole-Cole (1951) and Davidson-Cole (1951) functions. These functions are less successful with polymer data (Smyth, 1955; Davidson, 1961; Williams and Watts (1970), although Havriliak and Negami (1966) have shown that the combination of both Cole-Cole and Cole-Davidson expressions.

$$\frac{\epsilon(iw) - \epsilon_\infty}{\epsilon_S - \epsilon_\infty} = [1 + (i\,w\,\tau)^n]^{-m}; \quad (o < n,\ m < 1) \tag{1}$$

describes well a variety of $\alpha-$ and $\alpha\beta-$ dispersion data for polymers. Here ϵ_S, ϵ_∞, τ are the limiting low and high frequency permitivities and relaxation time respectively. On the other hand, the relaxation data of many amorphous polymers are better represented by Williams-Watts nonexponential decay function (Williams and Watts, 1970; Williams et al. 1971; Cook et al. 1970)

$$\varnothing(t) = \exp\,[-(t/\tau)^\gamma]; \quad (o < \gamma < 1) \tag{2}$$

A schematic representation of various data may be seen in Fig. 1. On the right is the practically non-existent-ideal Debye response (see next section) and then moving towards the left are the symmetric, the slightly asymmetric and the strongly asymmetric broad peaks all relating to the dipolar materials. The latter behaviour is called non-Debye response. Our discussion will be restricted to this type of relaxation data mentioned above which is classified under the name of $\alpha-$ and $\beta-$ dispersions, in polymers. Other responses shown further on the left of Fig. 1 will not be discussed. Even with these restrictions the existing literature on the subject, both experimental and theoretical is very large. The aim is doubtless presumptuous and the attempt can only be partially fulfilled.

The characteristics of α, β and $\alpha\beta$-dispersion data may be summarized as follows: It is well-known in dielctric literatures that the absorption observed above the glass transition temperature T_G in polymers is called α-dispersion, while below T_G β-dispersion. Although the criteria

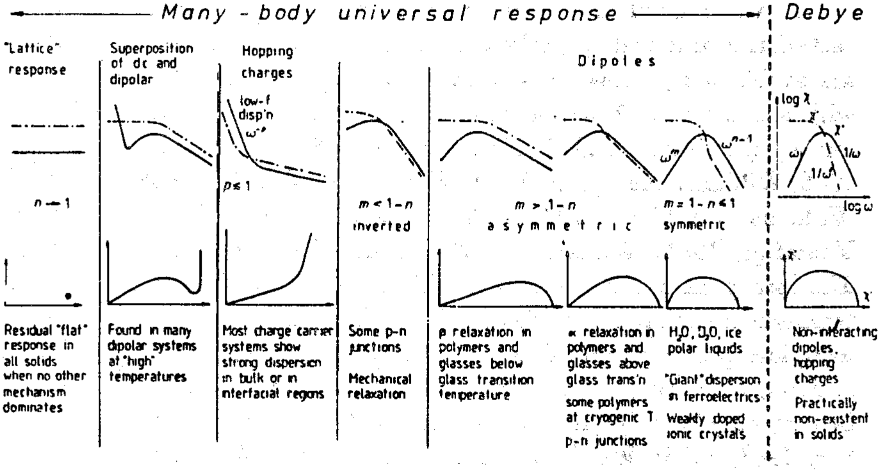

FIGURE 1. The general classification of all types of dielectric responses found in solids. The upper row gives the diagrammatic representation of the log $\chi'(w)$ (chain-dotted line) and log $\chi''(w)$ (solid line) against log w, the lower row gives the corresponding complex succeptibility plots. Typical materials giving the various types of response are indicated. The extreme right gives the practically nonexistent case of the Debye reponse, moving to the left we find increasingly broader loss peaks for dipolar systems, further to the left the charge carrier responses corresponding to the strong low-frequency dispersion and to dc conductivity. On the extreme left is the limiting case of "flat" frequency-and temperature- independent loss.
From Jonscher (1983).

for distinguishing α-peak from β-one is not well established in log (w) representation, the following empirical rules may be used for their selections in practice.

For α-absorption; (i) $T > T_G$. (ii) the half-width of the loss peak, λ, is less than 2.5 decades of frequency, (ii) a plot of log Wmax vs. T^{-1} (T: Temperature in Kelvin) results in slightly convex-line so that a single activation energy can not be derived from this plot, (iv) The average value of activation energy varies in the range of 50–250 KCal Mole^{-1} in polymers.

In the case of β-absorption (i) $T < T_O$, (ii) $\lambda > 3$ decades of frequency, (ii) The plot of log Wmax vs. T^{-1}, gives an Arrhenius behaviour, (iv) the activation energy is between 5 and 30 K Cal mole^{-1} in polymers and glasses.

The behaviour observed in the vicinity of T_G may arise from overlap of α-and β-peaks that is called αβ-peak, and the process is similarly named the αβ-absorption. Strictly speaking, these are all empirical classifications introduced for practical purposes.

In the light of the above empirical rules, some further typical characteristics of α and αβ-peaks exhibited by polymers with linear chains are as follows: (a) Loss curves are depressed, broad, and asymmetrical, with a half width, λ which varies between 1,6 and 2,5 decades of frequency (McCrum, et al, 1967; Jonscher, 1983; Havriliak and Negami, 1966; Williams and Watts, 1970; Williams, et al. 1971; Cook et al. 1970; Williams and Watts, 1971; Williams and Edwards, 1966; Ishida and Yamafuji, 1961; Williams, 1963; 1964, 1965; Jonscher, 1975). (b) The loss peak shifts towards the high frequency side with increasing temperature without significant change in shape (except where secondary loss processes interfere), but the peak-height of the α-absorption reduces, as a rule, slightly in magnitude with increasing temperature. So they may be superimposed to form a well-defined master curve (Jonscher, 1983, 1975; Williams and Edwards, 1966; Williams, 1963, 1964, 1965). (c) A plot of log Wmax vs. T^{-1} results in straight or slightly-convex lines with negative slopes (McCrum et al. 1967; Davidson and Cole, 1951; Williams, 1964; 1965). (d) The principal dispersion Wmax is independent of chain length (Stockmayer, 1967). (e) In addition to extensive studies on the relaxation in polymers over a wide range of frequencies and temperatures, several studies have also been made using pressure as an additional variable (Williams, 1964, 1965; Williams et al. 1971; Cook et al. 1970; Williams and Watts, 1970, 1971; Williams and Edvards, 1966). The following points are significant; (i) The shape of the loss curves at a given temperature is independent of pressure, as the pressure is raised the curves move gradually to lower frequencies without changing in shape. (ii) The plot of log Wmax vs. pressure at constant temperature resembles that against T. (iii) The plot of log Wmax vs. T at a given pressure results in convex lines. The foregoing features have to be explained by any proposed theories.

It is the purpose of this article to discuss to what extent the existing theories are capable of explaining and elucidating the experimental observations summarized above. By doing this we will touch inevitably to some of the problems such as internal field calculation, relaxations between macroscopic and microscopic parameters of bulk materials, Which are naturaly related somehow to the dielectric response.

THE PHYSICAL AND MATHEMATICAL BASIS OF DIELECTRIC RESPONSE

When a molecular system is placed in an electric field, there is always the tendency for any electrically charged species to migrate along the field in the appropriate direction. If the charged species are completely mobile this results in the conductivity familiar in metals, electrolyte solutions, or semiconductors. However, if the charged entities can move only a certain distance, and then for some reason become localized, the net result is an electric polarization of the samples.

For example, charge carriers may migrate across a sample, but be unable to cross the boundary between the sample and the electrodes. Under these conditions the trapped charges collect at the furface, causing interfacial polarization of the sample. At the other extreme on a distance scale, electrons may migrate across the atoms in a molecule but not between molecules. Thus, each molecule in the field suffers a slight distortion of electron distribution, called electronic polarization (forming in the molecules an induced dipole moment). The addition of each molecular dipole along the direction of the field again causes a resultant polarization of the whole sample. A third example of a polarization process, and the one of interest in this article, occurs when the two opposite charges in a molecular dipole attempt to migrate in the field, thus applying a turning couple to the molecule. This tends to align the dipole in the field. Again the resultant effect is an electric polarization of the sample, called, in this case, ‘orientation polarization’.

The migration of charges lowers the energy of the system in the field, and so is called ’relaxation’, and the adjective ’dielectric’ is added when polarization due to localized charges, is involved.

It is evident that the formation of the polarization can take place only at a rate determined by the charge mobility. This is unimportant if the electric field changes slowly, but if the electric field is altered sufficiently rapidly (as with a high frequency alternating voltage or in the field of electromagnetic radiation) there is no time for an equilibrium polarization to be established. So a study of the frequency dependence of the macroscopic phenomena resulting from polarization can yield information on the charge carries mobility. In the case of orientation polirization due to small field, this mobility is the rate of Brownian rotational diffusion.

For comprehensive accounts of the macroscopic theory of dielectric relaxation, the reader is referred to the text of Fröhlich (1958) and the articles of Scaife (1963). Further references are Glarum (1960), Hopkins (1876), Manning and Bell (1940), McCrum et al. (1967), Jonscher (1983), Böttcher and Bordewijk (1978).

The complex dielectric permittivity $\epsilon\,(iw) = \epsilon'(w) - i\epsilon''(w)$, where $w=2\pi\upsilon$ (Hz.), of a dielectric medium is given by the superposition relation (Fröhlich, 1958; Manning and Bell, 1940; Scaife, 1963; Hopkinson, 1976; Böttcher et al., 1978).

$$\frac{\epsilon(iw)-\epsilon_\infty}{\epsilon_S-\epsilon_\infty} = \chi(iw) = \int_o^\infty dt\ [\exp-iwt)]\left[\frac{-d\varnothing(t)}{dt}\right] \tag{3}$$

ϵ_S and ϵ_∞ are the limiting low-and high frequency permittivities, respectively. $\varnothing(t)$ is the normalized decay function of the polarization when a steady macroscopic electric field is removed from the medium. $\varnothing(t)$ contains contributions from relaxation processes only. $[d\varnothing\ /\ dt)$ may be regarded as the normalized transient current which flows when the steady field is removed from the medium. This forms the basis of transient experiments which are made (McCrum et al..., 1967; Jonscher, 1983) in order to obtain dielectric data in the low frequency range 10^{-3} to 10^3 Hz.

Equation (3) states that the normalized complex permittivity is given by the one-sided Fourier transform of the quantity $[-d\varnothing\,dt]$. This equation is the standart form of the equivalence between the complex dielectric permittivity $\epsilon(iw)$ and the decay function $\varnothing(t)$ or the response function $(-d\varnothing\ /\ dt)$. Eqn. (3) shows also that of one parts of the normalized complex permittivity is known over the entire relaxation range, then $[-d\varnothing(t)\,/\,dt]$ and $\varnothing(t)$ are also known over the entire relaxation range.

It is clear from eqn. (3) that a simple exponential decay function $\varnothing(t) = \exp\,(-\tau\,/\,t)$, $t>o$, where τ is a macroscopic relaxation time for the bulk material, which was first obtained from Debye's diffusive theory of dipolar relaxation for polar liquids (Debye, 1945) then the double potential well model for crystalline solids (Fröhlich, 1958), gives Debye's single relaxation time expression

$$\frac{\epsilon(iw)-\epsilon_\infty}{\epsilon_S-\epsilon_\infty} = \frac{1}{1+iwt}$$

and hence $$\frac{\epsilon'(w)-\epsilon_\infty}{\epsilon_S-\epsilon_\infty} = \frac{1}{1+w^2\tau^2};\quad \frac{\epsilon''(w)}{\epsilon_S-\epsilon_\infty} = \frac{w\tau}{1+w^2\tau^2} \tag{5}$$

Plotting log $\epsilon''(w)$ vs. log (w) gives a symmetric loss curve about its maximum value which occurs at Wmax $\tau=1$ and has a width at half-height of 1.144 decades. For fixed temperatures and at high frequencies, the real $\epsilon'(w)$ and imaginary parts $\epsilon''(w)$ of $\epsilon(i\epsilon)$ behave like $\epsilon'(w)\sim$

w^{-2} and $\epsilon''(w) \sim w^{-1}$ while at low freguencies, below the peak frequencies $\nu_{max} = \frac{\omega_{max}}{2\pi}$, the real part is almost one and the imaginary part, is propartional to w so the slope of the loss curve at low and high frequency site is (± 1), recpectively. The complex plane representation of ϵ'' against ϵ' falls on a half circle with the radius $(\epsilon_s - \epsilon_\infty) / 2$ centered on the real axis. At the peak frequency, the magnitude of the absorption is $\epsilon''(W_{max}) = (\epsilon_s - \epsilon_\infty) / 2$. The relaxation time τ, is generally thermally activated with an activation energy H and is given by

$$\tau = \tau_0 \exp (H / kt) \qquad (6)$$

where $\tau_0 = \nu_0^{-1}$ is some 'attempt-to jump' freguency and usually assumed to be associated with a phonon freguency, k Baltzmann's constant, and T is the temperatrue in Kelvin.

The relations (5 to 6) provide a useful check on the applicablity of the Debye equations and allow quantitative comparison with experimental observations.

We note that non of the properties of the α-, β- and $\alpha\beta$- absorptions given in the first section obeys Debye behaviour. Despite this fact, one success of Debye's diffusive theory of relaxation is that it gives us a graphical picture of fluctuations in a three dimensional assembly and links up with the theory of Brownian movements. In this model, a molecular dipole is expected to change its orientation by a series of small steps because of collisions with its neighbours, and this is described by a resistive couple which determines the microscopic relaxation time.

Both relaxation models of Debye may be criticized on the grounds that the influence of the interaction between dipoles has not been taken into account. Future developments of this model need to be concerned with this factor.

So far we have attempted to give a picture relevant to both time and frequency dependent polarization of the bulk material in the macroscopic sense. As a rule, the response of a system is not the sum of responses of individual components when interactions play a part. One is interested in obtaining as accurate information as possible about events at the molecular level from experimental data. This can only be achieeved by having an adequate theory of molecular processes and a precise relationship between macroscopic and microscopic parameters. In the next section, this aspect of the dielectric response will be considered in terms of "dipole correlation function" approach.

CORRELATION OF THE DIELECTRIC RESPONSE TO MOLECULAR PROCESSES

To relate the observed macroscopic phenomena to various molecular processes is, in general, a task of great difficulty, and has been the subject of considerable discussion and conflicting theoretical treatment during the last 30 years (Fröhlich, 1958 Powler, 1953; Glarum, 1960, 1972; Cole, 1965, 1973, 1974, 1980; Zwanzig, 1963, Nee and Zwanzig, 1970; Fatuzzo and Mason, 1967; Klug et al. 1969; Mazur and Mandel, 1959; Mandel 1971; Rivelson and Madden, 1975), Most of the treatment has been based on the dipole correlation function, which is simply the expectation value of a time-delayed product of values of the dipole moments. If m_j is the component, along the applied field of the dipole moment of the j-th molecule evaluated at time t, and m_j (0) is the value of the dipole moment at time t=0, the normalized 'auto-correlation function' for the j-th dipole is given by

$$\varnothing_j (t) = \frac{< m_j (o), m_j (t) >}{< m_j (o), m_j (o) >} \tag{7}$$

Here the brackets < > indicate an equilibrium ensemble average in the absence of an electric field. For the case that the n dipoles are the entire content of a shperical sample, the corresponsing macroscopic correlation function ∅ (t) is defined by

$$\varnothing (t) = \frac{< f_n m_j(o). \sum_{r=j}^{n} m_r(t) >}{< f_n m_j(o). \sum_{r=j}^{n} m_r(o) >} \tag{8}$$

where f_n is the canonical distribution of the dipolar system under equilibrium conditions. However, the most important question is how to calculate the relationship between ∅(t) and the corresponding molecular dipoles is considered. In recent years there has been much controversy on how best to calculate this relationship. An early attempt was presented by Glarum (1972) and a later approach by Cole (1973, 1974, 1980) using Kubo's linear response theory (Kubo 1957, 1961) for handling the external force in time-dependent statistical mechanics. This was subsequently criticized by Fatazzo and Mason (1967) and others (Klug et al, 1969; Mazur and Mandel, 1959) who derived more complex expressions than Glarul's by using the generalized Onsager models (Onsager, 1936). An excellent review of this general approach may be found in (Zwanzing, 1965; Cole, 1980).

The function $\varnothing_j$ (t) is usually obtained by considering the local field that acts on a molecular dipole or a microscopic sphere containing either one or a small number of such dipoles. This field is obtained by removing the microscopic sphere of material under consideration, and summing the fields arising from the free charge on the capacitor plates, those arising from the induced charge on the surface of the microscopic sphere and those which arise from the polarization effects upon the surroundings due to the reintroduction of the missing microscopic sphere of dielectric material (Onsager, 1936; Kirkwood, 1939). These has been some controversy on how best to calculate these local fields (Fröhlich, 1958; Powler, 1953; Glarum, 1960, 1972; Cole, 1965; 1973, 1974, 1980; Zwanzig 1963; Nee and Zwanzig, 1970; Fatuzzo and Mayson, 1967; Klug et al., 1969; Mazur and Mandel, 1959; Mandel, 1971) but Titulaer and Deutch (1974) have claimed to resolve this problem. However, none of these dielectric theories yields a truly single particle correlation function, $\varnothing_j$ (t), but rather a 'local' correlation function; the field is local insofar that a small sample volume is chosen, but it is nonmolecular in that the field is obtained in a cavity which is large compared to molecular dimensions so that a macroscopic dielectric theory can be used. An alternative treatment was given by (Kivelson and Madden, 1975) who attempted to relate $\varnothing$ (t) to a truly single particle $\varnothing_j$ (t) making use not of the local fields, but developing of a theorem which states that "if the molecular correlation function can be expanded as a sum of exponentials, the macroscopic correlation function has the same form with appropriately scaled parameters". However, their results are similar to the earlier ones and we propose to leave this matter in this rather undecided state.

It is important to note that all these complications arise when dealing with strongly polar materials. In such materials the relation of the macroscopic response te molecular behavior depends significantly on the mutual correlation of the motion of molecules through the short-range interactions. In electrically dilute materials, however, the discrepancy between macroscopic and molecular behaviour is often unimportant. Even for strongly polar liquids, the relation between the complex permittivity and $\varnothing_j$ (t) was often given in the from

$$X_j\ (iw)\ q(w) = \int_0^{\infty} \left[\frac{-d\,\varnothing_j}{dt}\right] \exp\ (-iwt)\ dt \tag{9}$$

where q (w) is a numerical factor which depends upon the detailed local field considerations (Glarum, 1960, 1972; Cole, 1965, 1973, 1974). To a good approximation q(w) may be taken to be unity (Cole, 1973, 1974; Cook et al., 1970). Consequently eqn. (9) and the macroscopic relation given by (3) are very similar in form. Writing $\varnothing_j\ (t) = \exp\ (-t\,/\,\tau)$, eqn. (9) gives the usual single relaxation expression if $q(w) = 1$. Note that the exponential decay is not an acceptable correlation function since its non-zero time derivative at $t = o$ predicts an instantaneous response to the field being turned off. In practice, from the definition it should be zero when t tends to zero. This anomaly arises because of the neglect of intertia terms, and has received much attention for nonpolymeric systems (Birnbaum, 1970).

Thus the dielectric relaxation of systems of small molecules in the liquid state may be considered in terms of the dipole correlation function and this has been done for a number of systems (Glarum, 1960), 1972), even including internal re-orientation processes within small molecules (Williams, 1968). The essential difference between the nonassociated molecules and polymer molecules lies in presence of correlations in the dipole orientations along a polymer chain.

The dynamic theory of the dielectric behaviour of dipolar polymers has been outlined by Cook, Watts and Williams (1970), using the dipole correlation for a flexible polymer chain containing only one kind of dipole. Eqn. (8) is then replaced by

$$\varnothing(t) = \sum_j \sum_r < m_j(o)\ m_r\ (t) > / < m_j(o)\ .\ m_r\ (o) > \tag{10}$$

Here $[m_r(t)]$ are the individual dipole moments along the polymer chain. The sums are taken over dipolar elements only. Egn. (10) consists essentially of two parts: The so-called auto-and cross correlation terms. The autocorrelation term $<m_j(o)\ .\ m_j(t)>$ was already mentioned and refers to the reorientation of a reference dipole j in the chain alone, while the cross correlation term, $<m_j(o)\ .\ m_r(t)>$, $j \neq r$ is the dynamic correlation between the dipole r and the reference dipole j. Hence there are two summations in eqn. (10).

Strickly speaking, eqn. (10) should be considered to be the more correct term than eqn. (7) and should apply everywhere, not only to polymers, on the condition that the interaction between dipole is not negligible. Eqn. (7) is the result of our ignorance of how to deal with cross-correlation function.

The relation between $\varnothing$ (t) given by eqn. (10) and the complex permittivity is made complicated by local field factors, but under certain assumptions one may write (Cook et al., 1970)

$$X(iw)\ Q(w) = \int_0^\infty \left[\frac{-\,d\varnothing(t)}{dt}\right] \exp\,(-iwt)\ dt \qquad (11)$$

$$Q(w) = [\epsilon_S\,(2\,\epsilon\,(w) + \epsilon_\infty)]\,/\,[(\epsilon(w)\,(2\epsilon_S + \epsilon_\infty)]$$

For cases of practical interest, ϵ (w) ϵ_S, Q (w) may be taken to be unity, so that eqn. (10) again similar in form to eqn. (3). Equations (9 to 11) relate the observed macroscobic complex permittivity to the dipole correlation function $\varnothing$ (t), and $\varnothing$(t) necessarily involves the dipole correlations along either a real chain (like polymer's one) or an imaginary one (such as the one often considered in ferro-electrics).

In fact, in ferro-electrics the permanent dipoles are strongly correlated to each other due to their long-range dipolar forces along the direction of the polarization axis (i.e. the easy direction). The physical nature of such a chain may be considered to be similar to the spin chains in ferromagnetics, and has a long-range character in space. However, a short-range chain order can also arise from forces due to chemical bonds, Van der Waals attraction and repulsion forces. These forces have a short range and play considerable roles in nearestneighbour interactions between molecules in polymers and glasses.

A simple model exhibiting short-range order is the Markoff chain, as it was pointed out by Domb (1955). In this, the essential interaction between units is accounted for by making the probability for the particular orientation of one unit to be dependent upon the orientation of the next. Therefore, such a short-range ordering is a natural consequence of the nearest-neighbour interaction between molecules, and should be considered in any rigorous calculation of the complex dielectric permittivity.

The dynamic behaviour of an infinite Markoff chain has been investigated by Glauber (1963) in terms of the Ising formalism by using time-dependent statistics. Its application to dielectrics may be found in (Bozdemir, 1981). It was shown that the exchange interaction has a considerable influence on the dielectric relaxation of one dimensional lineer chain molecular systems.

A CRITICAL EXAMINATION OF THE RELAXATION THEORIES ABOUT NON-DEBYE RESPONSE

In this section it is our aim to discuss the most important questions of dielectric: What physical processes are behind this non-Debye response?

As it is well-known that the commonly accepted answer to this question has been based on the concept of a distribution of relaxation times, DRT, which arises from the existence of more than one relaxation mechanism, each of which may be characterized by an exponential decay function with a single relaxation time. So the Debye dispersion functions are generalized under some fundamental assumptions regarding cause and effect, linearity and superposition. If the number of modes is sufficiently high mathematically the summation of Debye responses corresponsing to a distribution of relaxation times is carred out in terms of integration of a function G (τ) defining the distribution:

$$\frac{\epsilon\,(iw) - \epsilon_\infty}{\epsilon_S - \epsilon_\infty} = \int_o^\infty \frac{G(\tau)}{1+iw\tau}\,d\tau \tag{13}$$

and the loss factor is given by $\epsilon''(w) = \int_o^\infty G(\tau)\,\frac{w\ \tau\ d\tau}{1+w^2\tau^2}$ (14)

Here G (τ) is a real non-negative function of relaxation times. The real part of the complex permittivity is also written similarly;

$$\epsilon'(w) - \epsilon_\infty = \int_o^\infty \frac{G(\tau)\ d\tau}{1+w^2\tau^2} \tag{15}$$

From this, we obtain for $w=o$ $\epsilon_S - \epsilon_\infty = \int_o^\infty G(\tau)\ d\tau$

A simple molecular model leading to a discrete number of relaxation times is the multi-site model of Hoffman and his co-workers (Hoffman, Williams and Passaglia, 1966; Hoffman and Pfeiffer, 1954; Hoffman, 1955). This model is based on the fact that the force field experienced by a particular molecule is such that it can adopt a number of equilibrium positions seperated by a range of barrier heights. This situation is thought to exist such as in certain molecular lattices owing to anisotropy of the crystalline field in which the molecule reorients itself. This model has been notably successful where it has been applied with care. The parameters of the theory can also be analyzed in terms of molecular properties and intermolecular interactions. This has been made by Lauritzen (1958), interpreting the behaviour of long-chain dipolar compounds in urea chathrate complexes and the results are remarkably good. A great deal of works need to be done in such quantitative analysis of well-defined molecular environments. The various forms of clathrates are particularly attractive in this respect: the rotator phase solids and the spherical-molecule liquids derived from them represent further approachable stages in the direction of the typical polar liquid. It is reasonable to expect that much will be achieved by such further calculations for molecular models of dielectric relaxation. However the site-model theory and its further extension made by Ishida and Yamafuji (1961) as applied to polymers have been found unsuccessful to explain the nature of the broading and asymmetry of the loss curves. The rest of models for DRT such as Fröhlich (1958), Wagner (1913) Mrazek (1972) have used the idea of redistribution of barrier heights resulting normally from molecular complexity.

Although several important aspects of the observed loss behaviour may be explained by taking arbitrary functional forms of distribution in relaxation times indirectly in activation energies, the assumption of a distribution in activation energies is not based on any independent experimental evidence and has no molecular significance. Therefore this type of treatment of dielectric relaxation may be considered to be purely formal. For this reason, this approach has been found inadequate in a number of papers (Jonscher, 1975, 1977, 1980, 1983; Williams and Watts, 1970; Williams et al. 1971; Davidson, 1961; Glarum, 1960; Cole, 1961) and was particularly criticized by Jonscher (1980, 1983). Instead of DRT, Jonscher has, alternatively, suggested that non-Debye behaviour could arise from manybody interaction between dipoles or charged particles. Starting with this suggestion, we have recently studied (Bozdemir, 1981) the dielectric response of one dimensional dipolar chains by means of the "Time-dependent nearestneighbour Ising model theory" of Glauber (1963). In this relaxation model, each dipole is assumed to have two components: One is normally oriented between two localized states in a plane perpendicular to the chain axis, while the other is oriented along the chain. The model further presumes that the reorientation probability of any dipole located on the site chain has a time-dependent parameter, depending at any instant upon the momentary orientation of neighbouring dipoles. It was shown that the decay function of a single dipole located in either an infinite or a finite chain results in a non-Debye-type form, due to the many-body nature of the induced molecular moments. The model-results essentially have conformed the Jonscher's prediction, and the nearest-neighbour interaction in one-dimension seems sufficient to give rise to the observed departure from the Debye-Response in many order-disorder ferroelectrics, diluted linenear amorphous polymers, chain flexible dipoles consisted of the alkyl halides, and crystalline solids. In addition to this, the qualitative behaviour of the model studied shows similarity to the properties of some α-peaks observed in polmers, above T_G, but not the behaviours observed in 'solid like' situation below T_G so called β-peaks and also the one observed in the vicinity of T_G, named as αβ peaks.

Note that the time-dependent relaxation functions obtained from Kinetic Ising model of Glauber (1963) by a number of authors (Anderson, 1970; Isbister znd Mcquarrie, 1974; Bozdemir, 1981; Budimiz, 1985; Bahar, 1987) are nonexponential, and are similar to the Williams-Watts form. However, the deviation from exponential decay is not great enough to explain many experiments (Lacombe, 1980). Recently Hall and Helfand (1982) have studied the high temperature limit of a double spin flip kinetic Ising model (Haake and Thol, 1980). This model, which is based on the idea of cooperative conformational transitions in a polymer can be solved exactly, with time dependent relaxation functions similar to those of Glauber (1963)

In order to explain this aspect of experimental data, we have made several attemps to extend this dielectric Ising model theory further by including those neglected parts in the first treatment (Bozdemir, 1981) such as the long-range dipole-dipole interactions and the interaction between neighbouring chains. Not yet any successful result has been obtained, even that not much hope we have, because similar studies along this line (Zwanzig, 1963; Cole 1974) have already shown that only a limited effect on the departure from ideal Debye response is exerted.

For the αβ and β -absorptions of long- chain polar molecules we have recently suggested a new relaxation process on the basis of "a defect mechanism" (Bozdemir, 1985). In this model it is assumed that a dipole located on the site chain having interaction with its neighbours may be relaxed independently by either an Ising type mechanism (Bozdemir,

1981) or by a defect mechanism. The defect mechanism for dipolar relaxation which is that, at a site containing dipole, relaxation occurs when a defect diffuses to the dipole. For example if a defect is a 'hole' reaching a dipole, it can certainly increase the free volume within the dipole. Therefore the increased volume and also the lowered activation energy should allow the reorientation of the dipole more quickly than it would be otherwise. The turning of a dipole by a defect is assumed to cause whole chain motion as well. This may be explained as follows: As the defect moves along the chain by a diffusive mechanism, any part of the chain adjacent to the defect can undergo a turning motion. The rest fo the chain then rotates or attemps to turn from one localized site to the other due to this defect. If there are more than one such a defect in the chain, the rotation of the chain occurs likely by any one of these defects. So in this model, the relaxing unit considered is not only individual dipole associated with the chain but the chain itself as a whole. This relaxation mechanism is physically attractive because only a local section of the chain needs to be activated in order to bring the whole chain reorintation. From the analysis of this model a number of physically important results, such as the exact form of Williams-Whatts decay function (2) which may represent only α- and αβrelaxation data observed in amorphous polymers.

There is a number of one dimensional relaxation models, which involves the diffusion of "defects" (Bendler and Shlesinger, 1987). The early one is due to Glarum (1960) Hunt and Powles (1966). Their results are similar to the Cole-Cole and Cole-Davidson relations with m, $n >$ 0,5. Valeur et al. (1975) later obtained the same time-dependent relaxation function in their study of three-bond motions of a polymer backbackbone on a diamond lattice. Bordewijk (1975) improved the defect diffusion calculation by considering relaxation from all defects, not just the one that is nearest by, and found a relation function of the Williams-Watts form with the exponent $\gamma = 0.5$. This result was also obtained by Skinner and his co-Workers (1980) in their study of the dielectric relaxation by solutions of crystalline polyethylene and by Shore-Zwanzing (1975) in their study of the relaxation of perpendicular dipole polymers. More recently, Skinner (1983) has developed a one-dimensional model, which is based on both Glauber's kinetic Ising Model and Glarum's diffusion model to study the cooperative dynamics of linear chain molecules, Correlation functions are derived from the model well represented by the Williams-Watts function with γ between 1 / 2 and 3 / 4.

The results of the existing normal mode theories for the relaxation of polymers do not agree well with the experimental findings (McCrum et al., 1967). Also, the molecular basis of the normal mode theories is obscure. The theory of Yamafuji and Ishida (1962) for both α and β-relaxations is obly able to explain by this means the narrow α- peaks. In this model mathematical developments involve several approximations which tend to obscure the details of the model and cast doubt on the validty of the final expressions. The Dissade-Hill model (1979, 1980, 1983) of dielectric relaxation based on correlated states near phase transitions appears to be providing some basis for interpretation of the non-Debye behaviour in condensed matter, but we do not know how it can be extended to outside the critical region where the most dielectric data are measured.

DISCUSSION AND CONCLUSIONS

As in problems of kinetics generally, there is all too often an embarassingly large number of possible explanations of relaxation processes in dielectrics, with insufficient decisive evidence to reject or to favour any particular one. Regarding the multi-site models, multiple relaxation regions can result anisotropies of crystalline fields at a molecule, whether or not they can be represented by a one molecule barrier model, but often these are grounds for considering such possibilities as structural defects by vacancies or impuruties, proton transfer in hydrogen bonding systems, in homogeneties as in mixed crystals or partially crystalline aggregates, and liquid-like behaviour in amorphous solids. However the assumption of distribution in relaxation times due to the activation energies and other factors is arbitrary and has litte molecular significance.

The existing normal mode theories for the relaxation of parallel dipole components along the polymer chains do not agree well with the experimental findings summarized in the first section. Also, the molecular basis of the normal mode theories is obscure. The theory of Yamafuji and Ishida (1962) is only able to explain very narrow α-peaks without invoking the DRT.

The relaxation models based on cooperative relaxation processes such as Defect-Diffusion model of Glarum, Kinetic Ising model of Glauber appear to be providing some basis for interpretation of the non-Debye behaviours, but this field needs to be more firmly based on well-founded theoretical arguments rather than on ingenious conjecture.

Correlation function approach may be considered to be purely descriptive, i.e. describing the nature of the dielectric relaxation function in time after remowing the applied field. The actual time-dependent form of this function should be derived from first principles i.e. by using the Hamiltonian of the system for a given physical model. One possible derivation of the actual time dependent form of dipole correlation function for only a one-dimensional dipolar chain system has been achieved in terms of Glauber's formalism of the Ising model. This method leads to finite distorsions from the Debye shape and to considerable modification of the single-particle relaxation frequency. The works along this direction should be continued.

We finally come to the conclusion that the existing theories of dielectric relaxation appear not to offer a satisfactory interpretation of the experimental observations summarized in the first section. A much more satisfactory model for the interpretation of this type of dielectric relaxation data is strongly required.

NOMENCLATURE:

$\epsilon\ (iw)$	complex dielectric permittivity
$\epsilon'\ (w)$	frequency-dependent real permittivity
$\epsilon''\ (w)$	loss factor
w	radian frequency
$\varnothing\ (t)$	dielectric decay or macroscopic correlation function
ϵ_s	the equilibrium value of the total permittivity
ϵ_∞	high frequency part of the permittivity
$I(t) = -d\varnothing / dt$	electric current or after effect function
τ	macroscopic relaxation time
$X\ (iw)$	normalized complex permittivity
$X'\ (w)$	normalized real permittivity
$X''\ (w)$	normalized loss factor
ν	frequency,
ν_{max}	peak frequency of loss curve
ν_o	jumping frequency
H	activation energy
k	Boltzmann's constant
T	temperature in Kelvin

ϵ'' (Wmax)	maximum loss factor
$\varnothing_j(t)$	single particle correlation function
$m(t)$	dipole moment
f_n	cononical distribution of the system at equilibrium
T_G	glass transition temperature
$G(\tau)$	function of distribution of relaxation time.

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