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Review
A new understanding of the dielectric relaxation of solids

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The frequency dependence of the dielectric response of solids shows an apparently bewildering variety of patterns, virtually none of which corresponds to the classical Debye behaviour. However, a wide ranging critical analysis of the existing wealth of data shows that the dielectric loss obeys power-law dependences on frequencies, both below and above any loss peaks that may be present. This corresponds to power-law dependences on time under step-function excitation and it applies completely generally regardless of the detailed physical and chemical nature of the materials in question and also applies equally to dipoles, ions and hopping electrons as the polarizing species. Moreover, the power-law responses persist down to the lowest temperatures in the milliKelvin range, thus proving the importance of non-thermal transitions. The power laws are characterized by exponents in the range ± 1 and they cover as special cases the complete range of the observed types of response, from virtually frequency-independent "flat" losses often seen in low-loss materials, through various forms of asymmetric loss peaks to strongly dispersive behaviour in which both the real and the imaginary components of the susceptibility vary almost inversely with frequency. The "universality" of the power law strongly suggests the dominance in all materials of a common mechanism of dielectric relaxation and this is found in many-body interactions which provide a model capable of explaining the totality of the observed responses of solids, including both the frequency- and the temperature-dependence. In this interpretation, the classical one-particle Debye law represents but a singularity in a more general behaviour and is usually overshadowed by the new many-body mechanisms.

1. Introduction

The long-standing application of dielectric materials in many branches of electrical and electronic technology has led to a corresponding interest in the basic properties of these materials and, in particular, in the transient response of the polarization which covers as many as fifteen decades of time or frequency below the microwave region. A very wide range of materials has been investigated in a very wide range of temperatures extending from the highest that the materials may withstand down to cryogenic temperatures of 1 K and below. The wealth of experimental data may therefore be said to be truly overwhelming and the classification and characterization of these data present a challenge to those trying to understand the behaviour of dielectrics. It has to be admitted, however, that the theoretical understanding of the processes in question is rather primitive, being often confined to purely speculative models or resting on formal mathematical arguments without foundation in physical reality.

This situation is made even more difficult on account of the fragmentation of dielectric studies into smaller specialist areas which have little in common in terms of methods of analysis and accepted models. In addition, the materials themselves are often poorly characterized in terms of

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structure and composition and the various patterns of response appear to elude rational classification.

The present review outlines a recent attempt to produce an empirical classification of various types of dielectric response, based on the widest possible range of materials. This attempt appears to have been very successful in demonstrating the existence of a remarkably general or "universal" form of dielectric response which is only slightly affected by extrinsic factors such as impurities and structural defects and which leads to the inescapable conclusion that an overriding physical principle is at play which is applicable to all solid dielectrics regardless of their physical and chemical properties. The empirically observed universality of response is then shown to lead to a very natural theoretical interpretation in terms of many-body interactions which are expected to apply in all these different systems.

Here, the review will be confined to what may be described as the "low frequency" region in which "viscous" responses dominate and an arbitrary upper limit will be placed at a frequency of the order of 10 to 100 GHz. At still higher frequencies, in the THz range and above, phonon and lattice vibrational effects begin to dominate the response, also molecular and electronic excitations as well as interial and plasma phenomena come to the fore. All these processes are "strong" in the sense that their presence modifies very considerably the behaviour which is evident at the lower frequencies under consideration here and it would be very confusing to try to resolve their respective contributions. By contrast, it will be argued that the dominant processes in the low frequency region are many-body interactions which may be described as "weak" interactions. It is worth noting also that the frequency region extending for at least fifteen decades below our upper limit contains most of the frequencies of direct interest to electrical and electronic engineering, except for opto-electronic applications.

The review begins with a few basic concepts relating to dielectric polarization and this is followed by a brief description of the various, currently accepted, theoretical approaches to the observed strong departures of the response from the Debye model which appears to dominate much of dielectric thinking despite its manifest disagreement with experimental data. An outline of a new classification of all types of dielectric response will be given, showing typical examples of the various categories and the review will conclude with a presentation of the recently proposed many-body theory which promises to provide a unified model within which the entire range of experimental data may be interpreted.

At the start of the presentation it is necessary to clarify one essential point of principle relating to the "philosophy" of the approach taken here. Dielectric behaviour, especially taken over such a wide range of frequencies and materials as adopted here, is undoubtedly full of confusing complexities. Dielectric loss peaks abound whose shapes vary and whose overlaps in frequency seem to doom to failure any rational attempt at classification. In the face of this situation, one possible approach is to accept the complexity and to derive suitable empirical functions to model it, without attempting to produce a rigorous justification in terms of fundamental processes. This is the approach of the distributions-of-relaxation-times school, about which more will be said later. No other simple approach can account for the observed complexity in any significant range of frequencies.

However, the fundamental principle advanced in the present approach is that the dielectric response is basically *remarkably simple* when seen in terms of certain elementary "universal" responses. It will be pointed out that there exist many well documented examples of such universal behaviour covering the entire available frequency range, sometimes up to ten decades and that these simple examples constitute existence theorems for the universal response. Once such simple behaviour has been diagnosed and recognized as physically meaningful, more complex types of behaviour are easily understood in terms of a superposition of two or sometimes more such simple responses.

It is not claimed that this proposed universal approach can explain the actual behaviour of all materials in the entire frequency range in terms of a single mechanism. Such a claim would be utterly wrong and is one we have never made. It can be claimed however, that most materials show two, or at most three, partially overlapping universal mechanisms in the entire range of frequencies in which measurements are available; each of these mechanisms being understandable in terms of simple physical processes. The ability to analyse the apparently complex behaviour of dielectrics represents, in our submission, a decisive step forward towards the complete understanding of the dielectric response. In this sense, the general

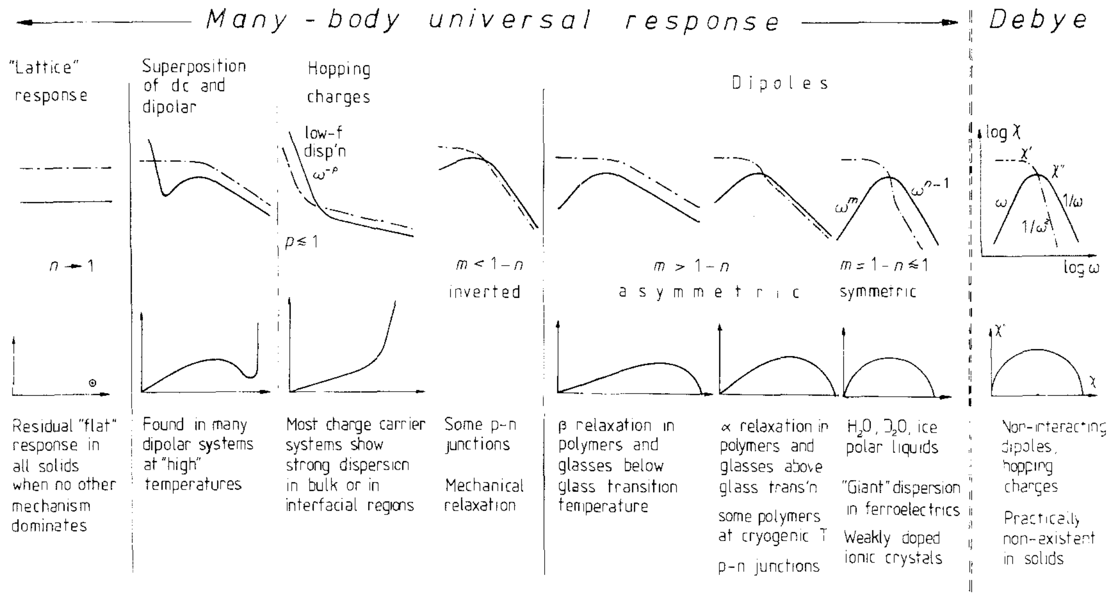

Figure 1 A general classification of all observed types of dielectric response in the entire range of solids. The upper diagrams represent the plots of $\log \chi'(\omega) - \log \omega$ as the chain-dotted lines and of $\log \chi''(\omega) - \log \omega$ as solid lines. They range from the ideal Debye response on the far right, which is very seldom, if ever, found in solids, through the α and β peaks in dipolar materials, the "inverted" peaks observed in p–n junction generation/trapping processes and in some mechanical loss peaks, and on to the universal dependence for charge carrier systems. The limiting forms of behaviour are represented by the strong low frequency dispersion for which $n \rightarrow 0$ and by the "flat" frequency response of low-loss materials for which $n \rightarrow 1$. The lower diagrams represent the corresponding complex χ plots. The various types of materials giving the respective responses are indicated, together with the principal mechanisms. See also [4, 5, 35].

classification of Fig. 1 is intended as a key to the understanding of more complex responses and not as a claim that all actual responses are as simple as those shown.

Some of our critics advance the proposition that merely to admit the existence of two or three overlapping universal mechanisms is to overthrow the very basis of our universal mechanism. This is neither fair nor reasonable and it could be compared with the statement that if two Debye mechanisms can co-exist, then the Debye mechanism is not valid at all!

2. Basic dielectric concepts

The dielectric response of any material may be defined in terms of the time dependence of the depolarization current following a sudden removal of a steady polarizing field, E_0,

$$i(t) = \mathrm{d}P/\mathrm{d}t = \epsilon_0 E_0 f(t), \qquad (1)$$

where $P(t)$ is the time-dependent polarization, ϵ_0 is the permittivity of free space and $f(t)$ is the dielectric response function. Alternatively, the response may be characterized in terms of the frequency dependence of the complex dielectric susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ which is the complex Fourier transform of $f(t)$ and ω is the radian frequency. The dielectric permittivity $\epsilon(\omega)$ of a material consists of the free space contribution and of the sum of all susceptibilities for the physical mechanisms operating in the material. The real and imaginary components of $\chi(\omega)$ and of $\epsilon(\omega)$ are related by the Kramers–Kronig relations which are valid for all responses which are linear in the applied electric field.

The archetypal form of dielectric response is that of the classical Debye model for which the frequency and temperature dependence of the susceptibility is given by

$$\chi(\omega, T) = \frac{A}{1 + i\omega\tau} = \frac{A}{1 + i\omega\tau_\infty \exp{(W/kT)}}, \qquad (2)$$

where τ is the relaxation time which is often thermally activated with an energy W. The dielectric loss $\chi''(\omega)$ represents a symmetric peak at $\omega_\mathrm{p} = 1/\tau$ with a width at half-height $\lambda_\mathrm{D} = 1.144$ decades in the logarithmic frequency representation. The response function is $f(t) \propto \exp{(-\omega_\mathrm{p} t)}$.

The following physical processes lead to the prediction of the ideal Debye response:

(i) identical non-interacting dipoles "floating" in a viscous medium with thermal randomization [1];

(ii) identical non-interacting dipoles "jumping" between preferred orientations with respect to the positions of the nearest neighbours;

(iii) a set of non-interacting charges, each hopping between identical potential double wells [2, 3];

(iv) a series combination of a resistance R and a capacitance C;

(v) the generation–recombination process for electron–hole pairs on a simple recombination level in a semiconductor.

The loss peak frequency, ω_p, is related to the viscosity η by $\omega_p = 2\eta kT$ in (i); is related to the natural frequency of thermally activated hopping in (ii) and (iii); is related to the product $1/RC$ in (iv) and is related to the recombination time in (v).

While mechanism (i) is clearly not applicable in solids, except possibly for some solid rotator phases, mechanisms (ii) and (iii) are classical solid-state processes. Mechanism (iv) would be expected to apply where a Schottky barrier or other chemical barrier exists in series with a resistive bulk medium, while (v) would be expected to be seen in semiconductor p–n junctions.

It is an undisputed experimental fact that the dielectric response of the overwhelming majority of solids does not follow the Debye relations and in many cases the departure is such that there is no resemblance to the ideal, so that the simple Debye model cannot possibly apply to these materials [4, 5].

3. Previously accepted theories

This evident discrepancy has long been recognized and as early as the turn of the century von Schweidler formulated the power law (see Equation 10) as the general form of time–domain relaxation, replacing the exponential law corresponding to the Debye process. This power law is known as the Curie–von Schweidler law. The existence of these serious departures from the Debye law has given rise to the development of a range of theoretical treatments seeking to provide explanations of the observed behaviour in terms either of modified Debye-like models or of other simple mechanisms [6]. The principal approaches may be listed as follows: (a) distributions of relaxation times (DRT's); (b) distributions of hopping probabilities; (c) correlation function approaches; (d) local field theories; (e) diffusive boundary conditions (Warburg impedance); (f) interfacial phenomena (Maxwell–Wagner) effects; (g) transport limitation at boundaries.

Of these, DRT's are the simplest and the least sophisticated and postulate the required form of DRT to explain virtually any result of $\chi(\omega)$, but this approach does not prove anything [7–11]. A few *ab initio* calculations have been made [12] for well-defined crystal structures, e.g. thio-urea, obtaining a reasonably good fit with experimental data in the GHz range. No comparable calculations appear to have been made at lower frequencies and wider frequency intervals. The most serious objection to the DRT approach is the broad similarity of the dielectric response of most materials, which is the central point of the present review, and this would require an "integrating" approach to DRT's showing why widely different materials should have similar DRT's. No such attempt appears to have been made. Moreover, low-temperature behaviour of dielectrics is equally incompatible with any form of thermally-activated response, as DRT's invariably are.

One of the most serious conceptual difficulties associated with the DRT philosophy is the virtual impossibility of furnishing a positive proof that a particular dielectric response does or does not involve a distribution. Among the indirect arguments may be cited the generally observed fact, known under the name of compensation rule, that where a physical parameter such as a relaxation time or the electrical conductivity can be expressed in the form implied by Equation 2, with a wide range of values, then the pre-exponential factor, τ_∞ in our case, and the activation energy are related by the equation

$$\tau_\infty = a \exp (W/kT_1), \qquad (3)$$

where T_1 and a are suitable constants. This means that the distribution must necessarily involve a variation of both the pre-exponential factor and the activation energy. This, however, would necessarily require a changing shape of the spectral response with temperature, since different parts of the frequency spectrum, corresponding to different relaxation times, move with different activation energies. This is clearly not the case in many situations in which the time–temperature superposition principle is applicable, e.g. in most

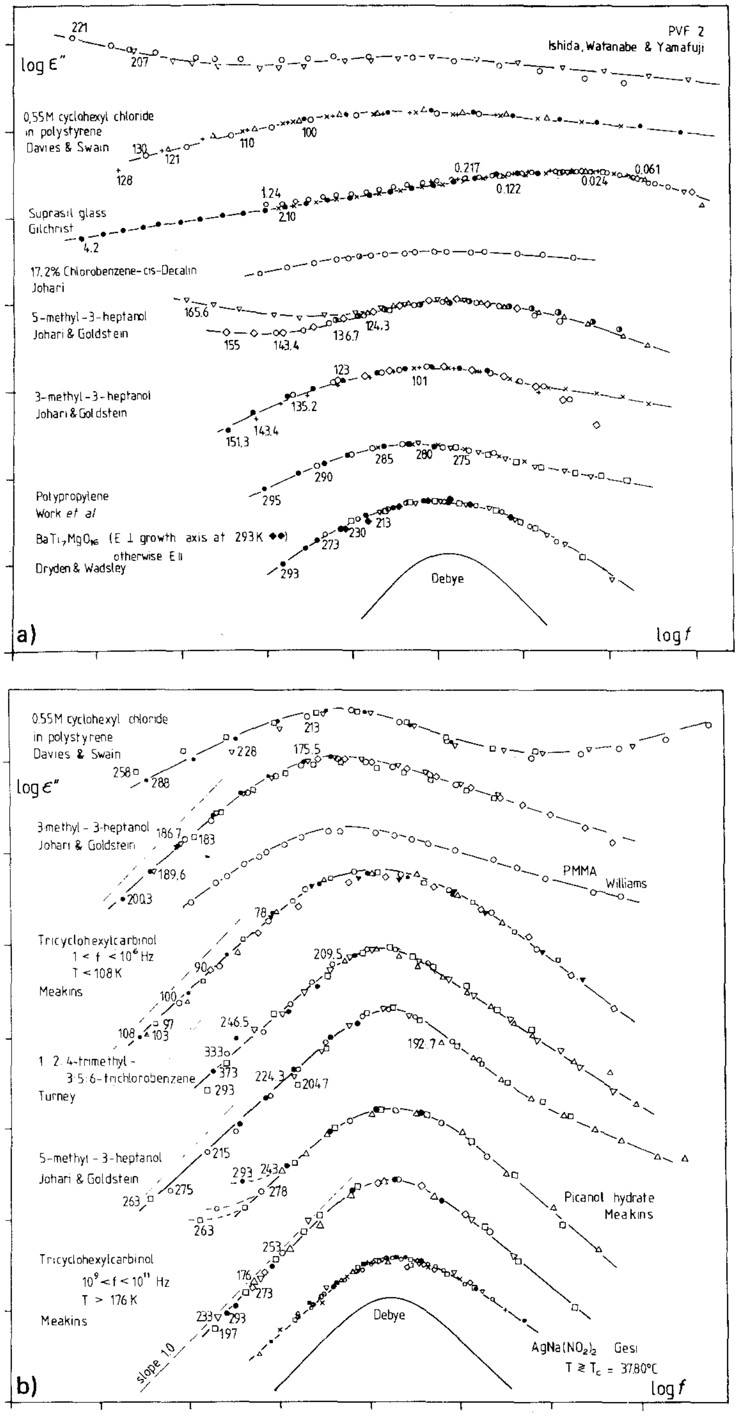

Figure 2 A compilation of dielectric loss data for a range of materials, solids as well as liquids, plotted as log $\epsilon''(\omega)$ against log ω, normalized for different temperatures and displaced vertically and horizontally for clarity. Temperatures are indicated at the corresponding lowest frequency points: (a) correspond to the lower temperature peaks, and (b) to the higher temperature. Slopes corresponding to $m = 1$ are indicated and so are the Debye responses. The sources of the data are indicated. The logarithmic plots and the normalizations were made by R. M. Hill who kindly supplied his diagrams.

examples quoted in Fig. 2. Further discussion of this topic and additional references are given by Jonscher [13].

As regards the various means of deriving the DRT's from the experimentally observed behaviour, and there are many such methods [6], it is noted that this procedure cannot possibly lead to the derivation of anything more specific or more precise that the original information obtained from the experiment. Thus it is wrong to argue, as some people do, that the DRT represents a more sensitive means of characterizing the dielectric behaviour than the original data.

The approach (b) is essentially DRT in the context of hopping charges [14–18] and similar arguments apply. Once again, however, despite the high mathematical sophistication, there is no independent check on the physical plausibility of the postulated distributions.

Correlation functions (c) are mathematically sophisticated methods [19–24] of following the time evolution of the orientation of a dipole, but the basic limitation is that, while it is possible to describe simpler forms of response, taking into account many-body interactions requires the summation of several terms in a series which is not well convergent and the mathematical difficulties of obtaining a realistic solution rapidly become prohibitive. There is therefore a tendency to make it into an "input–output" theory, where one puts in functions which in the end give the desired result, without being able necessarily to justify the use of these functions.

Local field theories attempt to describe the forces acting on dipoles [25] in terms of interactions with neighbours and they were initially introduced by Clausius and by Mossotti in the 1870's to describe the static response. Unfortunately, in the dynamic response they are capable of describing only the relatively small departures from the ideal Debye behaviour and to that extent they do not apply to the majority of dielectric data.

The diffusive boundary conditions (e), as developed initially by Warburg in 1898 for the case of the interface between a liquid electrolyte and a metallic electrode, can be modelled by a distributed R–C network and have the characteristic frequency dependence [26–28]

$$\chi'(\omega) = \chi''(\omega) \propto \omega^{-1/2} \qquad (4)$$

with $f(t) \propto t^{-1/2}$. This represents the first decisive break with Debye response and goes in the right direction but its limitations are that it requires the presence of two types of charges of opposite signs to maintain neutrality in a diffusive medium. Moreover, the particular exponent $\frac{1}{2}$ is found only exceptionally in practice and the model itself is quite inflexible in this respect.

An ingenious attempt to introduce diffusion into dipolar processes seeks to "trigger" the dipolar transitions by the diffusive motion of some "defects" in the material [29, 30] although the physical process in question is far from clear and the end result no more useful that in the straight diffusion.

The various Maxwell–Wagner models of interfacial polarization (*f*), [31, 32], represent basically an extension of the R–C network to a whole distribution, thus representing an unverifiable hypothesis capable of explaining in principle, any frequency dependence of dielectric polarization.

Transport limitation at boundaries (g) through selective transmission of certain carrier species, mainly ionic, has been developed in a series of papers by Macdonald [33, 34] discussing ionic conductors with a high degree of mathematical sophistication. While it is capable of modelling barrier responses in highly conducting electrolytes, it cannot explain strong departures from Debye behaviour found in many dielectrics, including ionic conductors. Once again there are many disposable parameters in the theory which cannot be verified independently, making the theory essentially conjectural.

This brief review of the currently accepted theories in various branches of the science of dielectrics suggests that those theories which postulate well defined physical models, in particular (e) and possibly (g) and (d), are incapable of accounting for the majority of experimental facts, while those that do succeed to "fit" the data tend to rely on unverifiable assumptions.

4. The need for an alternative approach

If it were a fact that the experimentally observed departures from the Debye model behaviour in various classes of materials were randomly irregular, then there would be little justification for going beyond the currently available theories, each of which may have some plausibility in its own particular field, such as low-loss polymers, high-density electrolytes, amorphous semiconductors and so on. This would be even more so if these very different materials showed completely different types of dielectric responses unrelated in any way to one another. It would be further objected that many data are of poor quality, refer to indifferently characterized materials and are available in a narrow frequency range, so that there is little point in developing an all-embracing theory generalizing the approach.

It is suggested, however, that the situation is far more favourable than this, and that the actually available range of up to 15 decades below the microwave region offers unrivalled scope for presentation of data and that the actual responses of all these very different materials show remarkable common features, or "universality" of frequency dependence, despite all the acknowledged shortcomings of the materials in question.

Most significantly of all, the laws of universal behaviour determined on the empirical basis are neither arbitrary nor inexplicable, but they point to a very meaningful physical mechanism which is uniquely capable of explaining the entire range of experimental data, including very low-temperature behaviour and the response of the low-loss materials. The case for a completely fresh approach to the entire theory of dynamic dielectric responses rests, therefore, on the synoptic view of the totality of dielectric responses leading to a theoretically meaningful universality. Therefore a representation of the synoptic classification of response types is given.

5. The empirical classification of response types

Fig. 1 shows this classification, beginning with the ideal Debye response on the far right. It is noted that this is hardly ever seen in practice and this is a serious assertion which often provokes strong reactions. It is suggested, however, that where data of sufficient quality exist, it is possible to show significant departures from the Debye law, for which $\chi''(\omega) \propto \omega^{-1}$ and $\chi'(\omega) \propto \omega^{-2}$ beyond the loss peak frequency, whereas the slightest departure from Debye means that $\chi''(\omega) \propto \chi'(\omega) \propto \omega^{-1+\kappa}$, where $\kappa \ll 1$. This is a very sensitive test [36, 37]. Certainly by that test, water and ice are not Debye systems.

5.1. Loss peaks in dipolar materials

The overwhelming weight of experimental evidence, when represented in the form of a $\log \chi'' - \log \omega$ plot, is that the empirical form of loss peaks may be approximated by the expression [36, 38]

$$\chi''(\omega) = \frac{A}{(\omega/\omega_p)^{-m} + (\omega/\omega_p)^{1-n}} \tag{5}$$

with

$$0 < \left\{ \begin{matrix} m \\ 1-n \end{matrix} \right\} < 1. \tag{6}$$

while the real part of the susceptibility follows the relations

$$\begin{aligned} &\chi'(\omega) \propto \omega^{n-1} && \text{for } \omega \gg \omega_p \\ &\text{and} \\ &\chi'(\omega) = \text{constant} && \text{for } \omega \ll \omega_p. \end{aligned} \tag{7}$$

Fig. 2 shows a collection of data for a range of polymers, normalized for different temperatures to bring the peaks into coincidence. These peaks comprise both the so-called α and β peaks, the former being found above the glass transition temperature, the latter below. While the widths and the temperature dependence of the loss peak frequency are different in the two regimes [38–40], Equations 5 and 7 are valid. It should be pointed out that any departures from the straight-line plots may be understood in terms of overlap of some other mechanism; there are certainly very many examples where the power law is obeyed rigorously over many decades of frequency.

The selection of peaks shown in Fig. 2 refer to systems in which the variation of temperature does not bring about any change in the shape of the loss spectrum: this is referred to as the principle of frequency–temperature superposition, or the equivalent time–temperature superposition. While there are many such systems, equally there are others with which the shape of the spectral response changes with varying temperature, usually in the sense of decreasing width of the peaks with increasing temperature. This type of behaviour is found among some of the examples in Fig. 2 where the same material is shown in both diagrams, e.g. cyclohexyl chloride in polystyrene and also methyl heptanol, but in these cases the change of shape occurs abruptly at the glass transition. However, there are also examples in which the slope changes gradually with temperature indicating a continuously changing structure of the system.

Fig. 3 gives the exponents m and $(1-n)$ in the form of the plot for one hundred different dipolar materials, solids as well as liquids [36, 41]. In this diagram, the ideal Debye response corresponds to the top right corner, while the empirical Cole–Cole [42] and Fuoss–Kirkwood [43] expressions corresponding to symmetric loss peaks in $\log \omega$ representation fall on the diagonal, while the top side represents the asymmetric peaks for which the Cole–Davidson expression [44], may be used, giving $m = 1$.

It is interesting to note that none of these empirical formulae fit the results very well, except the Cole–Davidson expression which relates, for the most part, to experimental points corresponding to very high frequencies and the significance of this will be seen later in the theoretical discussion. The other well-known empirical expression due to Williams and Watts [45] does not fit the data either. The general conclusion from this graph is

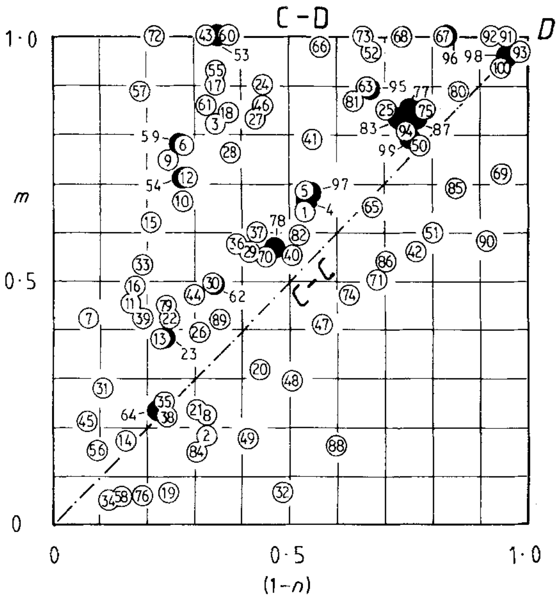

Figure 3 The representation of the dielectric response of one hundred dipolar materials, solids as well as liquids, in the form of the plot of the exponents m against $1-n$ in the empirical expression, Equation 5. Each material is represented by a circle with the number referring to the index to be found in the original reference by Hill [4]. In addition, acoustic absorption data are represented by triangles and mechanical modulus data by squares. The Debye response is represented by the point "D", the dotted diagonal corresponds to symmetric peaks given by the Cole–Cole, Fuoss–Kirkwood and Williams–Watts empirical expressions. The top side represents the empirical Cole–Davidson expression.

that the exponents m and n are uncorrelated and that they must therefore represent independent physical mechanisms [36].

There are very many other examples of dielectric loss peaks arising in dipolar materials other than polymers and here some examples will be mentioned without showing the data. Among materials showing near Debye responses may be mentioned Er-doped CaF_2 [37, 46], the "giant dispersions" observed in many ferroelectrics at GHz frequencies [47], liquid crystals parallel to, but not normal to, the orientation of the molecules [48], certain high purity p–n junctions [49]. There are, of course, many examples of Debye-like behaviour arising from the series $R-C$ configuration already mentioned and it is not proposed that they are discussed here. Broader loss peaks are found in glasses [50–52], in many p–n junctions [49, 53], in polymers at cryogenic temperatures [54–57], electrolytic capacitors [58] and many others. There are many examples of extremely broad loss peaks, with half-widths of four decades or more, among which may be mentioned suprasil glass at temperatures below 4 K [59] and various polymers at 4 K which are almost flat [57, 60]. The advantage of low-temperature measurements is that they are completely free of the disturbing influence of direct current conduction which tends to mask the low-frequency response at higher temperatures.

As a general observation it may be said that loss peaks are associated with dipolar systems in which the dipoles may be of molecular origin or may arise from "closely coupled" pairs of defects of opposite signs, such as may be found in doped ionic crystals. In particular, an anisotropic system may behave as a conductor in one direction and as a dipolar dielectric in another: an example is single-crystal sodium β-alumina [61] where a pronounced peak is observed in the direction normal to the highly conducting planes.

5.2. The dielectric response of charge carriers

A clear distinction tends to be made in dielectric literature between the dipolar responses which give rise to loss peaks, on the one hand, and the effect of charge carriers which result in purely direct current (d.c.) conductivity, σ_0, on the other hand. The effect of the latter is to add a singularity at zero frequency which tends to mask the low frequency "proper" dielectric behaviour by a term of the form σ_0/ω in $\chi''(\omega)$, while leaving the real part of permittivity unaffected. Such a distinction is certainly valid in the case of "free" electrons and holes in crystalline semiconductors, which move in a quasi-free motion between collisions and cover mean free paths of many interatomic spacings. These charge carriers, which are also responsible for the conductivity of metals, show a frequency-independent σ_0 at least up to the frequency corresponding to the reciprocal free time between collisions, beyond which the conductivity decreases as ω^{-2}.

A completely different situation arises, however, in those many solids in which a finite electrical conductivity is due to hopping motions of charges, such as localized electrons in strongly disordered semiconductors and all ionic charges in all materials. These charges execute rapid hopping motions between sites which may be determined by localized defects in the solid or may be due to the very presence of the charge itself, as in the case of polarons. The important feature is that the

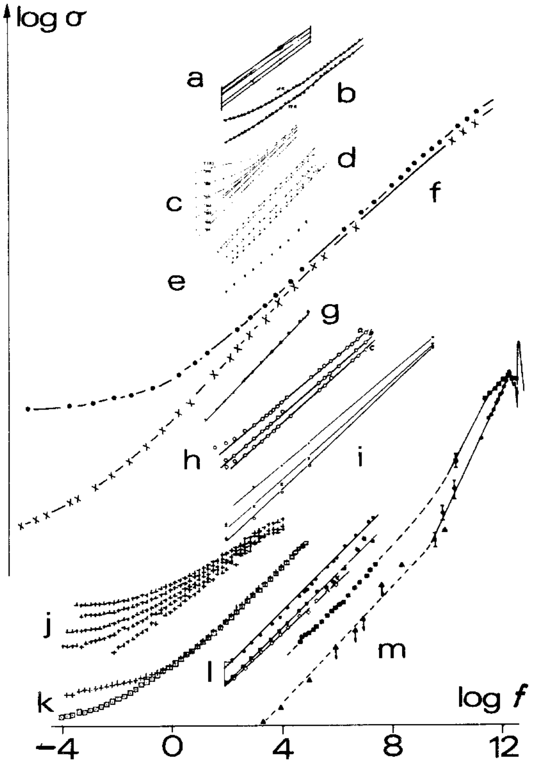

Figure 4 The compilation of a.c. conductivity data for a range of materials arranged on a common log *f* basis (in Hertz) but displaced vertically along the log σ axis for clarity. Data sets denoted by one letter are on a common log σ scale. (*a*) Single-crystal silicon in the impurity hopping range by electrons at (bottom to top) 3.0, 4.2, 8.0 and 12.0 K [62]; (*b*) single-crystal β-alumina at 77 and 87 K – a classic fast-ion conductor by Na^+ ion movement [63]; (*c*) glow-discharge deposited amorphous silicon in the temperature range 84 to 295 K [64]; (*d*) a range of chalcogenide glasses at 293 K, top to bottom: Sb_2S_3, $Sb_{30}As_{10}S_{60}$, $Sb_{20}As_{20}S_{60}$, As_2S_3, $Sb_{10}As_{30}S_{60}$ [65]; (*e*) single-crystal anthracene at 294 K with 1 M saline solution as contact – two sets of measurements are shown (not resolvable on the scale of the present diagram) [66]; (*f*) single-crystal anthracene (— X — X —) and evaporated β-carotene (– • – • –) at 294 K [67]. The two sets of data are on corresponding log σ scale, showing the close similarity of the results in the a.c. range, with significant departures in the d.c. levels. These results show the superposition of a very shallow peak at 10^6 Hz with an underlying trend $\sigma \propto \omega$; (*g*) trinitrofluorinone-polyvinyl carbazole (TNF PVK) [68]; (*h*) three glasses (i) 50 P_2O_5–50 FeO, (ii) 50 P_2O_5–40 FeO–10 CaO, (iii) 50 P_2O_5–25 FeO–25 CaO: room temperature [69]; (*i*) 80 V_2O_5–20 P_2O_5 glass at three temperatures [70]; (*j*) evaporated amorphous SiO_x (silicon monoxide) in the range of temperature (bottom to top) 211 to 297 K [71]; (*k*) stearic acid 9-layer film between Al and Au electrodes in the dark (□□) and in the presence of ultra-violet light (+ +) [72]; (*l*) three amorphous samples (top to bottom As_2Se_3, Se and As_2S_3. The measurements, taken at 300 K are believed to be those of the bulk material and not to be influenced by the electrodes [73]; (*m*) two samples of As_2Se_3 at room temperature [74] extending to far-infra-red frequencies and showing a steeply rising ω^2 region above 10 GHz, characteristic of lattice vibrational processes [4].

carriers spend most of the time in these localized sites, the transitions themselves being very rapid in comparison. In the limit of two-centre hopping, where the charges are each confined to two centres only, the situation is physically indistinguishable from the dipolar situation. As the probabilities of further hopping transitions increase, the motion in a low frequency electric field tends to include an increasing component of directed drift superimposed on the rapid to-and-fro jumps which are present in thermal equilibrium.

The study of the frequency dependence of the electrical conductivity became popular in the context of amorphous and glassy semiconductors which have been receiving a large volume of attention recently. In these materials the alternating current (a.c.) conductivity is normally expressed in the form of a sum of the d.c. contribution and the "true a.c." component which is directly related to the dielectric loss

$$\sigma(\omega) = \sigma_0 + \omega\epsilon''(\omega). \qquad (8)$$

It became known that the a.c. component of $\sigma(\omega)$ corresponded to a power-law frequency dependence [3, 104]

$$\epsilon''(\omega) \propto \omega^{n-1} \quad \text{for} \quad 0.6 < n < 1 \qquad (9)$$

and this type of frequency dependence became accepted as a "proof" of the applicability of the electronic hopping mechanism. However, this view was arrived at in apparent ignorance of the fact that exactly the same power law applies to ionic conductors and is also obeyed above the loss peak frequency in dipolar solids, Equation 6. Fig. 4 shows a compilation of the conductivity data for a range of materials, some of which are clearly electronic conductors, (*a*), (*c*), (*d*), (*g*), (*h*), (*j*) and (*l*); (*b*) is a classic example of an ionic conductor, while the others have at least a strong contribution from dipolar mechanisms. The underlying trend corresponding to Equation 9 is clearly visible, while the low-frequency response tends to a frequency independent conductivity which would represent d.c. It is clear, however, that the

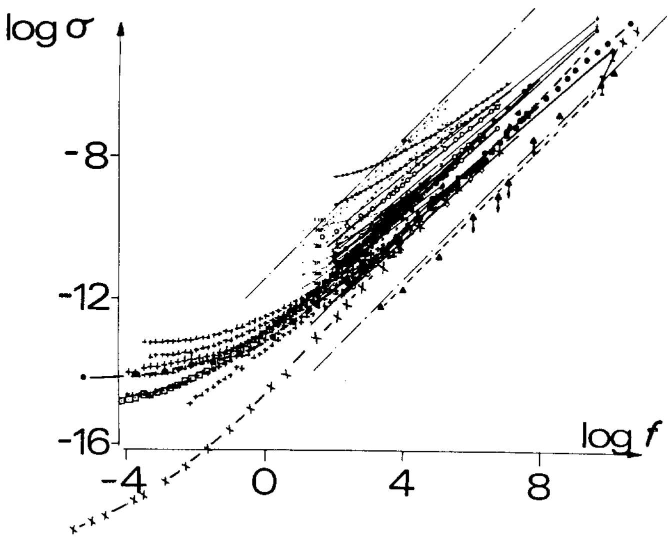

Figure 5 The compilation of the data for the a.c. conductivity of Fig. 4 on a common scale of log $\sigma(\Omega\,\text{cm})^{-1}$ showing the relatively narrow range of a.c. conductivity for a very wide range of materials. The upper and lower sloping chain-dotted lines correspond, respectively, to dielectric loss $\chi'' = 10$ and 10^{-3}, independent of frequency [5].

saturation of $\sigma(\omega)$ at low frequencies is by no means complete and a definite small slope is clearly discernible in some cases. This point will be returned to later.

What is even more significant, however, is the fact that the absolute values of $\sigma(\omega)$ fall in a remarkably narrow range for all these very different materials, as is evident from Fig. 5, suggesting strongly that some very general mechanism is common to all these systems.

The power law of Equation 9 is seen in a wide range of ionic conductors, especially the class known as "fast" ionic conductors which are characterized by relatively high ionic mobilities. The generally accepted method of presentation of these data is in the form of a complex impedance plot which gives typically an inclined circular arc, sometimes followed at low frequencies by an inclined "spur", the former corresponding to the "bulk" and the latter to some "barrier" response. It has been shown [75–78] that this behaviour is exactly equivalent to the power law, Equation 9, with very similar values of the exponent n to those in the electronic mechanism. It is remarkable in this connection, that the dielectric response of the relatively conducting bulk is characterized by a similar type of frequency dependence as the much more insulating barrier region; they correspond to the same basic "lattice" but with and without the prevailing ionic charge carriers, respectively.

The question naturally arises as to what is the relation between the d.c. and a.c. components of the conductivity in hopping systems [79] and, while it is difficult to generalize, it may be said that in materials with dipole dominated polarization there is clearly no relation, while in strongly carrier dominated materials there must be some relation in the sense of a monotonic increase of the a.c. component with the d.c. conductivity. However, it is clear from Fig. 5 that this relation, if it exists, is much less rapid than linear and there is also the evident complication that the d.c. conductivity is normally much more strongly temperature dependent than the a.c. component.

Injection and exclusion of charge carriers plays an important role in determining the level of dielectric loss in materials, as has been shown in many situations [80]. A distinction between dipolar contribution and charge carrier contribution can sometimes be made on the basis of the fact that the former is much less strongly temperature dependent than the latter. This means that one may subtract the loss data obtained at two temperatures from one another and the difference corresponds to the injected charges at the higher temperature. This is shown in Fig. 6 where the incremental real and imaginary components of the capacitance show a Kramers–Kronig compatible power-law relation with an exponent $n = 0.67$ which is typical of charge carrier responses.

Other examples of the power-law relation being found without any sign of loss peaks include ferroelectric triglycine sulphate both below and above the Curie temperature [81] and ferroelectric ceramics of the lead zirconate–niobate type [82].

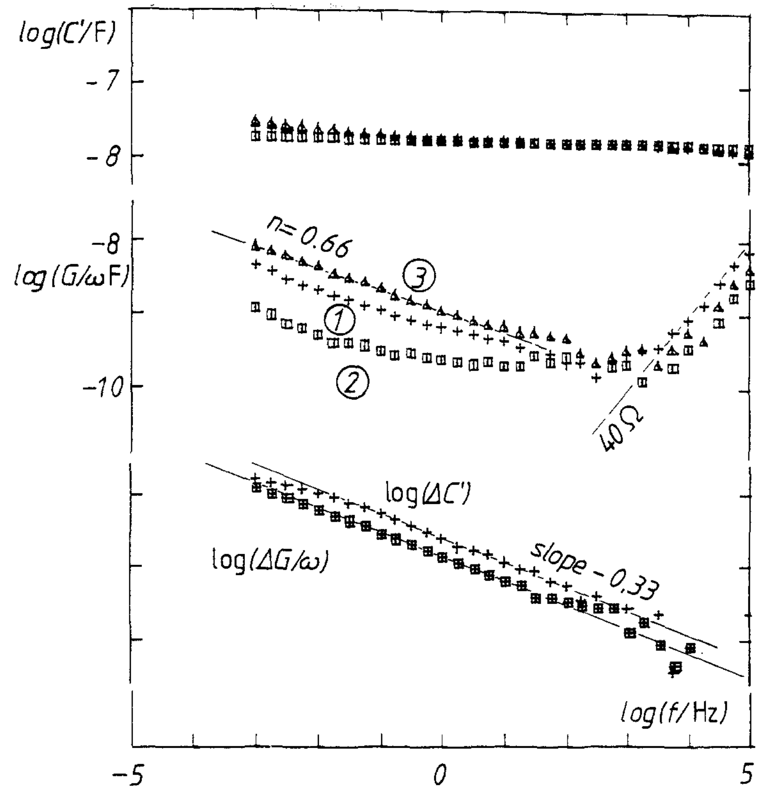

Figure 6 The dielectric response of a three-layer stearic acid film between aluminium electrodes at three temperatures: (1) 293 K, (2) 91 K and (3) 325 K. The upper diagram shows the capacitance $C'(\omega)$, the middle diagram the loss $G(\omega)/\omega$ and the lower diagram gives the incremental complex capacitance $\Delta C'(\omega)$ and $\Delta G(\omega)/\omega$ obtained by subtracting the 91 K data from the 325 K data. The two straight lines are drawn in Kramers–Kronig compatible ratio, showing agreement over seven decades of frequency, even though the original data show some complicating features. Taken from Millany and Jonscher [89].

5.3. Frequency independent low losses

It is a general fact that the dielectric loss in relatively low loss materials tends to become very "flat" in frequency, as shown in Fig. 1, corresponding to the value of the exponent $n \to 1$. It is impossible to distinguish between this and the case of a very flat loss peak, the fact remains that many materials show losses varying by not more than a factor of 3 to 10 over many decades of frequency. While it is possible to discern some "fine structure" in the form of slight peaks in the spectrum, there can be no doubt that these peaks are superimposed on an almost constant background loss. One example of this type of behaviour is given in Fig. 7 for a range of polyethylenes over five decades of frequency [83]. Another very typical example is shown in Fig. 8 where the presence of moisture gives rise to a very pronounced loss peak which is slightly broader than Debye, but the progressive removal of water molecules leads ultimately to a virtually flat loss [84]. Similar flat loss is found in hot-pressed ceramics [85] and in many pure

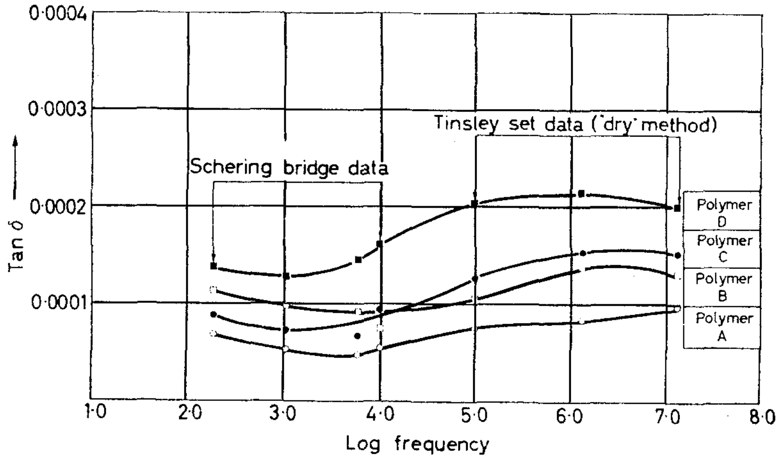

Figure 7 Examples of almost frequency independent losses in a range of polyethylenes at room temperature, covering five decades of frequency in the audio and radio ranges. The loss scale is linear and the variation over the frequency range does not exceed a factor of two. Taken from Reddish [83].

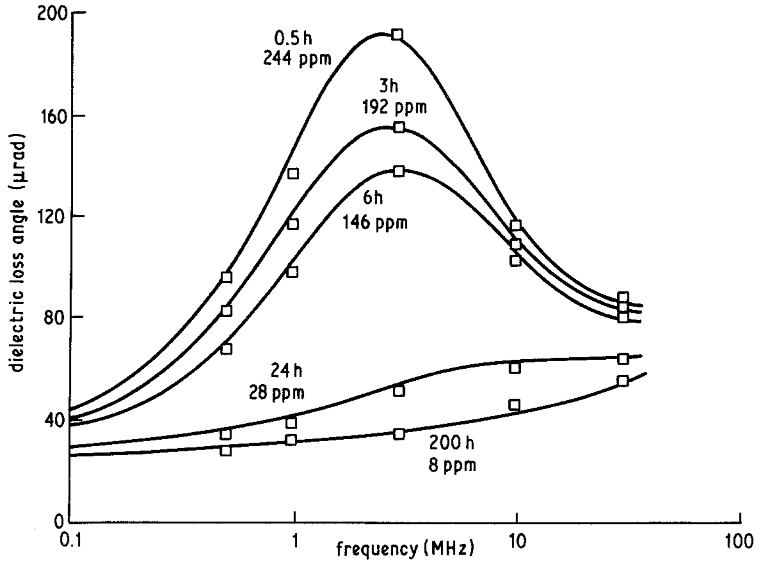

Figure 8 The effect on dielectric loss of successive drying of a sample of polyethylene quenched in water at 95° C, with drying times and water content indicated. The large initial peak due to water molecules disappears, leaving behind a flat loss at the level of 20 to 40 μ radians. Taken from Ayers [84].

materials at very low temperatures. In fact, this flat loss response is very insensitive to temperature and may be regarded as the limit of loss in highly pure materials at low temperatures.

It is our understanding that under no known circumstances does the loss in any solid descend below the limit of detection of the best equipment, while the same is not true of liquids, where "holes" of loss are found between successive loss peaks [86].

This flat loss represents a natural limit for our power law, Equation 9, wheras it would require a very broad and flat distribution of relaxation times to be interpreted in terms of the DRT theory.

5.4. Strong low frequency dispersion

Another limit of the power-law relation, Equation 9, is obtained when the exponent n tends to zero so that both $\chi'(\omega)$ and $\chi''(\omega)$ show a strong dispersion at low frequencies. This behaviour is in complete contrast with the situation in which d.c. conductivity is present where the real part is constant and the loss goes as $1/\omega$. This type of behaviour is found quite generally in dielectric materials in which hopping electronic or ionic charge carriers are present in appreciable quantities and it has been identified as a specific case of the general power law, Equation 9 [87]. It is found in most dielectric materials at elevated temperatures, when charge motions are encouraged by thermal excitation [88], but it may also be seen at very low temperatures. One example of this type of behaviour in a semiconducting glass may be seen in Fig. 9, another is shown in Fig. 10 which refers to the dielectric loss of an ionic conductor of the Hollandite structure [91] in a wide range of temperatures [92]. At the lowest frequencies there is a perfect example of the power law with $n = 0.84$, while at the highest temperature there is $n = 0.07$. At intermediate temperatures a loss peak is superimposed on the power-law trend.

A very similar type of behaviour may be seen in some of the examples shown in Fig. 4 in terms of the a.c. conductivity, where it is noted that the strong low frequency dispersion manifests itself as a weakly frequency dependent conductivity, other reported examples are in single crystal alumina [93], in wet sand [94], in many organic materials and, in fact, in most dielectrics at sufficiently high temperatures and low frequencies, provided that there is a significant density of charge carriers [87].

It is stressed that this type of dielectric response, as well as the flat low loss behaviour, has not been previously recognized as a specific form of response; it was being interpreted in terms of the Maxwell–Wagner behaviour [31, 32] which cannot account for the exact power-law relationship which is being found experimentally.

It is difficult to be sure whether the observed strong low frequency dispersion is a genuine bulk phenomenon or whether it is due to interfacial processes. One test is the linearity with the amplitude of the applied voltage, since barrier effects would be expected to be non-linear at voltages exceeding a few kT/e per barrier. This would also lead to a breakdown of Kramers–Kronig relations which only apply to linear systems.

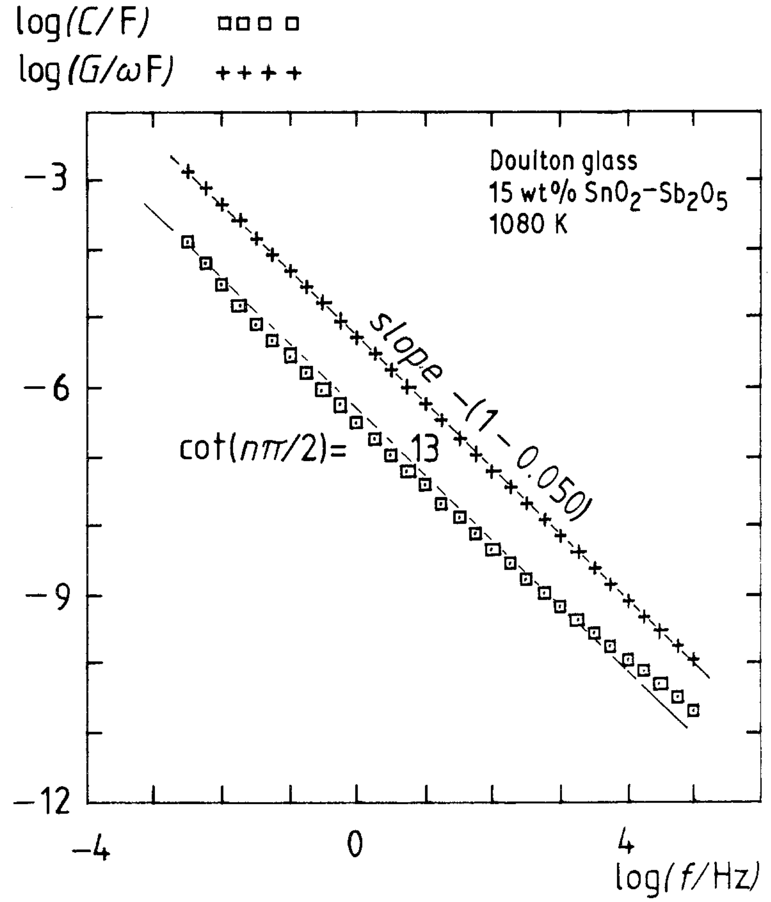

Figure 9 Low frequency dispersion in a glass doped with Sn and Sb oxides, at 800 K. The slope corresponds to a value of the exponent in Equation 9, $n = 0.050$ and appears to be constant within experimental error over seven decades of frequency and of loss and capacitance. The agreement with the Kramers–Kronig compatible ratio cot $(n\pi/2)$ is satisfactory, in view of the sensitivity of this ratio to very small values of n. Taken from Doyle [90].

5.5. The dielectric response of p–n junctions

Semiconductor p–n junctions represent one of the most interesting dielectric systems whose study may be of considerable importance both from the point of view of the theoretical understanding of the polarization processes as such and with regard to the characterization of p–n junctions as important electronic elements. In particular, p–n junctions have two most important advantages as vehicles for the advancement of the understanding of dielectric phenomena. Firstly, transistor quality semiconductors such as silicon, germanium, gallium arsenide and others are among the most perfect and best characterized solids in existence, so that their physical properties are known with much greater precision and certainty than those of any other materials. This goes especially for the crystalline perfection and for the content of impurities present in them, both as a result of deliberate doping and arising from accidental admixtures. Secondly, a junction diode represents the only capacitor structure in existence which does not require metallic contacts to be made directly to the active dielectric region, with the resulting uncertainty regarding the precise nature of this interface and the various physico-chemical reactions that may complicate the interpretation of the results obtained. In a typical p–n junction, the "contacts" to the space charge region are made by means of the neutral bulk p- and n-regions on either side of the space charge region which constitutes the proper "dielectric" material. The entire structure is a single crystal of high quality and there is no question of any interface arising between the "dielectric" and the "contact". In addition, p–n junctions have the added advantage that the width of the space charge region and therefore the capacitance may be adjusted by the application of a steady bias superimposed on the small signal voltage used for the measurements of the dielectric properties. The application of this bias alters the occupancy of the deep localized levels in the junction and therefore gives the opportunity to carry out "electronic doping" of the space charge region.

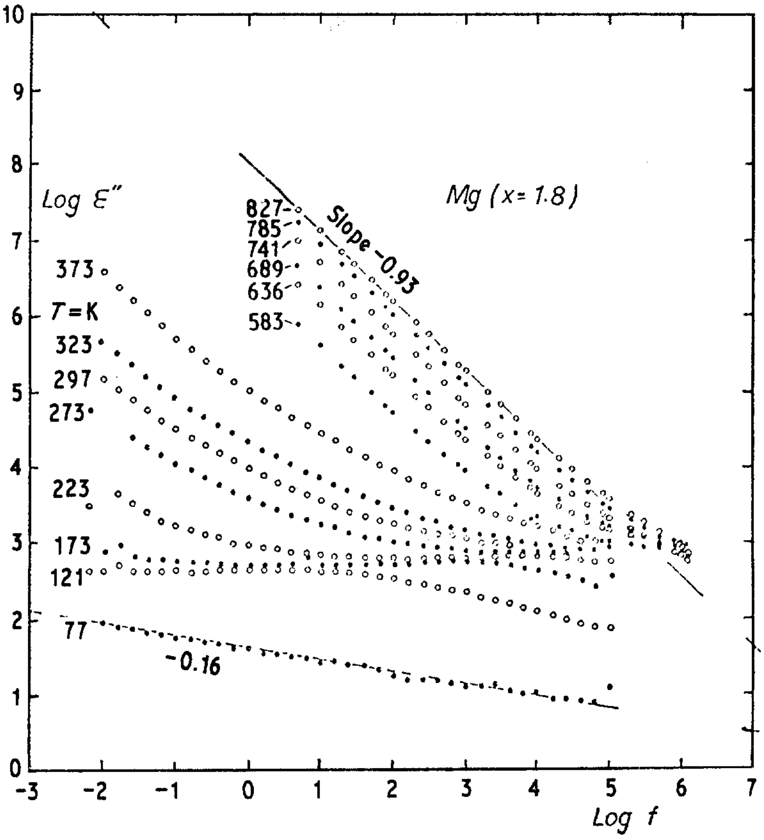

Figure 10 The frequency dependence of the dielectric loss of an ionic conductor of the Hollandite type, $K_{1.8}Mg_{0.9}Ti_{7.1}O_{16}$ over extended frequency and temperature ranges, showing the complete range of behaviour from the power law with a small value of the exponent $(n-1)$ through dipolar loss peak and on to large values of the exponent $(n-1)$. Taken from Deori [92].

In our experience [49] semiconductor p–n junctions show a remarkable variety of dielectric responses: an almost Debye-like loss in a high purity silicon diode, strongly asymmetric peaks of the type shown in Fig. 11 in both a silicon and a GaAlAs/GaAs heterojunction laser diode, and in the latter an almost "flat" response at around 50 K was seen. However, the remarkable feature of this behaviour is that there is clear evidence of only one loss peak in all those diodes over a frequency range of nearly ten decades after normalization for temperature. This should be contrasted with the presence of three loss peaks in a silicon diode which had been irradiated with

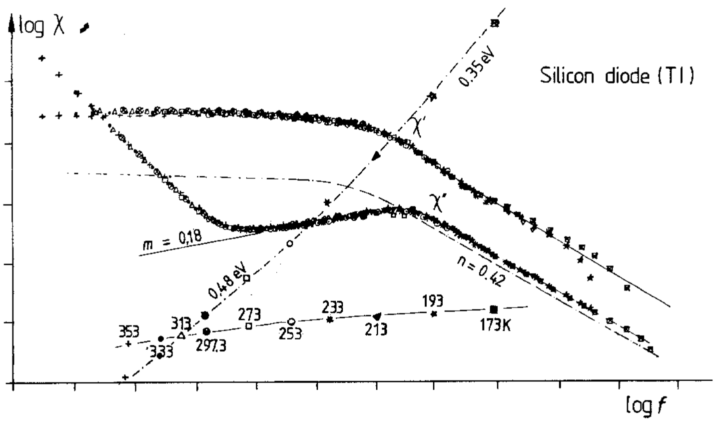

Figure 11 The dielectric loss of a silicon p–n junction, normalized at several temperatures indicated on the locus of the displacement point. At low frequencies and high temperatures d.c. conduction dominates the response, the dielectric behaviour is characterized by a single loss peak with a very small value of the exponent $m = 0.18$ and a much larger values of $(1-n) = 0.58$. The $\chi'(\omega)$ plot is displaced vertically for clarity and the chain-dotted line indicates the proper position of the Kramers–Kronig transformed loss peak. The activation energies are shown. Note that the effective frequency range covers ten decades and no other loss mechanism is visible [49].

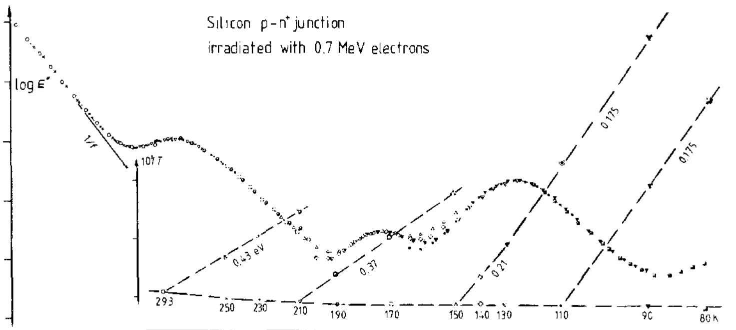

Figure 12 The normalized data for the dielectric loss of a silicon p–n junction irradiated with 0.72 MeV electrons, showing three distinct loss peaks with the activation energies indicated. The normalization was carried out with respect to the peaks and, in view of the different activation energies, the fit of points between the peaks is not so good. The low frequency response is dominated by d.c. conduction. Note that the total effective frequency range covers over thirteen decades [49].

0.7 MeV electrons, as shown in Fig. 12. The activation energies obtained from the dielectric measurements agree well with those determined by other methods.

5.6. Dielectrics at very low temperatures

It is an experimental fact that the dielectric response persists down to the lowest temperatures; certainly well below 4 K and measurements exist down to the milliKelvin range. In this respect the dynamic response differs essentially from most forms of steady state current flow, except pure tunnelling of electrons across potential barriers a few nanometres wide. Several examples of dielectric loss at cryogenic temperatures [54–57, 59, 60] have already been mentioned where the frequency dependence showed the whole range of response types from the "flat" behaviour characteristic of low loss materials, to sharply defined near-Debye peaks. Here it is proposed that an example of a similar Hollandite material [92] as shown in Fig. 10 but taken to lower temperatures [95] is discussed. Fig. 13 shows that the response remains virtually independent of temperature between 77 and 5.2 K and the loss follows the power law with $n = 0.93$ over more than five decades, while at the

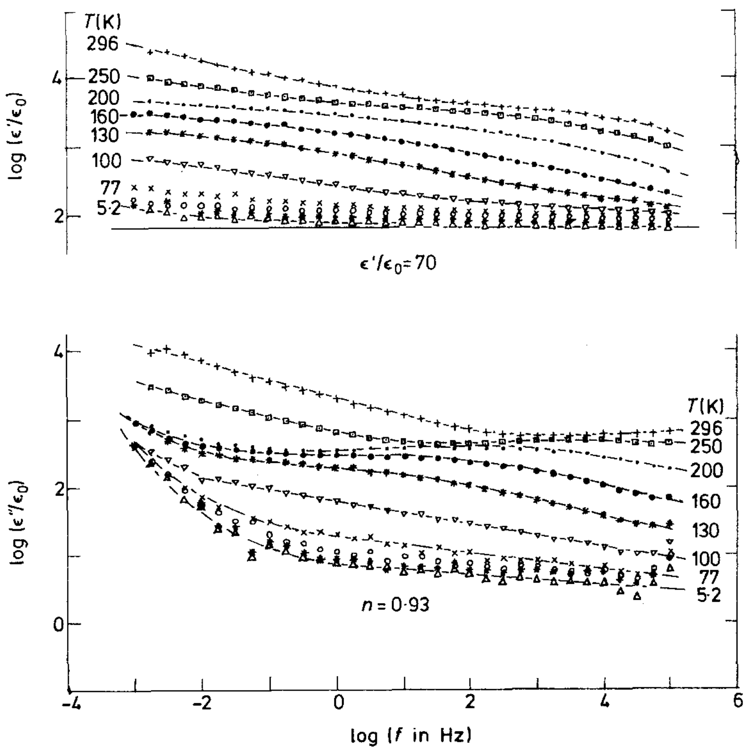

Figure 13 The frequency dependence of the real and imaginary components of the complex dielectric permittivity of the ionic conductor $K_{1.6}Mg_{0.8}Ti_{7.2}O_{16}$ in log–log representation, with temperature as parameter. The symbols for the lowest four temperatures are × 77 K, ○ 60 K, ∗ 30 K, △ 5.2 K. The other curves are annotated [95].

lower frequencies there is clear evidence of strong dispersion, with the real part $\epsilon'(\omega)$ showing the concomitant rise which proves that this is not the case of d.c. conductivity, which would have been very unlikely in an ionic conductor at these temperatures. The importance of this experimental evidence lies in the fact that a high level of dielectric activity persists down to the lowest temperatures, even in the case of ionic materials in which conventional tunnelling is impossible.

6. The formulation of the "Universal" law

It has been shown that the totality of dielectric responses of all materials falls into the broad class of power-law relations for the dielectric loss given by Equations 5 to 7 and this power-law relationship is called the "Universal law" of the dielectric response, since it is found quite regardless of [5]:

Physical structure – single-crystal, polycrystalline, amorphous and glassy;

Types of bonding – covalent, ionic, molecular;

Chemical type – organic, inorganic, biological;

Polarizing species – dipoles, hopping electrons, polarons, ions;

Geometrical configurations – from "bulk" dimensions to monomolecular layers, planar and intricate geometries, continuous and granular media;

A very wide range of temperatures – from the lowest attainable to the highest compatible with the stability of the materials in question.

This universality of the power-law response constitutes the strongest argument for the pursuit of our alternative approach to the interpretation of the dielectric behaviour of solids; it is just too difficult to envisage that any or all of the classical explanations should always give the same "magic" form of relationship.

It is now noted that all these different materials obeying the universal relation satisfy two extremely general criteria relating to the motions of the polarizing species in them [96–98]:

(i) The dipoles or charges responsible for the polarization execute sudden hopping or jumping transitions between preferred orientations or sites. The time scale of these transitions is very rapid in comparison with all other processes taking place in the material, in particular with the externally applied variable fields. The nature of these transitions is completely different from the "slow" motions of Debye dipoles in a viscous medium.

(ii) Any sudden transition of an individual dipole or charge excites a much slower delayed response of the totality of neighbouring dipoles or charges through co-operative many-body interactions.

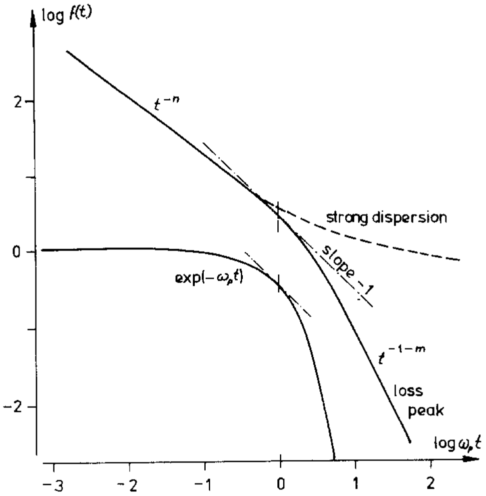

Figure 14 The response function $f(t)$ for the Debye process and for the "universal" response with the same loss peak frequency ω_p. In both cases ω_p is given by the reciprocal time at which the logarithmic slope goes through the value -1. While the entire Debye loss peak is generated by a single exponential process in time, the universal peak requires two separate sequential processes. Strong low frequency dispersion shown by the dotted line corresponds to a negative exponent m in the second power law, Equation 11.

This division of the medium into *slow* and *fast* responders will be seen to be of fundamental significance to the new interpretation of the physical nature of the dielectric response.

The contrast between the classical Debye mechanism and the proposed many-body responses is further enhanced by considering the nature of the time–domain response corresponding to the frequency–domain behaviour given by Equation 5. This may be described by two power laws, as shown in Fig. 14:

$$f(t) \propto t^{-n} \qquad \text{for } t < 1/\omega_p \qquad (10)$$

and

$$f(t) \propto t^{-1-m} \qquad \text{for } t > 1/\omega_p. \qquad (11)$$

These two laws correspond to two sequential physical processes which are different from one another and independent, in view of the information contained in Fig. 3. This is a completely different concept of the significance of the loss peak in the frequency domain, by contrast with the classical Debye approach in which the loss peaks correspond to some "principal" mechanism in a distribution [99].

It is noted, furthermore, that the power law of Equation 10 has the unique feature that its Fourier transform into the frequency domain is

$$\begin{aligned}\chi(\omega) &\propto (i\omega)^{n-1}\\ &= \{\sin(n\pi/2) - i\cos(n\pi/2)\}\omega^{n-1}\end{aligned} \qquad (12)$$

so that the real and imaginary components have the same frequency dependence, in complete contrast with the Debye response. This implies the independence of frequency of the ratio

$$\frac{\chi''(\omega)}{\chi'(\omega)} = \frac{\text{energy lost per radian}}{\text{energy stored}} = \cot(n\pi/2) \qquad (13)$$

in the frequency range in which this law is applicable, as shown in several of the experimental diagrams reproduced here.

The immediate physical significance of the energy relation (Equation 13) is that every individual dipolar or charge transition altering the dielectric polarization entails a finite energy loss, regardless of the rate of change of the polarization under the action of the sinusoidal applied field. This leads to the constant phase angle between polarization and field, independently of frequency, in complete contrast with the constant time delay, τ, postulated in the Debye model.

7. The many-body model

The intuitive predictions of the early papers relating to the many-body nature of the dielectric response [96–99] were confirmed and considerably extended by subsequent developments of a much more rigorous and quantitative theory. The first of these proposed the analogy with the well-known concept of infra-red divergence [35] which is characterized by the same power-law dependence as Equation 10. This model made direct reference to the general criteria (i) and (ii) outlined above and it provided the first basis for a completely new approach to the interpretation of the universal dielectric response. Further development of these ideas, including the treatment of the two independent mechanisms which are present wherever there is a loss peak or a strong low frequency dispersion, were provided by the work of Dissado and Hill [100–102], referred to as D and H. The principal concept in this theory is the existence of correlated states which arise from interactions between individual dipoles or charges in an interactive system. These states form a narrow band in energy, much narrower than the thermal energy kT at room temperature, and they are half-filled. The excitation of these states can take place only through the action of the sudden changes of potential resulting from dipolar or charge transitions characterizing the dielectric behaviour of solids. Excitations of the correlated states are capable of storing a considerable amount of energy, which is only slowly released to the system, part of it being lost in the process.

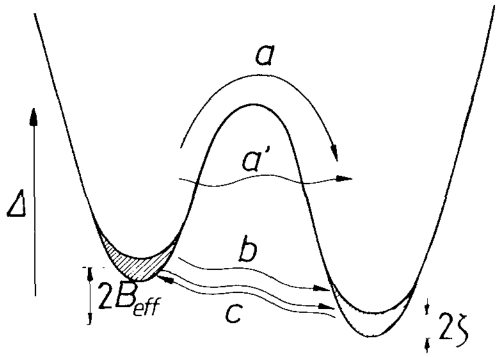

Figure 15 The potential energy diagram of a many-body two-level system, representing the energy of a large number of individual interacting systems. The potential wells correspond to preferred orientations for dipoles or positions for hopping charges. The shaded regions at the bottom of the wells represent correlated states of width 2ζ. The arrows a and a' denote thermally-assisted transitions in which a significant amount of energy is exchanged with the phonons. Arrows b and c denote configurational tunnelling transitions of the "flip" and "flip-flop" types, respectively.

The collective system may be represented schematically by the energy diagram of Fig. 15 in which the two potential wells correspond to the preferred orientations of the system and the total polarization is determined by the relative occupancies of the two wells. Dissado and Hill distinguish three types of transitions between the wells denoted by the arrows a, b and c. Transition a corresponds to the classical thermally-excited transition of a single particle from one well to the other and this is the transition which would be involved in the classical Debye process. The particle in question makes a "large" transition involving typically an interatomic spacing, the relevant energy Δ being of the order of 1 eV. By contrast, Transitions b and c do not involve any thermal excitation and they correspond to *configurational tunnelling* in which large numbers of interacting particles undergo small adjustments which collectively give the result of a large transition of a single particle. Configurational tunnelling becomes easier,

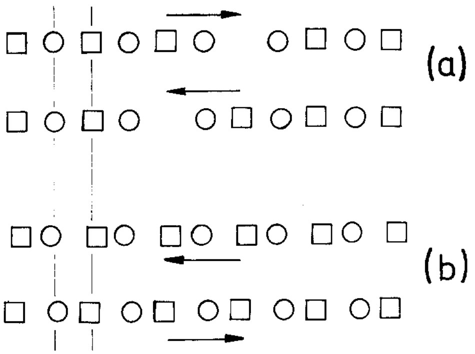

Figure 16 Schematic illustration of (a) "large" and (b) "small" transitions with the corresponding changes in the dipole moment shown by arrows. Detailed discussion in the text.

the more disordered is the system in question and it has been shown that all dielectrics involving orientational polarizations due to charges or dipoles are necessarily disordered [102]. A very important property of configurational tunnelling is the fact that it may involve very heavy particles such as ions and dipoles and it is therefore not confined to the very light electrons.

The principle of configurational tunnelling leading to a change of the dipole moment in a system of interacting particles is illustrated by the simple diagram of Fig. 16 relating to a hypothetical one-dimensional lattice. Fig. 16a refers to the situation in which oppositely charged ions occupy "regular" positions in the lattice but one ion is missing leaving a vacancy with a resulting net dipole moment, defined as the difference in the centres of gravity of the relevant distributions of the positive and negative ions. This dipole moment is indicated by the upper arrow. If this vacancy is now filled by transferring the nearest like ion by means of a "large" transition over the restraining potential barrier, the dipole moment is reversed as indicated by the lower arrow. This large ionic transition is equivalent to a dipolar rotation which also requires a thermal excitation to overcome the barriers preventing free rotation in solids.

Fig. 16b shows a fully occupied but slightly "disordered" lattice in which the oppositely charged ions have been slightly displaced in opposite senses from their regular positions in Fig. 16a. This corresponds to a finite net dipole moment, as indicated by the upper arrow. If now all the ions were to be translated by small amounts to equivalent sites on the opposite side of their respective regular positions, the sum of all these small transitions would amount to a change of dipole moment of the same order of magnitude as the single large transition in Fig. 16a. The essential point is that these small transition do not require as much thermal energy as the large transitions and they may occur even without any thermal excitation; hence the term configurational tunnelling.

In Fig. 15, Transitions *b* are denoted as "flip" transitions and they change the total dipole moment of the system with the characteristic time dependence given by Equation 10 and they dominate the response at "short" times, storing the energy in the excitations of the correlated states, denoted in the diagram by the shaded regions near the bottoms of the wells. After the lapse of a sufficiently long time, the other type of configurational tunnelling sets in, denoted by the arrow *c* and involving "flip-flop" interactions, in which synchronous configurational tunnelling transitions occur in opposite senses at different spatial positions, leaving the total dipole moment unchanged. Because of the resulting excitations of the correlated states, however, the flip-flop transitions do affect the rates of the momentum-changing flip transitions and of the thermally-excited large transitions, giving the final power law of decay of Equation 11.

Mechanisms *a* and *b* occur in parallel, while *c* competes with *b* and a detailed analysis by D and H shows the following form of the time dependence of the depolarization current

$$i(t) = \exp(-\omega_{\mathrm{p}} t) t_1^{-n} {}_1F_1(1-m; 2-n; \omega_{\mathrm{p}} t) \times \frac{\Gamma(1+m-n)}{\Gamma(2-n)\Gamma(1+m)}, \tag{14}$$

where ${}_1F_1(\;;\;;\;)$ is the confluent hypergeometric function and Γ is the Gamma function. The Fourier transform of this relation gives the following expression for the complex dielectric susceptibility

$$\chi(\omega) = A \cdot G(\omega/\omega_{\mathrm{p}}), \tag{15}$$

where A is an amplitude factor defining the strength of the dielectric response in unit electric field and is given by

$$A = \omega_{\mathrm{p}}^{n} \cos\left(\frac{n\pi}{2}\right)(\zeta)^{-n} Nd(M'(0)/E) \times \frac{\Gamma(1+m-n)}{(1-n)\Gamma(1+m)} \tag{16}$$

while $G(\omega/\omega_p)$ is the spectral shape factor of the reduced frequency ω/ω_p

$$G(\omega/\omega_p) = \frac{\omega_p^{1-n}}{(\omega_p + i\omega)^{1-n}} \times {}_2F_1\left(1-n, 1-m; 2-n; \frac{\omega_p}{\omega_p + i\omega}\right), \tag{17}$$

where ${}_2F_1(\ ;\ ;\ ;)$ is the Gaussian hypergeometric function and $M'(0)/E$ is the static deviation linearized per unit of electric field, N is the number of dipoles per unit volume and d is their length.

The ability to express the susceptibility as a product of an amplitude factor and a shape factor constitutes the theoretical justification for the widely used process of normalization of dielectric data with temperature, or pressure, as the variable parameter. This justification did not exist explicitly in the older theories and it is very gratifying to be able to obtain it from a very general theory. The applicability of normalization to any given material depends, of course, on the m and n values not changing appreciably with temperature: if this is satisfied, then we refer to "time–temperature superposition". It has been seen that in many cases this condition is sufficiently well satisfied to provide very good normalization, while in others this is not true [38], this point will be discussed in more detail later.

The D and H theory gives an explicit formula for the loss peak frequency which enters into the general expressions, Equations 14 and 15,

$$\omega(T) = \hat{\nu}_\infty \exp(-\Delta/kT)h(T), \tag{17}$$

where $h(T)$ is a function of temperature which may not be very rapidly varying, so that the loss peak frequency is essentially thermally activated with the energy Δ of the barrier in the double well in Fig. 15, as found in Equation 2.

The general theoretical expressions, Equations 14 and 17, may now be evaluated in certain limiting cases in terms of simple functions. It turns out that the following relations apply:

$$f(t) \propto t^{-n} \qquad \text{for} \quad t \ll \omega_p^{-1}; \tag{18}$$

$$f(t) \propto \exp(-\omega_p t) \qquad \text{for} \quad t \simeq \omega_p^{-1}; \tag{19}$$

$$f(t) \propto t^{-m-1} \qquad \text{for} \quad t \gg \omega_p^{-1}; \tag{20}$$

where we have set $i(t) \propto f(t)$ to bring out the similarity with our earlier expressions in terms of the dielectric response function.

Equation 18 is exactly the empirically derived Equation 10, while Equation 20 is the empirically derived Equation 11. To that extent, therefore, the theory gives a complete account of the experimentally determined universal laws of dielectric behaviour. What is equally significant, however, is the fact that the theory gives, through Equation 19, a region of Debye-like exponential behaviour near the loss peak frequency. This preserves, therefore, the significance of the loss peak frequency in terms of Debye-like processes which has long been regarded as the cornerstone of the classical interpretation of the dielectric response.

The limiting forms of the frequency–domain response are similarly obtained as follows in terms of the dielectric loss spectrum

$$\left.\begin{aligned} \chi'(\omega) &\propto \chi(0) - a\omega^m, \\ \chi''(\omega) &\propto \omega^m \end{aligned}\right\} \quad \text{for} \quad \omega \ll \omega_p, \tag{21}$$

$$\chi(\omega) \propto \frac{1}{1 + i\omega/\omega_p} \qquad \text{for} \quad \omega \simeq \omega_p, \tag{22}$$

$$\chi(\omega) \propto (i\omega)^{n-1} \qquad \text{for} \quad \omega \gg \omega_p, \tag{23}$$

which are exactly the expressions found empirically, with, once again, the exception that the region "between the two power laws is identified with a Debye-like response near the dielectric loss peak".

The point of fundamental significance in this new approach to the interpretation of dielectric relaxation is the fact that the power-law time dependence and the corresponding frequency dependence which were so clearly established experimentally as the universal form of response, are *direct* and *natural* manifestations of the type of many-body interactions which are being described here. Given the ubiquitous presence of power-law relations, there is no other evident way in which one can envisage the interpretation on the basis of physically plausible assumptions. The complete description of the time–domain response of Fig. 14 or the corresponding generalized loss peaks shown in Figs 1 and 2 follow directly from the interplay of the three types of processes a, b and c in Fig. 15. The many-body processes described as flip transitions determine the early stages of the time response or the high frequency side of the loss peak, the flip-flop transitions determine the long time responses or the low frequency side of the loss peak. The "large" thermally-assisted transitions a, which by themselves would give the Debye response, retain their vital role in the new analysis, providing the "hinge" or link between the power-law processes and dominating the response in the transition region. This result, following directly from the complete analysis of Dissado and Hill, preserves the link with the traditional interpretation of the dielectric loss peaks in terms of Debye-like processes while explaining the modified shape of the loss peaks away from the loss peak frequency ω_p.

8. Discussion of the many-body analysis

8.1. The nature of the many-body interaction

One of the difficulties of presenting the many-body interactions is the essentially unfamiliarity of this concept and the lack of direct sense—perception experience from daily life of many-body systems. This means that any models that may be constructed and on which our physical intuition relies for a deeper understanding of the processes involved in dielectric relaxation are necessarily of very limited validity. In this respect the classical "ball-and-stick" models of vibrating molecular bonds or turning polymeric crank-shafts are much more appealing to the imagination and it takes a considerable intellectual effort to place oneself in the essentially unfamiliar framework of many-body interactions. Many of the concepts involved are much more easily understood in terms of the abstract ideas derived from the quantum mechanical theoretical analysis than in terms of more pictorial representation. However, we should make at least some attempts to render the new concepts acceptable to the practically oriented minds without taking in the whole theoretical complexity of the general model.

The first useful concept to be developed is the idea that in an interactive system "nothing can move without everything else moving as well". It is helpful to note here that at least one essentially many-body system which has attained sufficient familiarity to have become acceptable without undue difficulty are gaseous plasmas, and particularly the phenomen of plasma oscillations. Another closely related concept is the screened Coulomb potential, which requires a self-consistent solution to be obtained taking into account the interaction between potential and charge carriers.

Another important point is that many-body interactions involve low energies and very large numbers of particles. This means that the correlated states involved in our analysis represent a band of very large density but covering a small energy, of the order of a few millivolts. This band does not "fit" into the familiar band model of solids, since that model is, by definition, a one-particle model which does not contain the correlated states any more than it does the plasmon excitations. While one-particle states, such as those describing electrons and holes in the band model, relate to motions of individual particles, and the energies in question are typically of the order of electron-volts, the correlated states describe the motions of centroids of particle assemblies and their energies are much lower.

8.2. The magnitude of the exponents *m* and *n*

It was found empirically that the exponents m and n fall in the range between zero and one and this has its direct significance in the present theory. It is found that these exponents relate to the degree of correlation between the flip-flop processes and the flip processes, respectively. In both cases, fully correlated transitions correspond to the higher value of unity, completely uncorrelated transitions correspond to the exponents zero.

The concept of the degree of correlation is closely related to the degree of order in the system. The higher the state of perfection, the more difficult it is to see weakly correlated motions, since perfect order does not admit of any motion without ensuing "domino reactions". On the other hand, the less perfect the system, the easier it is for an uncorrelated event to take place without correlated events following in its wake. This means that the exponent n would be expected to increase, i.e. the response beyond the loss peak frequency to become flatter as order increases, e.g. as the temperature decreases. This would also explain why the behaviour of liquids, in which the correlations are largely destroyed because of the rapid fluctuations of structure, approaches that of the Debye model, with the exponent $n \rightarrow 0$.

The situation is more complicated with flip-flop transitions, since these involve two simultaneous events taking place and this means that a highly ordered system with strong flip correlations has very weakly correlated flip-flops, and vice versa. Thus small values of m go with large values of n and vice versa, but it should be remembered that the limit of vanishing flip-flop interactions corresponds to a frequency dependence of loss $\chi''(\omega) \propto \omega$, i.e. it appears as if $m = 1$. The latter

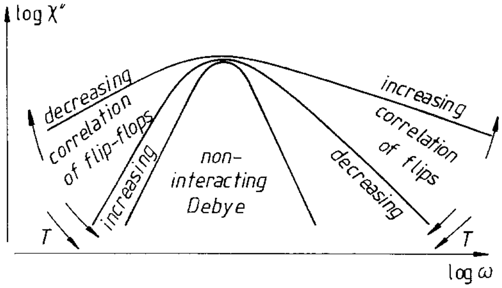

Figure 17 The effect of temperature on the loss spectrum in a dipolar material, as a consequence of changing correlation of flips and flip-flops. The non-interacting Debye response is shown as a singular case. This diagram relates to the shape of the spectral distribution, its amplitude may change in a different manner, e.g. it may decrease with decreasing temperature, according to the strength of the thermally-assisted transition.

situation arises in those cases where the loss peak frequency ω_p is higher than 10^8 to 10^9 Hz, since under these conditions the flip-flop interactions do not have time to develop and these cases correspond to the points on the top side of the square in Fig. 3, which all fall in that frequency range.

The effect of increasing temperature on the form of the shape function is therefore expected to be as shown schematically in Fig. 17, giving rise to a narrowing of the peak with increasing temperature. However, it should be noted that experience shows that there are many dielectric materials in which the shape of the peak is remarkably independent of temperature, indicating that the short-range order and interactions are not strongly affected by temperature.

8.3. Dielectric responses at very low temperatures

The co-operative tunnelling model provides a very natural explanation of the dielectric loss remaining finite at temperatures in the cryogenic range, down to milliKelvins, even in situations where the dielectrically active species are sufficiently heavy, e.g. K^+ ions, to make quantum mechanical one-particle tunnelling completely unlikely. One form of low temperature response is the "flat" loss already mentioned, without any "large" transition being involved in view of the absence of thermal excitations to provide the required energy. However, it is often observed that a loss peak is preserved down to the lowest temperatures [103] although its temperature dependence is not exponentially activated. In these cases we have to consider the presence of non-activated electronic or protonic tunnelling and these are very likely to account for the many examples of this behaviour, although the behaviour of loss away from the loss peak region may be modified by many-body interactions in the usual way.

8.4. Strong low frequency dispersion

The many-body theory of this very interesting type of behaviour is not yet completely developed at the present time but it is noted that this response is obtained formally from the loss peak expression below the loss peak frequency, Equation 21, by setting $m = -p$, with $\chi'(\omega)$ and $\chi''(\omega)$ maintaining the Kramers–Kronig determined ratio, $\tan(p\pi/2) \gg 1$. Mathematically this transformation may be derived if the flip-flop transitions should aid the flips instead of competing with them as in the dipolar case. It is believed that this is the case in hopping systems, in which the strong low frequency dispersion is observed and it is expected that theory may be adapted to this situation without much difficulty.

8.5. The dielectric response of p–n junctions

The dielectric behaviour of p–n junctions is of particular interest in the present context, since their response follows very closely that of other dipolar systems, while the physical mechanisms involved are completely different; there are no dipolar species in the space charge regions of p–n junctions and the dielectric loss is caused essentially by generation/recombination processes. The inference drawn is that these processes must also obey the power-law devolution in time, despite the fact that they do not involve two-level dipole-like alignments.

8.6. Relaxation as a solution of a differential equation

The point is sometimes made that a physically meaningful solution of the relaxation problem should represent the solution of a "simple" differential equation or an equally evident extension of one. This is the case with the Debye mechanism which corresponds to the solution of a first-order differential equation, while the DRT corresponds to an integral transform of the Debye solution. Now it is not evident that this limitation of the validity of a physically admissible solution should be justified on any fundamental grounds, especially when the physical situation corresponds to a many-body system.

9. Conclusions

This concludes the present, necessarily very limited, account of the new theory of the dielectric relaxation in solids. It was started with a detailed description of the nature of the experimental results in order to convince the reader that they warrant a serious fresh approach to the otherwise very old subject of dielectric response. We regard the remarkable universality of the response as conclusive proof that a common mechanism is responsible for the relaxation and that this mechanism is not of the Debye type. By focussing attention on the essential characteristics of all condensed matter, and especially of solids, namely the discontinuous nature of dipolar and charge transitions, and the inevitable interactions between the individual dipoles or charges, it was possible to develop a completely new approach to the theory of interactive systems which is in remarkable agreement with a very wide range of experimental data not otherwise easily understandable in terms of conventionally accepted models. Although a good deal more remains to be done on the new theoretical model, it may be said already now that the fundamental outline is sufficiently well developed to give us a firm basis for the assessment of the true nature of the dielectric response. Thus a very important stage in the understanding of the dielectric stage has been reached.

Having established the proposition that the entire range of dielectric behaviour may be explained in terms of many-body interactions without recourse to distributions of relaxation times, the question has to be asked whether real dielectric systems show any evidence of the existence of several relaxation times for the "large" transitions of the type *a* in Fig. 15. A large body of experimental and theoretical evidence, developed over the years to underpin the DRT theories, strongly suggests that activated processes exist which have different relaxation times. Our comment to this is that, quite evidently, there are many examples of dielectric behaviour with more than one loss peak in evidence and that this is the result of the presence of more than one activated process. There are also examples of dielectric response in which a "fine structure" is present on an otherwise very broad loss characteristic following the universal law and similar arguments apply there.

It remains a fact, however, that very many loss peaks show no evidence of a multiplicity of contributing mechanisms, being very well represented by the empirical relation, Equation 5, over many decades of frequency. If subsidiary thermally-activated transitions exist there, their presence is very effectively masked by the "wings" of the universal processes and it is concluded that the available experimental evidence offers no support for the presence of large distributions of relaxation times as the primary cause of the dielectric response. It is concluded, therefore, that although the existence of different thermally-activated processes cannot be ruled out, experimental evidence for their effective role in causing the dielectric relaxation in solids is very limited.

This does not exclude the possibility that the dominant thermal mechanisms responsible for the appearance of individual loss peaks are not themselves composed of a relatively narrow distribution of processes; the available experimental evidence is insufficiently sensitive to enable us to distinguish between a single mechanism and two or three closely spaced mechanisms.

This review is concluded by mentioning the highly significant fact that the dielectric response represents but one facet of a very much wider class of time–dependent relaxation phenomena involving many-body interactions. It so happens that the experimental material at our disposal is very much richer in dielectrics than in these other branches, e.g. in mechanical and magnetic relaxation, in nuclear magnetic resonance and optical absorption, so that the development of the necessary theory was best achieved on the basis of the dielectric data. However, now that this development has been made, it can be applied very successfully to these other branches and it is hoped that significant advances will be seen there.

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