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Low-loss dielectrics

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Low-loss dielectrics are important technologically as insulators but there is little understanding of the physical causes of this property and even their spectral response is not well documented—this study has revealed a number of different types of behaviour which do not appear to have been recognised previously. Most low-loss materials show a "flat", nearly frequency-independent loss, but while some follow the "universal" fractional power law of frequency dependence which is widely applicable to more lossy materials, some are very different and require a fresh approach to their interpretation. It is pointed out that low-loss behaviour is not necessarily connected with the absence of impurity dipoles and the recently introduced concept of dipolar screening may explain low-loss behaviour in impure materials. The universal response is shown to be only one of several forms of dielectric behaviour and examples are given of possible alternative forms which may explain the apparent incompatibility of some experimental data with Kramers-Kronig relations. © *1999 Kluwer Academic Publishers*

1. Introduction

Low-loss materials play an important role in technology and yet the understanding of what conditions have to be satisfied to obtain them and what mechanisms dominate their response is far from complete. A simplistic approach would demand the lowest possible concentration of dipoles and charge carriers, and in the latter, the lowest possible mobility. However, it is a fact that most technically important insulating materials are far from very pure and often contain deliberate or accidental admixtures of substances which are necessary in their processing.

Broadly speaking, it is possible to distinguish two classes of low-loss materials:

(a) polymers in which the dielectrically active species are dipoles while ionic and electronic carriers have very low mobilities and

(b) inorganic ceramic and similar materials in which dipolar contributions are probably negligible while typically electronic charge carriers may have a relatively high mobility.

In this paper we propose to examine the spectra of both these types in order to see what conclusions may be drawn from them. A discussion of the underlying interpretation will also be given.

It is convenient to begin the present enquiry from the standpoint of the "universal" formalism [1, 2] according to which the real and imaginary components of the complex susceptibility

$$\tilde{\chi}(\omega) = [\tilde{\varepsilon}(\omega) - \varepsilon_\infty]/\varepsilon_0 \tag{1}$$

are given by the fractional power-law relations

$$\chi'(\omega) = \tan(n\pi/2)\chi''(\omega) \propto \omega^{n-1} \tag{2}$$

Here $\varepsilon_0 = 8.845 \times 10^{-12}$ F/m is the permittivity of free space, ε_∞ is the high-frequency limit of ε' beyond the range in which appreciable losses occur and $\omega = 2\pi f$ is the angular frequency, f is the circular frequency and the exponent n falls in the range $(0, 1)$. An immediate consequence of Equation 2 is the independence of frequency of the ratio

$$\chi''(\omega)/\chi'(\omega) = \cot(n\pi/2) \tag{3}$$

which implies that for low-loss materials we require that $n \to 1$. It should be noted that the technically important loss parameter

$$\tan\delta(\omega) = \varepsilon''(\omega)/\varepsilon'(\omega) = \chi''(\omega)/[\chi'(\omega) + (\varepsilon_\infty/\varepsilon_0)] \tag{4}$$

differs in its frequency dependence from the loss $\chi''(\omega)$. In the case of very low loss systems, where $\chi'(\omega) \ll (\varepsilon_\infty/\varepsilon_0)$, the frequency dependences of $\chi''(\omega)$ and of $\tan\delta(\omega)$ are practically identical and the two differ only by a numerical factor. Several examples of low-loss behaviour are quoted in Ref. [2].

2. The significance of ε_∞

All dielectrics must have the low-frequency limit of permittivity greater than the free space permittivity, $\varepsilon(0) > \varepsilon_0$ and the difference between the two, $\varepsilon(0)/\varepsilon_0 - 1 = \chi(0)$ is equal to the integrated loss over the entire logarithmic frequency range [1]:

$$\chi(0) = \frac{2}{\pi}\int_{-\infty}^{\infty} \chi''(\omega)\,\mathrm{d}(\log\omega) \tag{5}$$

which states that any increment of $\chi(0)$ must be "paid for" by a finite loss somewhere in the frequency range. A very important mechanism of this is the inevitable loss arising from the lattice absorption bands in the visible and the UV regions of the spectrum, compared with which the lower frequency dielectric losses may be relatively trivial. Any loss processes occurring below the GHz region, say, cannot be associated with the lattice process and the corresponding permittivity at the top of this range, $\varepsilon_{\infty 1}$, must necessarily be significantly higher than ε_0.

This is illustrated schematically in Fig. 1, where the loss consists of two processes, each characterised by its own frequency dependence. Now if an empirical relation such as that given by Equation 2 is found to apply to the susceptibility of, for example the low-frequency process in Fig. 1, it would be unrealistic to expect that it should also apply to some very different process such as the high-frequency one. Thus, one would expect Equation 2 to apply to the *susceptibility* of each separate process, regardless of what happens at higher frequencies. This is shown schematically in Fig. 2 where the assumed power law relation has an exponent -0.02 for which the ratio (3) is 0.0314.

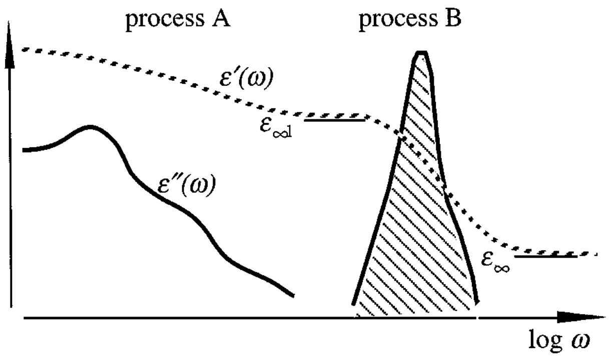

Figure 1 A schematic representation of the relationship between loss processes $\varepsilon''(\omega)$, shown by continuous lines, and the permittivity $\varepsilon'(\omega)$ shown by the dashed line. The low-frequency process "A" is followed at much higher frequencies by a strong process "B", such as lattice absorption and each of these has its characteristic frequency dependence. In the frequency range where the losses are negligible, $\varepsilon'(\omega)$ tends to a constant value $\varepsilon_{\infty 1}$, while the ultimate value ε_∞ beyond the lattice absorption lies lower.

Most low-loss materials are characterised by relatively "flat" frequency dependence, which in a sense is a logical necessity since any other dependence would necessarily be lossy. We have pointed out [2] that a flat loss is consistent with a constant energy loss per reversal of every *microscopic* orientation, regardless of the frequency of these reversals. This constant loss appears to be a ubiquitous phenomenon since it is found as a limiting condition in all low loss systems and a discussion of this broad question will be given later in the present paper.

3. Experimental data

There are many examples of low-loss behaviour which follow the "universal" law, that is one for which it is possible to find a value of ε_∞ such that the resulting susceptibility obeys the universal relation, possibly with some additional features. This is well illustrated in Fig. 3 which refers to pure polyethylene (PE), PE with 12% C and PE with 17.5% C [3]. The values of C_∞ are chosen so that the plots of $C'(\omega) - C_\infty$ and of $C''(\omega)$ are parallel lines in the logarithmic presentation and the values of tan δ are shown in Table I. The general conclusion from these data is that the universal fractional power law of frequency dependence of $\chi'(\omega)$ and $\chi''(\omega)$ is obeyed in all three cases, with the surprising result that the exponent $1 - n$ is higher for the pure PE than for PE with C.

Fig. 4 shows the response of PVDF α [4] at two temperatures of 103 and 163 K, where simple universal behaviour is seen after subtraction of C_∞ and correction for some series resistance. At higher temperatures the behaviour is complicated by the presence of some loss peaks.

In some *low loss* systems we find a very different type of behaviour, where C' does not admit of any meaningful substraction of C_∞ and there are no signs of any power-law relationship for either $\chi'(\omega)$ or $\chi''(\omega)$.

Our first example of this shown in Fig. 5 concerns a sample consisting of 55% of graphite suspension in 45% of its mechanical isomorph BN, being subjected to variable pressure giving variable thickness and resulting in variable inter-particle spacings, all below

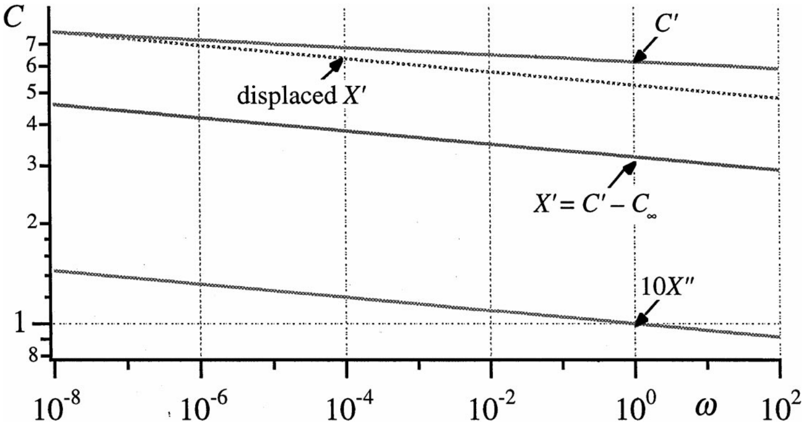

Figure 2 The idealised frequency dependence of $C'(\omega)$ for a capacitor consisting of a "universal" element $X'(\omega) = 3.18\omega^{-0.02}$, for which the ratio Equation 3 is 0.031, in parallel with $C_\infty = 3$ (the numbers are purely arbitrary). The real part of the susceptibility $X'(\omega)$ is given by the sloping line and its "ghost" is shown next to $C'(\omega)$ to stress the growing deviation of the latter as the importance of C_∞ increases with falling $X'(\omega)$. The loss component is plotted as $10X''(\omega)$ to increase the resolution of the plot. To test the KK compatibility of the susceptibility one has to plot $X'(\omega) = C'(\omega) - C_\infty$ together with $X''(\omega)$ and check the consistency of the slope and the ratio (3).

TABLE I Summary of experimental data on “flat” loss materials

Material	Reference	Frequency dependence	$\tan\delta$, mrad	Comments
Polyethylene	Fig. 3	Universal		Excellent fit over 8–10 decades of frequency, Equation 2 fit with regular dependence on graphite content
+ graphite	0% graphite	$1-n=0.10$	≈ 1	
	12%	0.04	≈ 4	
	17.5	0.04	≈ 20	
PVDFα	Fig. 4	Universal		Good fit over 8 decades few complicating features
		$1-n=0.060$ @ 103 K	6	
		0.063 @ 163 K	20	
45% BN + 55% graphite	Fig. 5	No particular trend difficult to subtract ε_∞	0.8–3	Variable pressure gives variable thickness with a slight effect on $\tan\delta$
CaTiO$_3$:Al	Fig. 6	Power law on $\varepsilon'(\omega)$ with $1-n=0.00035$ to 0.00060	0.5–1	No power law in $\varepsilon''(\omega)$, slope zero or positive, but Equation 3 obeyed
PSTZ	Fig. 7 a) $T<T_c$	Both $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ flat	20–40	No subtraction of ε_∞ possible
	b) $T>T_c$	$\varepsilon'(\omega)$ practically flat over 6 decades	6–17	Some variation in $\varepsilon''(\omega)$
PST	Fig. 8	$\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ flat over 5 decades	2–3	No subtraction of ε_∞ from $\varepsilon'(\omega)$ possible
Pure polyethylene	Fig. 9	Universal with $1-n=0.043$ for $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$	0.1–0.3	Subtraction of ε_∞ gives power laws over 10 decades of frequency but not the corresponding ratio (2)
Al$_2$O$_3$/Co	Fig. 4.2 of [2]	No discernible trend in $\varepsilon''(\omega)$	4–6	No data available for subtraction of ε_∞ from $\varepsilon'(\omega)$
Polystyrol	Fig. 4.8 of [2]	Flat over 7 decades	0.1	No data available for subtraction of ε_∞ from $\varepsilon'(\omega)$
Vinoflex	Fig. 4.8 of [2]	Variation by a factor of 2 over 6 decades	10–20	No data available for subtraction of ε_∞ from $\varepsilon'(\omega)$
Polypropylenes	Fig. 4.3 of [2]	Variation by a factor of ≈ 2 over 6 decades	0.05–0.2	No data available for subtraction of ε_∞ from $\varepsilon'(\omega)$

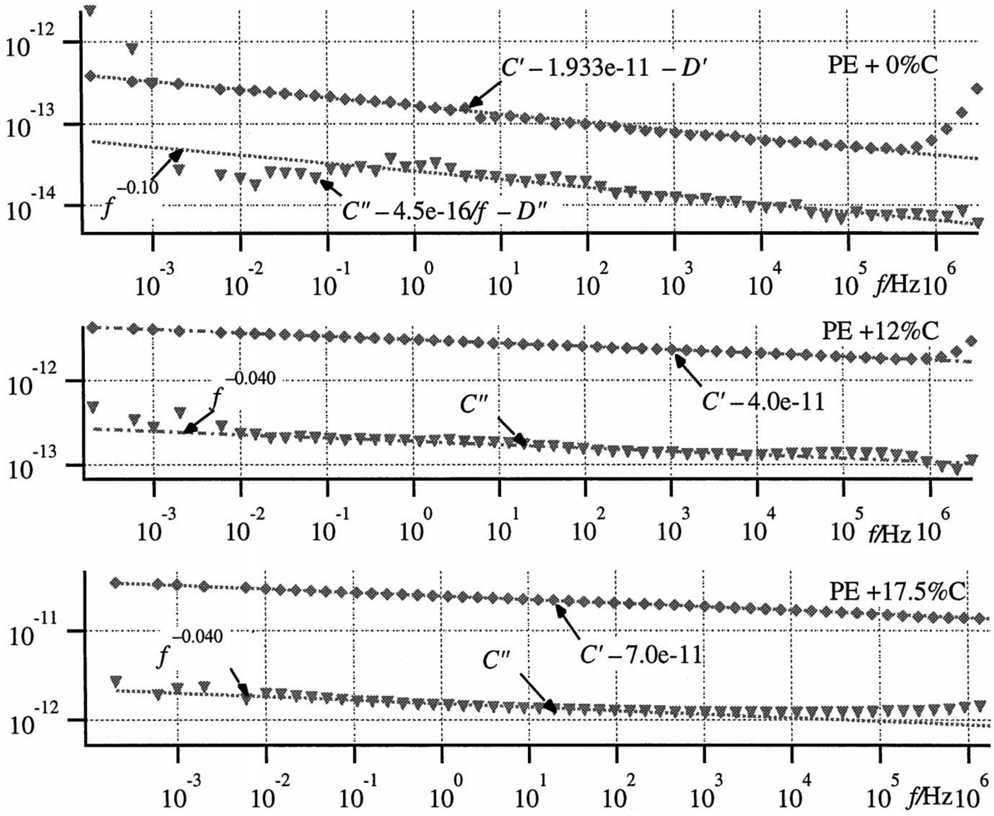

Figure 3 The spectra of polyethylene with variable admixtures of graphite, plotted as $\chi'(\omega)$ and $\chi''(\omega)$ with the values of ε_∞ indicated. The respective C', C'' and $\tan\delta$ data are shown in Table I. Values of $\tan\delta$ @ 1 Hz: 0.0015 in pure PE, 0.005 at 12% C and 0.02 at 17.5% C From [3].

percolation level [5]. Here the mean $\tan\delta$ is of the order of 0.3 to 1 mrad and there does not appear to exist any sensible power law relationship between $C'(\omega)$ and $C''(\omega)$ and the data are not amenable to any “conventional” analysis of the type used in deriving the universal relations in similar circumstances [6, 7].

Fig. 6 gives the data for single crystalline CaTiO$_3$: 30%Al from Lim *et al.* [8] for a range of temperatures

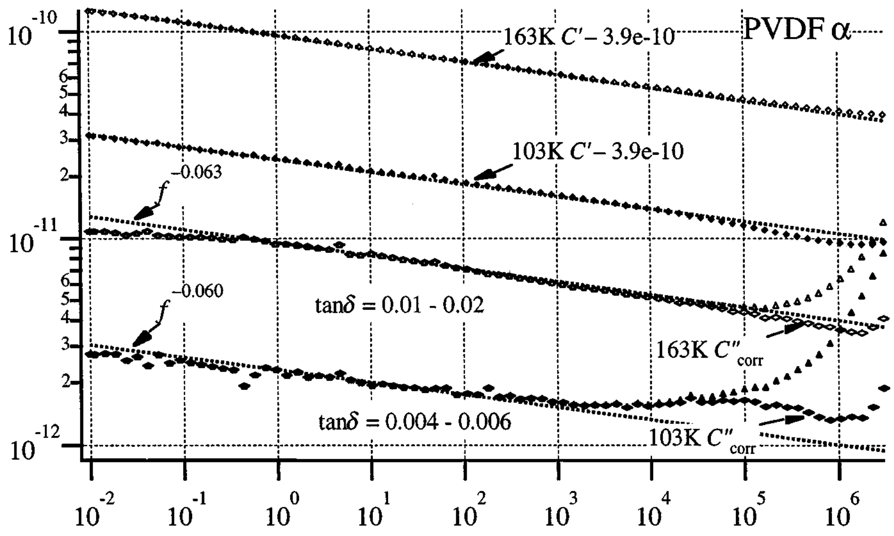

Figure 4 The spectra of PVDFα at two temperatures of 163 and 103 K, with correction for a series resistance and with a value $C_\infty = 3.9 \times 10^{-10}$ subtracted. The values of tan δ are indicated. Menegotto, unpublished data.

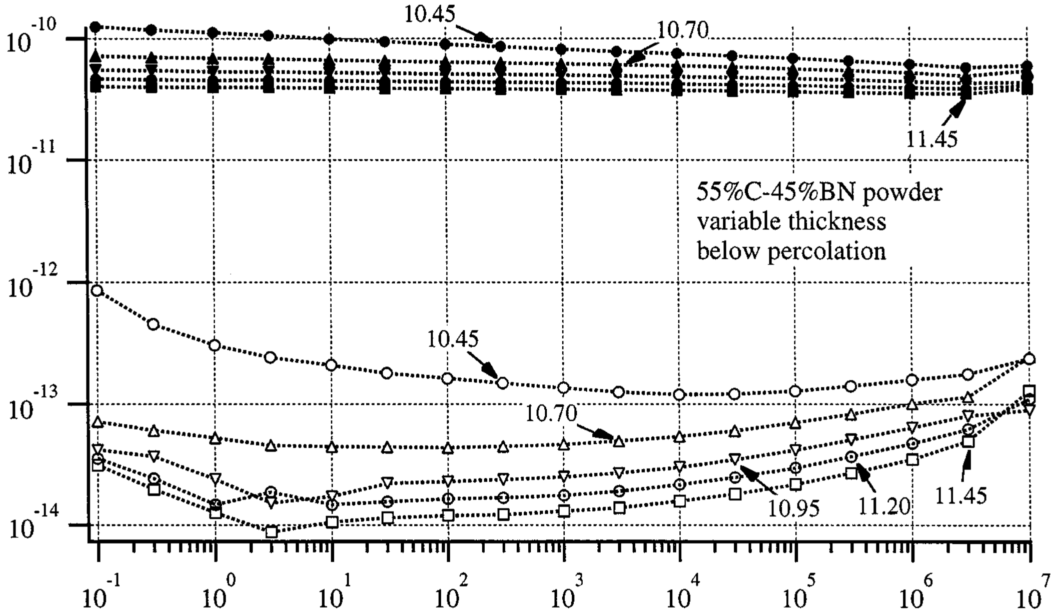

Figure 5 The spectra of C-BN powder mixtures under conditions below percolation with variable compression to give a variable sample thickness indicated by numbers and therefore variable inter-particle distances. These show an almost “flat” frequency dependence over nine orders of magnitude of frequency. tan δ values of the order of 3×10^{-4} are typical and we note that there is no trace of a fractional power law in the $C''(\omega)$ plots, with a predominance of *positive* slopes. From Mclachlan [5].

where $C'(\omega)$ in (a) follows an excellent power law over four decades of frequency, with the limiting slopes $1 - n = 0.000325$ and 0.000625 indicated on the plot. In diagram (b) $C''(\omega)$ follows a rather complex pattern with the low-frequency slopes ranging from positive to negative and a flattening at higher frequencies. The remarkable feature is that, although there is no sign of a universal relationship, applying the multiplier $\cot(n\pi/2)$ to the slopes shown in (a) one obtains the positions marked with the chain-dotted lines in (b), which show clearly that the ratio $C''(\omega)/C'(\omega)$ obeys the classical relation, even though the power-law relations do not apply to $C''(\omega)$ but to $\chi''(\omega)$.

A different example is shown in Fig. 7 referring to a ferroelectric ceramic of composition $Pb_2Sc_{0.875}Ta_{0.875}Zr_{0.125}O_6$ below and above the Curie temperature of $T_c = 68\,°C$ [9]. Below T_c both $C'(\omega)$ and $C''(\omega)$ are virtually flat over five to six decades of frequency and the tan δ is remarkably high, 0.02–0.04 which, on the face of it, appears incompatible with the virtually zero slope. A meaningful subtraction of a value of C_∞ likewise appears difficult since this would make the ratio $\chi''(\omega)/\chi'(\omega)$ even larger. There is no question in this instance of a construction like that in Fig. 6, showing at least an apparent agreement with the $\cot(n\pi/2)$ value, since no value of n can be derived. Above T_c in the paraelectric state in diagram (b), tan δ is significantly lower, but it is likewise impossible to substract a meaningful value of C_∞. The rise of $C''(\omega)$ at high frequencies, which could be attributed to series resistance, may not be due to this cause, since the difference between (a) and (b) would be difficult to justify in what is the same sample. Note the different behaviour below and above the Curie temperature.

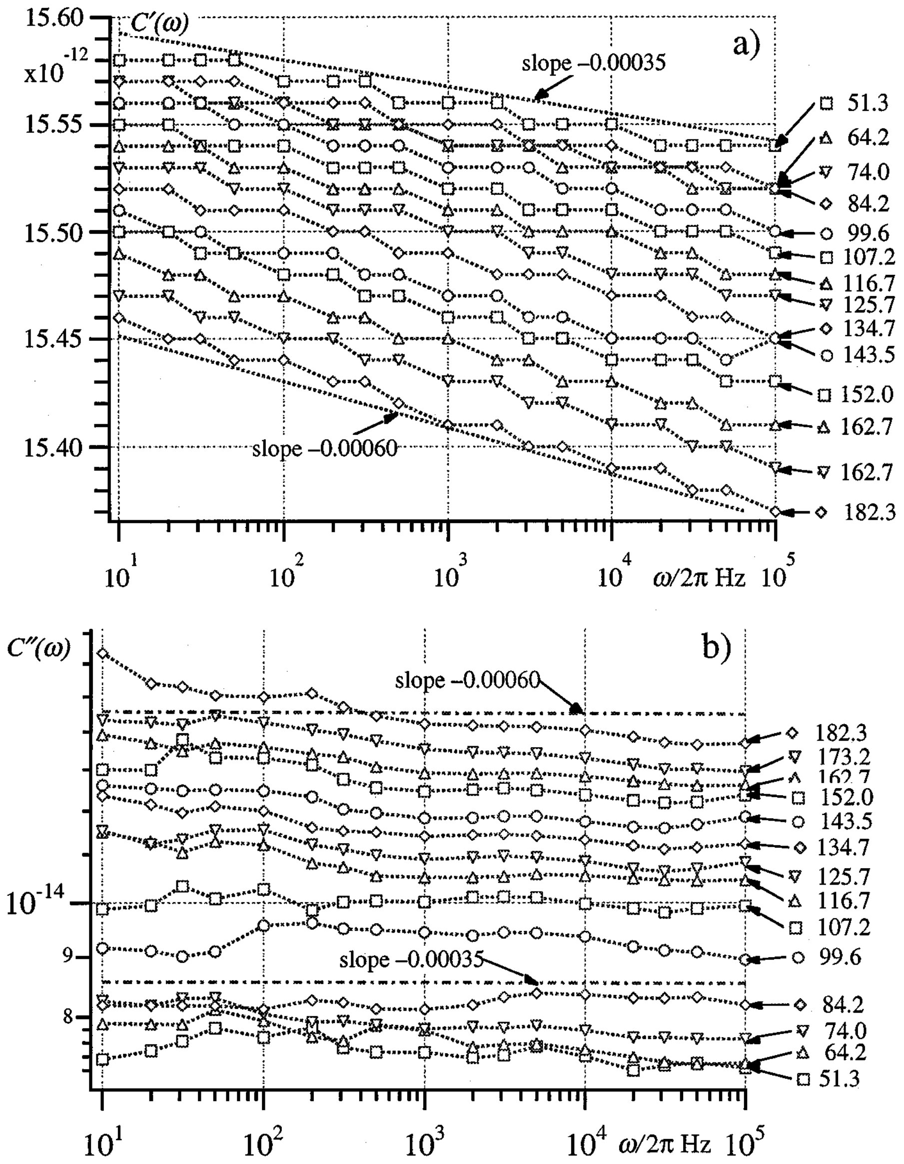

Figure 6 The spectra of $CaTiO_3$:30%Al showing in (a) $C'(\omega)$ without any subtraction of C_∞ and in (b) $C''(\omega)$ corrected for series resistance, over a range of temperatures in K. $C'(\omega)$ follow good power laws with the limiting slopes being indicated, $C''(\omega)$ have slopes at low frequencies ranging from positive to negative, with steep rise at higher frequencies. The latter could be the consequence of a finite series resistance. The arrows in (b) correspond to K-K compatible positions to the respective slopes in (a). From Lim *et al.* [8].

Fig. 8 shows the data for a ferroelectric sample of composition Pb_2ScTaO_6 in which it is not possible to subtract any value of C_∞ and, in any case, the logarithmic slopes of $C''(\omega)$ range from positive to negative values.

Our last example in Fig. 9 shows the data for polyethylene kindly supplied by D. S. McLachlan, where the tan δ falls between 0.1 and 0.3 mrad and there are clearly discernible trends to $C''(\omega)$ and $C'(\omega) - 9.50 \times 10^{-10}$ which are both proportional to $\omega^{-0.043}$. However, the similarity of power law exponents is not compatible with the ratio of these quantities, showing clearly that the "universal" law is not applicable in its classical form.

4. Summary of response types

We conclude that there exist several types of low-loss responses, among which we may distinguish the following, in progressive order of complication:

(a) The "classical" type which obeys the universal relations with clearly identifiable exponent n, and with corresponding ratio $\chi''(\omega)/\chi'(\omega)$ and also with an identifiable value of ε_∞;

(b) The response in which $\varepsilon'(\omega)$ has an identifiable slope although there is no means of subtracting ε_∞ and the ratio $\varepsilon''(\omega)/\varepsilon'(\omega)$ is consistent with that slope, even though the frequency dependence of $\varepsilon''(\omega)$ does not agree with that of $\varepsilon'(\omega)$;

(c) The response consisting of essentially "flat" loss which may, nevertheless, correspond to even relatively large values of $\varepsilon''(\omega)/\varepsilon'(\omega)$, without any means of associating an exponent with it, and therefore there is no ratio $\chi''(\omega)/\chi'(\omega)$ to be expected from these data;

(d) the power law is clearly present in both $\chi''(\omega)$ and $\chi'(\omega)$ but their ratio is not consistent with that power law.

On the face of it, cases (b), (c) and (d) are incompatible with the traditional "universal" approach to dielectric

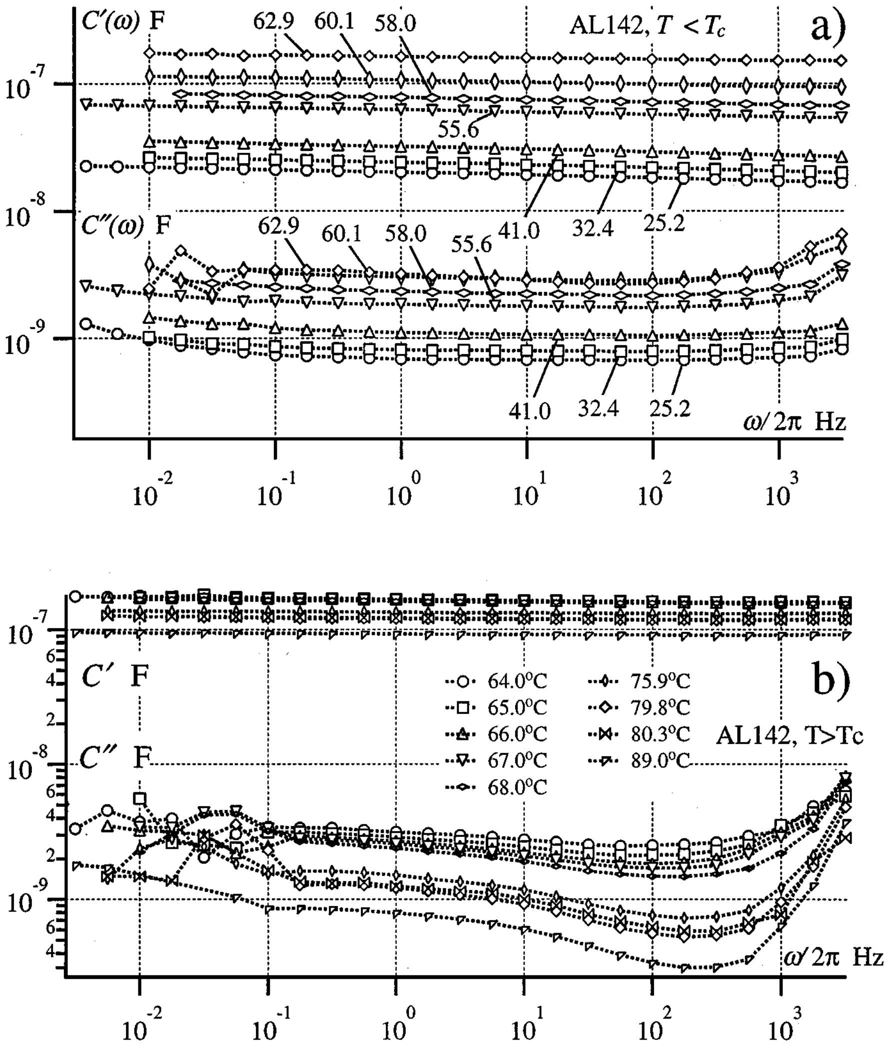

Figure 7 The spectra of $C'(\omega)$ and $C''(\omega)$ for a ferroelectric ceramic of composition $Pb_2Sc_{0.875}Ta_{0.875}Zr_{0.125}$ below the Curie temperature of 68 °C in (a) and above the Curie temperature in (b), showing a remarkably flat $C'(\omega)$ from which it is not possible to subtract C_∞, broadly flat $C''(\omega)$ and relatively high values of tan δ. The slopes of $C''(\omega)$ in (b) range from positive to negative regardless of the slope of the real part. From [9].

theory and we shall propose fresh approaches which may be capable of explaining these discrepancies.

5. Theoretical interpretation

Our next objective is to provide an understanding of the widespread existence of low-loss dielectric materials and to explain the "flat" or nearly frequency-independent character of these low loss spectra. A discussion is also given of the significance of deviations from the universal fractional power-law frequency dependence, particularly on the basis of the data presented in this paper. On this basis we shall formulate the following four questions relating to this subject—the main problem is that no-one seems to have posed them so far:

1. What material conditions must be satisfied for the low-loss property to be observed;
2. What characteristic forms of frequency-domain response are found experimentally in low-loss materials;
3. Can these forms be interpreted within the framework of the "universal" dielectric response or is it necessary to go beyond this framework;
4. What are the likely physical interpretations of this type of behaviour.

Dipolar losses depend on the ability of dipoles to reorientate themselves in external fields and this is determined by the magnitude of energy barriers preventing such orientations. In materials in which the dipoles form part of the structure of the material, such as in polar polymers, the steric forces preventing re-orientation may be very high, and the same may be true of rigid structures such as glasses. On the other hand, the situations of particular interest in the present paper are where the dipoles are extrinsic to the structure, for example impurity dipoles in most materials, when such constraints may not apply to the same extent.

The term dipole is to be understood to comprise *ionic dipoles* constituted by charged localised ions with their countervailing opposite charges constrained to hop around them, such as aliovalent substitutional impurities in crystalline materials or interstitial ions.

5.1. Review of experimental data

We begin with a review of some experimental data presented in Table I which sums up the principal

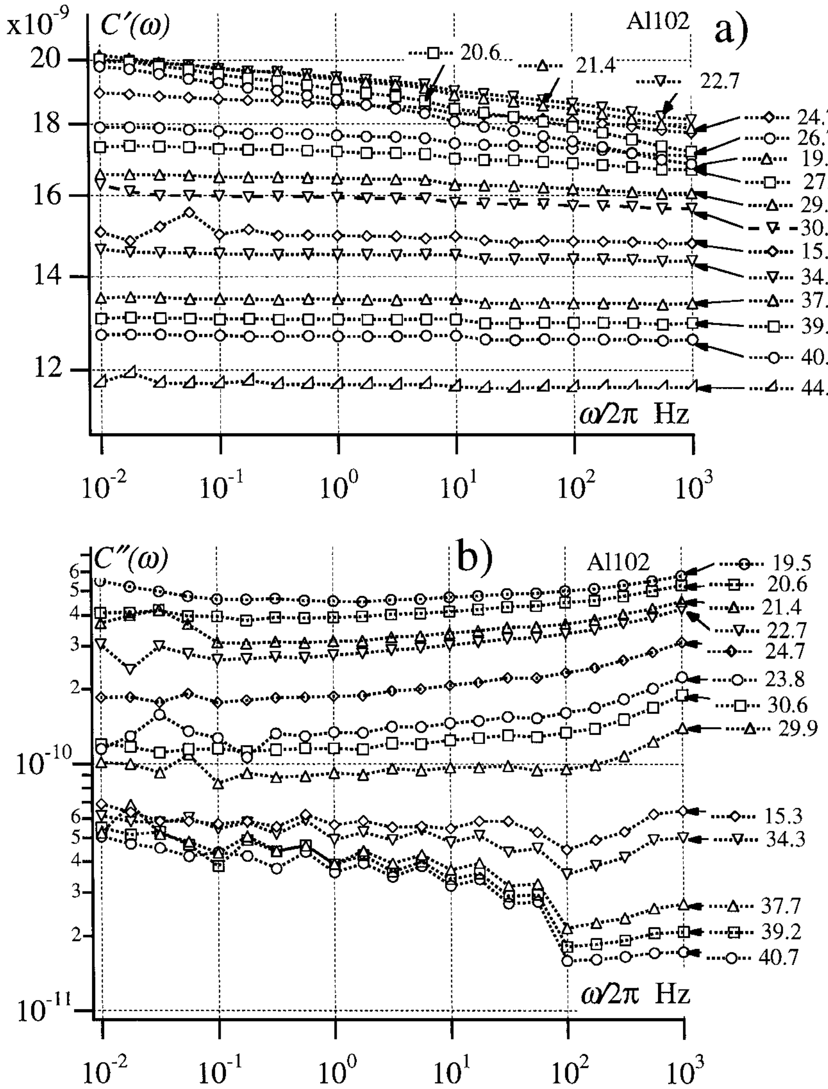

Figure 8 The spectrum of a ferroelectric ceramic of composition Pb_2ScTaO_6 which does not follow any "universal" tendency and in which it is not possible to subtract a sensible value of C_∞ at any temperature.

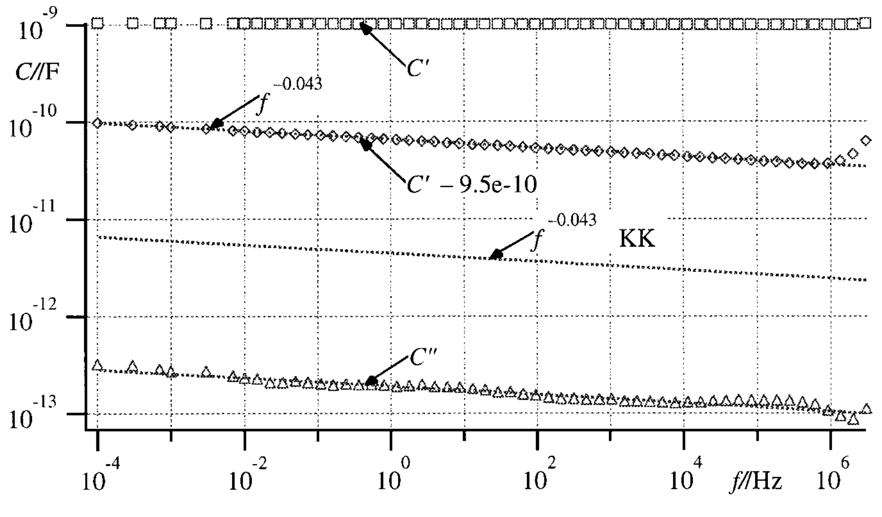

Figure 9 The loss data for polyethylene showing a different deviation from the "universal" trend, in that the subtraction of a value of $C_\infty = 9.5 \times 10^{-10}$ F give parallel logarithmic $C'(\omega)$ and $C''(\omega)$ plots with a slope -0.043 over ten decades of frequency, but with a ratio which some 20 times larger than the KK compatible value shown by the dotted line. The values of $\tan\delta$ cover the range 1–3 × 10^{-4} and the loss goes as $C''(\omega) \propto \omega^{-0.043}$ shown by the dotted line. Data kindly supplied by D. C. McLachlan.

characteristics and the orders of magnitude involved. We note that the range of $\tan\delta$ values for materials showing "flat" loss ranges from less than 0.1 to more than 40 mrad, in other words, the flatness of losses is not in any way confined to very low loss materials but is found regardless of the value of $\tan\delta$.

Likewise the spectral shape is independent of the level of loss—we see perfect universal law in PE with various admixtures—including zero—of graphite, while a different sample of pure PE gives the same power laws for $\chi''(\omega)$ and $\chi'(\omega)$ but not a consistent ratio $\chi''(\omega)/\chi'(\omega)$. Several of the examples show no power laws for both $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ while some show power laws for $\varepsilon'(\omega)$ but not for $\varepsilon''(\omega)$ while still retaining an approximate fit of $\varepsilon''(\omega)/\varepsilon'(\omega)$.

The conclusion from this is that "flatness" and loss level are not linked directly, at least not for $\tan\delta \leq 30$ mrad. For higher values of $\tan\delta$ the variation of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ is becoming pronounced, as would be expected from their KK compatibility. It is also evident that the universal law of polarisation is only one limiting form of behaviour and that other models are acceptable. We shall attempt to outline some possible alternative solutions, although the full clarification of this complex picture would require further work, mainly because this type of behaviour had not been properly recognised before.

5.2. The "universal" law

The complex dielectric susceptibility of many low-loss dielectrics follows a limiting form of the "universal" relaxation law given by Equation 2 with its KK consequence of Equation 3. The case of low-loss dielectrics corresponds to the limit $n \to 1$, where the ratio (2) tends to zero and many examples of such behaviour have been found [2, 3]. It is important to note that the *empirically observed* power law frequency dependence does not in any way *explain* the physical mechanism underlying these processes, it merely states that most materials happen to follow this law.

However, we have shown earlier in this paper that many low-loss materials deviate significantly from the universal relation, either by not following the fractional power law at all, or when following it, failing to maintain the KK compatible ratio (2). Some even show that a different ratio obeys the slope relation

$$\varepsilon''(\omega)/\varepsilon'(\omega) = \cot(n\pi/2) \qquad (6)$$

This relationship is very surprising, since its literal interpretation would require that the same fractional power law of frequency dependence should be applicable all the way to the optical region of the spectrum and beyond, since no subtraction of ε_∞ is involved. In some examples quoted by us relation (3) applies to the slope n of $\varepsilon'(\omega)$ but the slope of $\varepsilon''(\omega)$ may be completely incompatible with that of $\varepsilon'(\omega)$.

We shall propose some alternative approaches which may help to remove the apparent breakdown of KK relations.

5.3. Earlier theoretical treatments

There exist many theoretical treatments of the frequency dependence of dielectric susceptibility, some based on quantum-mechanical analysis of vibrations in disordered systems [10–12], others on a variety of fractal arguments [13], on dynamics of hopping charge carriers [14–18], on stochastic arguments [19–21] and on a logarithmic hierarchy of relaxation kinetics [22], to name but a few. All these treatments relate to the time-dependence of the relxation process under specified assumptions, but they are not very helpful in defining the criteria for low loss response. Only the quantum mechanical vibration theories [10, 12] and the stochastic analysis give the "universal" fractional power law of Equation 2, while the others, most of which are specifically applicable to relatively conducting, i.e. high loss systems, lead to various forms of logarithmic laws. It is relevant to point out that, while deriving $\chi''(\omega)$ or $\sigma'(\omega) = \omega\chi''(\omega)$, most of these treatments do not trouble to derive explicity the functional form of $\varepsilon'(\omega)$, so that it is not easy to obtain a closed-form expression for the ratio $\chi''(\omega)/\chi'(\omega)$, but it is evident that the form given by Equation 2 which is characteristic of the "universal" law represents but one special case of all possible forms, even though the most frequently encountered experimentally. Therefore one should not be discouraged from pursuing other possible models as examples of what is possible, without immediately being concerned with the particular physical model which may give rise to this behaviour.

The analysis in Ref. [10] comes to conclusions which are moderately close to those advanced in the present paper, envisaging an effective reduction of the number of available dipoles in the limit of $n \to 1$, even though it arrives there on a rather different path. The fact that there exist several analogies between these treatments strengthens our confidence in the validity of these arguments. In particular, Ref. [10] postulates a very general model, while the present analysis provides a more specific example. There are also some similarities with an earlier analysis by Bozdemir [23, 24].

5.3.1. Physical basis of low loss

There does not appear to exist a physically satisfactory *rationale* for the existence of low dielectric losses and simple "common sense" arguments that what is needed is a low density of polarisable species do not provide satisfactory answers, since low-loss materials are not necessarily very "pure". As a result of this we have suggested that the key to the understanding of low-loss behaviour lies in dipolar screening [2, 25] which leads to interactions between dipoles in materials with sufficiently *low* dipole densities. Briefly stated, the proposition is that electrostatic interactions between dipoles even at large distances from one another "lock" these dipoles so that their response to external alternating fields is weakened.

This dipolar screening is closely analogous to the well known phenomenon of screening by *charged particles* which leads to the concept of Debye screening radius λ_D and the related notion of the number ν of particles in a Debye sphere. Classical analysis leads to the conclusion that ν *increases* with *decreasing* density n of particles, going as $n^{-1/2}$-dense plasmas screen particles very effectively so that $\nu < 1$, no particle "sees" any of the others. On the contrary, in dilute plasmas Coulombic interaction extends further and many particles are found in the field of any one of them.

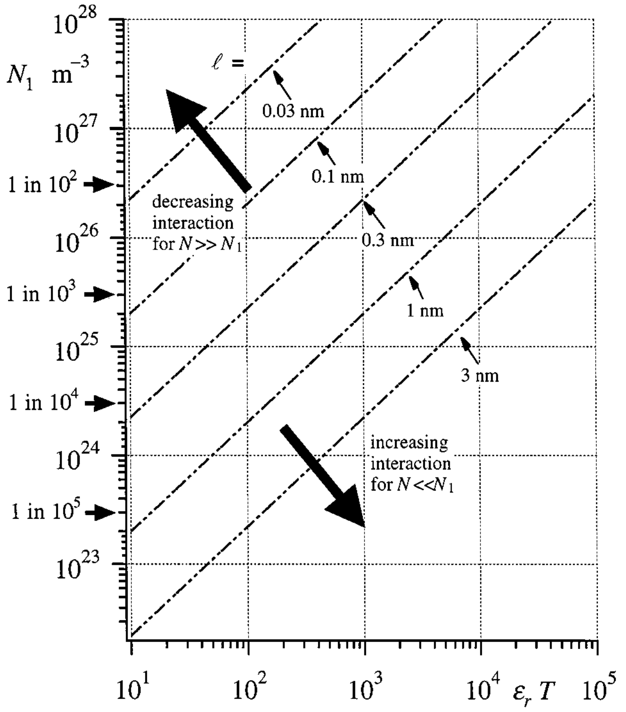

Figure 10 The critical density N_1 given by Equation 7, below which interactions between dipoles become strong and above which they are weak. The density N_1 is shown as function of the product of the temperature T and of the relative permittivity ε_r, with the "length" ℓ_{nm} of the dipole in nanometres as parameter. Marked on the density axis are densities as fractions of the "molecular" density 3×10^{28} m^{-3}. For $N \ll N_1$ dipolar fields interact strongly, individual dipoles are unlikely to follow external fields, thereby reducing their influence on polarisation and giving strongly interactive "flat" spectra. For $N \gg N_1$ individual dipoles do not "see" their nearest neighbours and each dipole behaves independently of all the others, giving Debye-like spectra. Note that $\ell_{nm} \approx 0.1$–0.3 is typical of most molecular dipoles, $\ell_{nm} = 1$ relates to larger molecules and $\ell_{nm} = 0.03$ is typical of induced atomic and molecular dipoles.

The analysis in Ref. [25] shows that the situation with dipoles is similar but much more drastic, in that there exists a critical density N_1 of dipoles given by

$$N_1 = \frac{3\varepsilon kT}{\mu^2 \ln 2} = 2.03 \times 10^{22} \frac{\varepsilon_r T}{\ell_{nm}^2} \qquad (7)$$

where ℓ is the dipole "length" defined by the magnitude of the dipole moment $\mu = \ell q$, where q is the dipolar charge and ℓ_{nm} is the value of ℓ in nanometres. As the dipole density falls below N_1, the number of dipoles within the field of any one dipole increases almost exponentially, so that any dipolar system of density $N < N_1$ is dominated by strong interactions (see Fig. 10). This relation is shown in Fig. 10 as a logarithmic plot of N_1 against the product of relative permittivity ε_r and temperature T, with ℓ_{nm} as parameter.

The effect of this is to delay the response of dipoles to external fields, at least on a sufficiently short time scale, while they remain "trapped" in the fields of their neighbours. Given sufficiently long time of interaction with the field, an equilibrium will always be reached eventually, but at shorter times and higher frequencies the *effective density of dipoles* is bound to be much smaller than their actual density.

Taking typical values $\varepsilon_r = 3$ and $\ell = 0.1$ nm and $T = 300$ K, we find $N_1 \approx 2 \times 10^{27}$m^{-3} which corresponds to nearly 1% of molecular density, and the dipole density N needs only be smaller than this rather high density in order for strong interactions to dominate.

According to this argument, a dipolar system does not need to be "ultra-pure" in order to have low losses, it is sufficient for the dipole density to fall below the critical density N_1 appropriate to ℓ, ε and T, for the effective number of dipoles to be reduced by the interaction. It is worth noting that in this context the para- or ferroelectric nature of the material itself does not play any major role, since the dipoles that we are considering are *impurity* dipoles embedded in the lattice of the material, and not the *intrinsic* dipoles of a ferroelectric material.

5.4. A particular model of flat loss

In the past we have tended to regard the flat loss as the limiting case of the universal power law relation with the exponent $n \to 1$, which would lead to the logical conclusion that $\chi''(\omega)/\chi'(\omega) \to 0$. However, there is no reason to regard this as the only possible situation since all the alternative treatments mentioned in Refs. [14–18] likewise do not follow the universal law and do not exhibit the relation (2). The latter has the unique physical significance that the loss is directly related to polarisation regardless of frequency, which may be interpreted as signifying a constant loss per reversal of microscopic polarisation [2, 26].

Consider a system which, due to specific physical conditions, has a genuinely "flat" loss in a certain spectral range. It cannot be truly flat in the entire range $[0, \infty]$, since it has to satisfy the conditions $\chi''(0) = 0$ and the finite integral given by Equation 5 (see Fig. 11).

We shall derive the functional form of $\chi'(\omega)$ corresponding to constant $\chi''(\omega) = A$ over a frequency range which we shall assume to be sufficiently large to justify calculating $\chi'(\omega)$ from this law and ignoring regions at lower and higher frequencies.

The Kramers-Kronig expression for $\chi'(\omega)$ in terms of $\chi''(\omega)$ is from Ref. [1]:

$$\chi'(\omega) = \frac{2}{\pi} \int_0^\infty \frac{x}{x^2 - \omega^2} \mathrm{d}x \approx \frac{2A}{\pi} \int_0^\Omega \frac{x}{x^2 - \omega^2} \mathrm{d}x \qquad (8)$$

where we have replaced the upper limit of integration with Ω assumed to be the limit to which the constant loss is valid. The integral in Equation 8 is to be taken in the sense of Cauchy's principal value, ignoring the imaginary contribution arising from integration over the pole at $x = \omega$. The integral is evaluated as the limit for $\omega_- \to \omega$ and $\omega_+ \to \omega$ of

$$\int_0^\infty \frac{x}{x^2 - \omega^2} \mathrm{d}x = \frac{1}{2} \ln(\omega^2 - x^2)\Big|_0^{\omega_-} + \frac{1}{2} \ln(x^2 - \omega^2)\Big|_{\omega_+}^{\Omega}$$
$$= \ln \Omega - \ln \omega \qquad (9)$$

so that

$$\chi'(\omega) \approx \frac{2A}{\pi} (\ln \Omega - \ln \omega) \qquad (10)$$

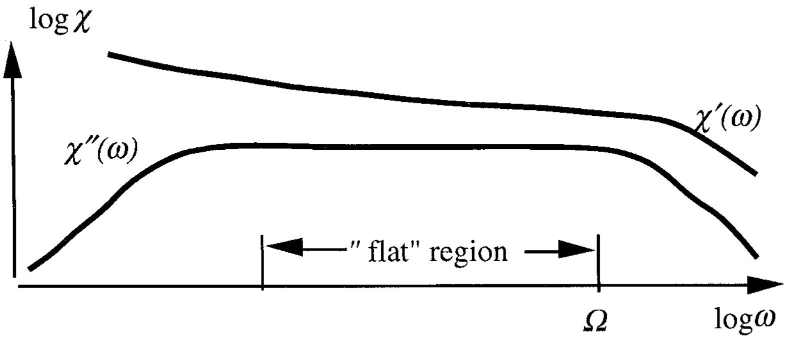

Figure 11 A schematic representation of a dielectric spectrum with a “flat” loss range covering several decades of frequency up to Ω. $\chi''(\omega)$ must go to zero at very low and very high frequencies. The corresponding $\chi'(\omega)$ remains relatively shallow in the chosen range but its relation to $\chi''(\omega)$ depends on boundary conditions which are not readily ascertainable.

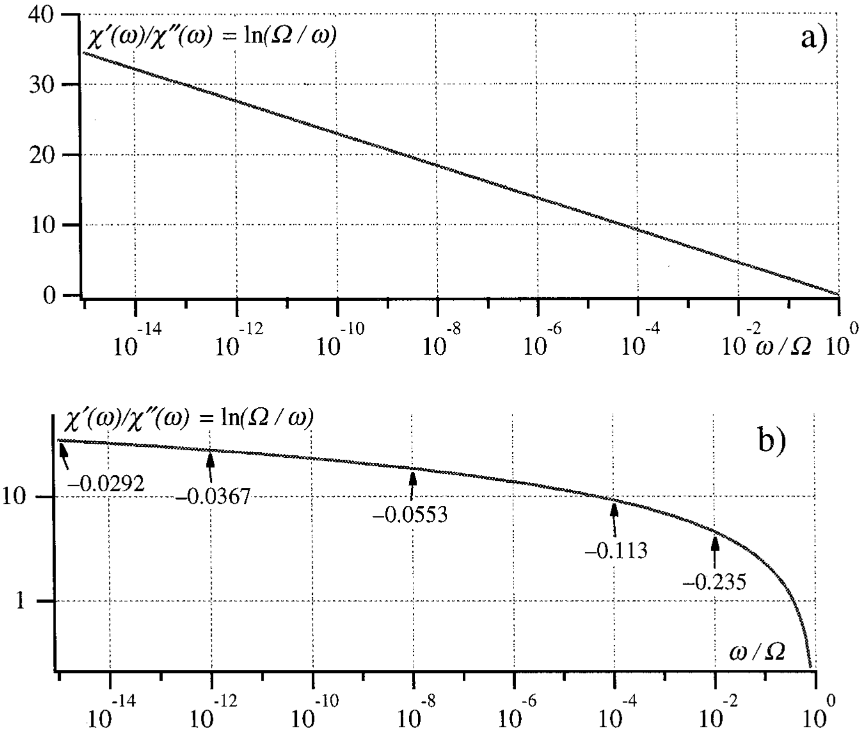

Figure 12 The calculated frequency dependence of the ratio $\chi'(\omega)/\chi''(\omega)$ with an assumed constant value of $\chi''(\omega)$, plotted linearly in (a) and logarithmically in (b) against the logarithm of the ratio ω/Ω. The tags in (b) give the values of the logarithmic slope at the points indicated.

This may be expressed as the ratio

$$\chi'(\omega)/\chi''(\omega) = \frac{2}{\pi}(\ln\Omega - \ln\omega) \approx \ln\Omega - \ln\omega$$
$$= \ln(\Omega/\omega) \qquad (11)$$

and this is shown as a plot in Fig. 12a. Since $\chi''(\omega)$ is assumed to be constant, the plot also gives the scaled graph of $\chi'(\omega)$ showing its functional form to be very flat or flat, depending on the value of the ratio in Equation 12. The logarithmic plot in Fig. 12b is more informative here, since it corresponds to the customary form of plotting the experimental data.

The value of the ratio $\chi'(\omega)/\chi''(\omega) \to 1$ as $\omega \to \Omega$, in other words as the frequency approaches the limit of applicability of the flat loss approximation, which is not surprising. As the frequency moves away from the limiting value Ω so the ratio (12) increases slowly and $\chi'(\omega)$ becomes progressively more constant. The values of the logarithmic slope at various points are indicated in diagram (b).

Taking limited ranges of frequency of, say four to six decades, it should be possible to obtain reasonably straight log-log plots with variable ratios $\chi'(\omega)/\chi''(\omega)$. It is necessary to bear in mind that the experimentally important ratio is the $\varepsilon'(\omega)/\varepsilon''(\omega)$ since we do not know *a priori* the values of ε_∞. The effect of this is seen in Fig. 13 as a decrease of the dispersion of $\varepsilon'(\omega)/\varepsilon''(\omega)$ in comparison to that of $\chi'(\omega)/\chi''(\omega)$.

It is clear that the proposed “flat loss” form with its KK-compatible $\varepsilon'(\omega)$ represents a much better approximation to the experimentally observed forms of dielectric response such as in Fig. 7 and possibly also in Fig. 8, and in many other sets of data, than the “universal” fractional power law which is seen, for example, in Fig. 3. The data of Fig. 6 could likewise fit into this picture but the extremely low value of the ratio $\varepsilon''(\omega)/\varepsilon'(\omega)$ makes it unlikely to be the correct choice. Finally, it is worth

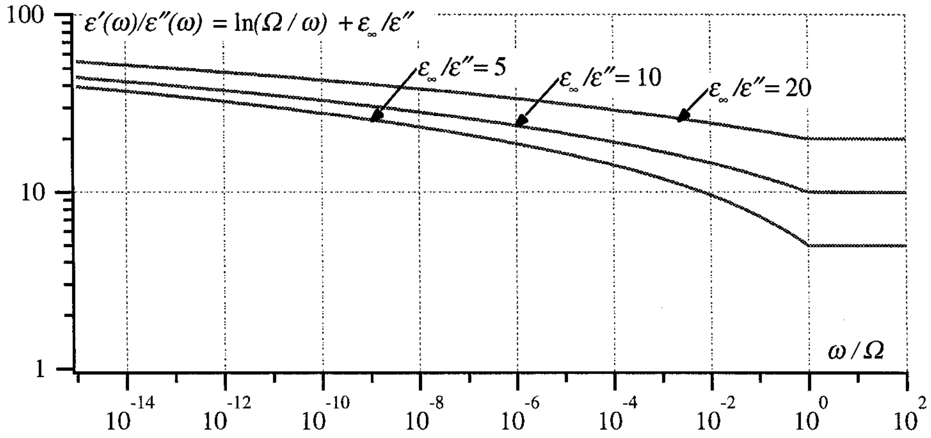

Figure 13 The graph of $\varepsilon'(\omega)/\varepsilon''(\omega)$ which differs from that of $\chi'(\omega)/\chi''(\omega)$ shown in Fig. 12 by the addition of various values of $\varepsilon_\infty/\varepsilon''$ as indicated by tags. The sharp kinks in the curves are due to the arbitrary truncation at zero of the data for $\chi'(\omega)/\chi''(\omega)$ which rapidly fall to $-\infty$ for values of ω/Ω where they are no longer valid. The important point is the gradual reduction of the dispersion of $\varepsilon'(\omega)/\varepsilon''(\omega)$ with rising ε_∞.

stressing that the data of Fig. 5 defy any simple form of classification.

It is also worth noting the remarkable behaviour shown in Fig. 9, where the fractional power law is obeyed by both $\chi'(\omega)$ and $\chi''(\omega)$ but the corresponding relation (2) is not obeyed, once again showing that there is more to this than meets the eye. It appears quite generally, therefore, that low- and very low-loss materials represent a special category of dielectric behaviour which does not fit entirely into the "universal" pattern. A full theoretical significance of this observation has yet to be developed.

The principal purpose of showing the example of constant loss is to demonstrate the potential of this line of approach—any number of possible frequency dependences could be tried and they may lead to promising alternatives to the universal form which manifestly does not fit the requirements of many low-loss materials. There would then remain the task of finding the physical framework in which the promising spectral dependence could be accommodated.

There remains a further possible approach to the interpretation of non-universal processes—termed "trans-universal" [2, 9], where the equivalent circuit of the model system contains an additional universal capacitor in series with the universal fractional power law element. It is not clear what the physical significance of this process could be and more analysis is needed to elucidate this aspect.

5.5. "Flatness" of low loss

We now turn to the other property of low-loss dielectrics—the "flatness" of their $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ spectra, ascertained experimentally over five, seven or more decades of frequency, notwithstanding the presence in some cases of *small* deviations from almost constant response in the $\log\varepsilon - \log\omega$ representation. Typically, $\log\varepsilon''(\omega)$ plots, many of which are quoted in Ref. [2], show more variation than $\log\varepsilon'(\omega)$ plots and may fluctuate over 1/5th to 1/3rd decade in five or six decades of frequency. These small deviations can be attributed to weak dipolar processes which may be present and which in no way invalidate the concept of the flat loss.

Our experience shows that residual losses remaining after elimination of more dominant loss processes [6, 7], such as large dipolar peaks, low-frequency-dispersion (LFD) [2] or direct current conduction, give a flat distribution over appreciable ranges of frequencies. This irreducible flat loss background falling well above the detection limit seems to be a characteristic of all solid dielectrics.

It is important to stress that there is *no necessary reason* why the universal relation given by Equations 2 and 3 should apply to all low-loss dielectrics. Apart from the fact that most dielectrics of any level of loss seem to obey this relation, it is a matter of empirical evidence that some low- and very-low-loss materials exhibit this type of behaviour to a large extent. Equally, however, there is convincing evidence of deviations from the universal relation, manifesting itself primarily by the inapplicability of the same fractional power-law relations to both $\chi'(\omega)$ and $\chi''(\omega)$, with consequential inapplicability of the ratio of Equation 3.

To the extent to which the universal relation is seen to be applicable, the flatness of low-loss response is an evident and inescapable consequence of Kramers-Kronig relations: if the loss is low, both $\chi'(\omega)$ and $\chi''(\omega)$ must be almost flat, corresponding to $n \to 1$, and in the correct ratio. The physical causes of this flatness are then directly linked to the fact that the universal relation is based on the assumption that every reversal of microscopic polarisation entails the same amount of energy loss regardless of the frequency of reversals. If very few reversals take place because of long-range interactions and the absence of screening, the loss is correspondingly low and flat.

Thus, the conclusion is that in the case of solid dielectrics the inevitable limiting condition is a flat, frequency-independent loss and permittivity, something that does not appear to arise in the case of liquids. This phenomenon requires a fundamental explanation.

Our starting point is the inevitable consequence of the fractional power law relation given by Equation 2, which can be interpreted as the ratio of energy lost per radian to energy stored in the system [2] and this is equivalent to the statement that the energy lost per reversal of microscopic polarisation is independent of frequency.

One process which could apply to low-loss systems is some form of piezoelectric mechanism where the application of an electric field gives rise to mechanical strain and this in turn brings with it energy loss on reversal of polarisation. This mechanism is very likely to operate in ferroelectrics where the piezo-electric coupling is strong and there is good experimental evidence for it [6] but it is possible that some form of piezoelectricity is present even in conventional dipolar materials, since dipolar orientations should have an effect on mechanical strain [27].

No detailed work appears to have been done on this process and yet the experimental evidence is compelling to consider this or some similar loss process as responsible for the observed behaviour of solid dielectrics. In this connection it is particularly relevant to note that flat loss is not seen in liquids, in which dipolar peaks appear to decrease indefinitely with progressive removal of dipolar species. This may be understood in terms of the absence of electrostatic ordering in liquids.

The flatness of loss may need to be further justified in the case of materials not following the universal relation.

6. Conclusions

We suggest that low-loss dielectrics owe their behaviour not so much to a particularly low density of dipolar species, which manifestly does not apply to many of them, but to the effect of dipolar screening which produces interaction between neighbouring dipoles, thereby preventing a significant fraction of them from following external alternating fields. The critical density for the screening effect is higher than would be needed for a very low loss in non-interacting dipolar systems.

Our study has revealed, we believe for the first time, that the "universal" fractional power law which applies to a large majority of all dielectrics regardless of their physical and chemical nature, appears not to be equally generally applicable to low-loss materials, with tan $\delta \leq 0.03$, say. This suggests that in the low-loss limit other processes take over and dominate the behaviour. Deviations from the universal law may take the form of failure to follow the fractional power law by $\chi'(\omega)$ and/or by $\chi''(\omega)$, and it may even lead to a failure to maintain the correct ratio $\chi'(\omega)/\chi''(\omega)$ expected of the universal law. There are also examples of the ratio $\varepsilon'(\omega)/\varepsilon''(\omega)$ being consistent with the power law trend of $\varepsilon'(\omega)$, the physical significance of which is not at all clear as yet.

The "flat" spectral character which is the widely observed concomitant property of low loss behaviour, is interpreted in terms of constant loss per reversal of polarisation, which is independent of the frequency of reversals. It is suggested that one such processes may be due to piezoelectric coupling between polarisation and mechanical loss, but there may well be other processes.

Generally, it is evident that the response of low-loss materials leaves a great deal of unanswered questions which should be investigated with a corresponding increase in the detailed systematic study of the experimental situation.

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