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Dielectric relaxation with dipolar screening

A. K. JONSCHER
Physics Department, Royal Holloway College, University of London, Egham, Surrey TW20 0EX, UK

The phenomenon of dipolar screening does not appear to have received sufficient attention in the past, in a manner comparable to charged particle screening, and yet it is shown that it is capable of explaining some forms of dielectric response to which no other evident explanation exists. While reorientations of mathematical dipoles of zero "length" do not entail any charge displacements, physical dipoles of finite length, l, do produce charge displacements and therefore screening. A theory of dipolar screening is presented and it is shown that relatively "dense" systems give complete screening so that neighbouring dipoles do not "see" one another, while in more dilute systems many dipoles fall within a screening radius, R_s, of any one dipole. Dipoles within R_s tend to adopt energetically favoured configuration and the entire system "seizes up" in a "domain", thus reducing the number of dipoles which can be reoriented at finite frequencies.

1. Introduction

The dielectric response of solids deviates considerably from the classical Debye form and the cause of this is to be found in interactions between the dipoles and the medium in which they are embedded. There are several theories dealing with this problem but they will not be discussed in the present context; the principal point which we wish to raise now is the fact that the phenomenon of dipolar screening does not appear to have entered into any of these. The guiding idea of the present treatment is to determine the effect of the density of dipoles on possible interactions between them, because these interactions are the dominant influence on the deviations, sometimes very drastic, of the dielectric response from the Debye spectrum. No relevant theoretical analysis of this problem has been found, and we are therefore proposing a highly simplified approach which provides relatively simple analytical results capable of application to specific situations. This theory is then applied to specific examples of dielectric behaviour which do not appear to have been otherwise explained.

The term "dipolar" here includes permanent molecular dipoles as well as ionic dipoles like an aliovalent impurity in a lattice with a compensating ionic charge in the neighbourhood, and this may apply to many inorganic ceramic and similar materials. It also refers to induced atomic and ionic polarization. Specific examples include the near-Debye behaviour in the opposing extremes of high-density systems such as polar liquids, and of certain very low-density systems, as well as the remarkable tendency to "flat" loss in polar materials at low temperatures. Our theory will be applied to both these extreme situations.

We begin with a very brief outline of screening by charged particles, because this provides a convenient analogous situation.

2. Screening by charged particles

The phenomenon of screening of charged particles by other such particles plays an important role in many physical situations in that it leads to the limitation of the range of interaction between charges by means of Coulombic fields [1]. Screening by charged particles leads to the concept of Debye screening length

$$\lambda_D = \frac{(\varepsilon kT)^{1/2}}{qN^{1/2}} \tag{1}$$

where N is the density of particles, q their charge and ε is the permittivity of the medium. Screening arises from the fact that the field of a given particle causes a self-consistent repulsion of like charges and attraction of opposite ones which leads to a modification of the potential in the neighbourhood of the particle, giving the "self-consistent" field

$$\phi(r) = \frac{q}{4\pi\varepsilon r}\exp(-r/\lambda_D) \tag{2}$$

implying that the unscreened Coulomb potential $q/(4\pi\varepsilon r)$ is attenuated by the exponential term and this the more rapidly the higher is the density N. The physical significance of screening is that the field of the particle cannot be "seen" beyond a few distances λ_D, in contrast with the unscreened Coulombic potential which decays sufficiently slowly to be "visible" at large distances. An important concept in this connection is the number, ν, of particles within a sphere of radius λ_D which is given by

$$\begin{aligned}\nu &= \frac{4\pi}{3}N\lambda_D^3\\ &= \frac{4\pi}{3}\frac{(\varepsilon kT)^{3/2}}{q^3}N^{-1/2}\end{aligned} \tag{3}$$

implying, somewhat paradoxically, that ν increases as N decreases.

3. Theory of dipolar screening

Dipolar interactions have been the subject of countless theoretical treatments since the dawn of dielectric science, beginning with the classical work of Clausius and Mossotti and continued both in terms of theoretical analysis (see, for example, the discussion in Titulaer and Deutsch [2] and Fulton [3]) and also through numerical modelling [4]. The problem is that these treatments do not lend themselves to a simple evaluation of the effect of screening, which means that it is not possible to infer from them the effect of dipole density on the interactions between dipoles. Most of these theories appear to relate to static situations and none of the predictions of the dynamic behaviour go beyond the classical Debye response which is hardly ever seen in solids.

We approach dipolar screening from the purely electrostatic classical standpoint and it is evident that the analogy with charged particle screening is only tenuous, because dipoles do not have any net charge and cannot change their density in response to external fields, at least not uniform ones. Moreover, the reorientation of ideal dipoles with zero length does not lead to any charge displacement and therefore cannot give rise to screening. Physical dipoles of finite length, l, on the other hand, can give rise to screening as was first proposed by Jonscher [5]. In the absence of screening the dipolar potential is given by

$$\phi_D(z, \theta) = \frac{q}{4\pi\varepsilon l z}\{[1 + (2z)^{-2} - \cos\theta/z]^{-1/2} - [1 + (2z)^{-2} + \cos\theta/z]^{-1/2}\} \tag{4}$$

where $z = r/l$ and the angle θ is the angle with respect to the direction of the dipole axis. At distances $r \gg l$ the potential is approximately

$$\phi(r, \theta) \approx \frac{\mu}{4\pi\varepsilon r^2}\cos\theta \tag{5}$$

and the radial and azimuthal components of the electric field arising from this potential are

$$E_r(r, \theta) \approx 2E_0(r)\cos\theta \tag{6a}$$

and

$$E_\theta(r, \theta) \approx E_0(r)\sin\theta \tag{6b}$$

Our proposition is that in contrast with ideal dipoles, *physical* dipoles of *finite* length, l, and charges $\pm q$, with a dipole moment, $\mu = ql$, can give rise to screening because a reorientation of a physical dipole necessarily gives rise to some charge displacement.

Dipoles in solids are not able to reorient freely as if they were in a liquid but are constrained to preferred orientations dictated by the dispositions of nearest neighbours. Let two preferred orientations of a dipole in a solid lattice be described by a potential double well as shown in Fig. 1, with a field, E, superimposed. The probability of such a dipole being oriented along/against the field is $1 \pm p$, given by

$$\frac{1 + p}{1 - p} = \exp(\mu E/kT) \tag{7}$$

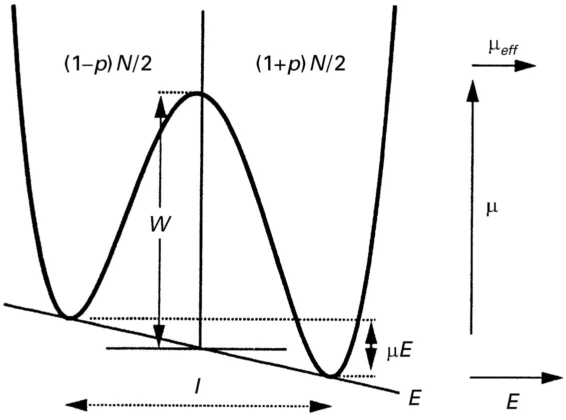

Figure 1 A potential double well defining the preferred orientations of a dipole with moment μ in the presence of an electric field E, indicating the occupancies of the two minima. The barrier energy is W. The inset shows the orientation of the dipole in an external field, E.

The net dipole moment induced along the field $\mu_{\text{eff}} = 2qpl = 2\mu p$ is given by the solution of Equation 7

$$\mu_{\text{eff}} = \mu\frac{e^{\mu E/kT} - 1}{e^{\mu E/kT} + 1} \approx \frac{q^2 l^2 E}{2kT} \tag{8}$$

This result refers to the *time-averaged* dipole moment under the action of the field due to dipole 1 and we have neglected here a term of the order $2/\pi$ arising from the averaging of the cos θ term in Equation 6a.

Now consider a regular array of dipoles of moment, μ, disposed on a square lattice shown in Fig. 2, with the lowest energy dispositions corresponding to antiparallel orientations of nearest neighbours shown shaded.

The amount of charge displacement involved in the reorientation of the dipole by μ_{eff} is, from Equations 8 and 6

$$\begin{aligned}\delta\mu &= \mu_{\text{eff}} \\ &= \frac{\mu^2 E}{2kT} = \frac{\mu^3}{4\pi\varepsilon kTr^3} \\ &= \frac{q^3 l^3}{4\pi\varepsilon kTr^3}\end{aligned} \tag{9}$$

and this is the screening dipole moment due to the finite length l, of the physical dipole. The total screening, Δμ, due to all other dipoles has to be calculated on the basis of the dependence of the field, E, arising from the original dipole at the distance, r, from that dipole which is given by Equation 6, so that the density, N, of dipoles between the radii r_1 and R contributes a total screening:

$$\begin{aligned}\Delta\mu &= 4\pi\frac{N\mu^3}{4\pi\varepsilon kT}\int_{r_1}^{R}\frac{r^2}{r^3}\,\mathrm{d}r \\ &= \frac{N\mu^3}{\varepsilon kT}\int_{r_1}^{R}\frac{\mathrm{d}r}{r} = \mu\frac{l^2}{\lambda_D^2}\ln(R/r_1)\end{aligned} \tag{10}$$

The summation of displacements from the individual dipoles in an array is shown in Fig. 2 corresponding to a square array, with the equilibrium dispositions of dipoles being shown shaded as the lowest energy antiparallel configuration. With the central dipole

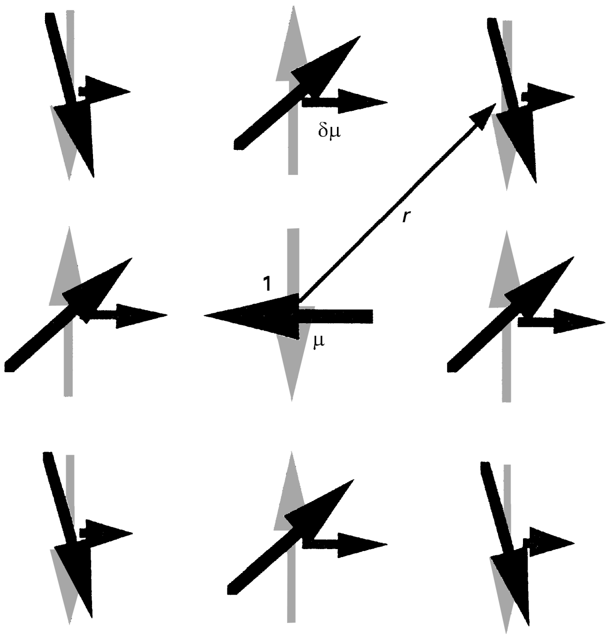

Figure 2 An array of identical dipoles of moment μ distributed on a two-dimensional square lattice, with initially antiparallel orientations of nearest neighbours for lowest energy, shown shaded. If the central dipole marked as **1** flips through 90°, the neighbouring dipoles change their orientations marginally under the influence of the dipolar field of the central dipole, the resulting incremental dipole moments, δμ, being shown by the arrows. The magnitudes of these dipolar reorientations depend on the distance from dipole **1** as r^{-3}. All the individual δμ point in the same direction, and may therefore be summed algebraically. Their orientations do not depend on the precise orientations of the individual dipoles.

1 changing its orientation through a right angle, the neighbouring dipoles undergo reorientations which depend on their distance, with the incremental dipoles δμ shown as arrows. We note that all δμ are oriented parallel and therefore their summation is a simple algebraic one.

The lower limit of integration is defined as $r_1 = (4\pi N/3)^{-1/3}$ which is such that a sphere of radius r_1 contains just one dipole, $4\pi/3\, r_1^3 N = 1$. Integration below r_1 would have no physical meaning, because there can be no contributions to screening below that distance.

Equation (10) is unbounded as $R \to \infty$, but the essential physical requirement is that the integration may not proceed beyond a value of $R = R_s$ for which $\Delta\mu = \mu$, when the dipole in question is completely screened and cannot be "seen" at larger distances. This "dipolar screening radius" R_s is to dipolar screening what λ_D is to particle screening and is defined by

$$R_s = r_1 \exp(\lambda_D^2/l^2) = (4\pi/3)^{-1/3} \exp(\varepsilon kT/\mu^2 N) \quad (11)$$

The numerical expression for the bracketed term in the exponential is

$$\frac{\varepsilon kT}{\mu^2 N} = 4.7\times 10^{21}\,\frac{\varepsilon_r T}{l_{\mathrm{nm}}^2 N} \quad (12)$$

where l_{nm} is the value of dipolar length in nanometres. Fig. 3 gives plots of R_s versus N for a range of parameters $\varepsilon_r T$ and l_{nm}, together with two plots of the

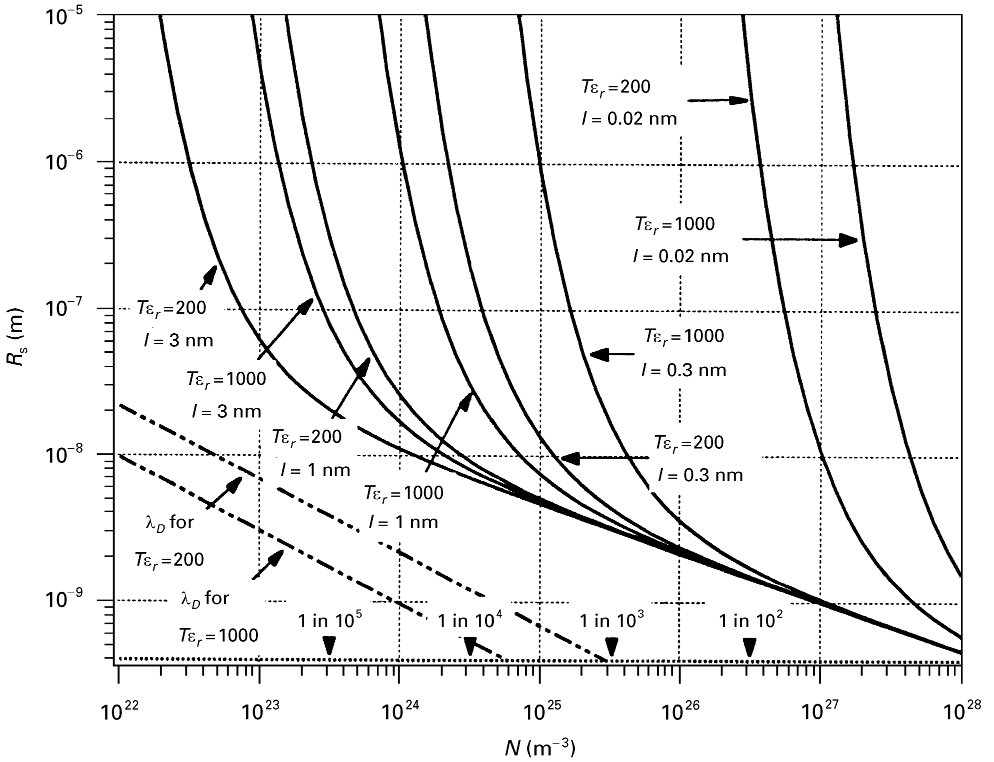

Figure 3 The screening distance, R_s, for dipoles and the Debye screening length, λ_D, for charges as functions of the density, N, of dipoles or charges for typical values of the dipolar length l, and of the product $\varepsilon_r T$. The "lattice" density, which is the maximum possible density corresponding to one dipole or charge per molecule, is taken as $3\times 10^{28}\ \mathrm{m}^{-3}$ and four levels of density are indicated at 1%, 0.1%, 0.01% and 0.001%. Note the rapid rise of R_s with falling N, compared with the much more gradual rise of λ_D.

particle Debye screening radius, λ_D. We note the rapid increase of R_s with N falling below a critical value, by contrast with the much more gradual rise of λ_D.

By analogy with ν defined by Equation (3), we now define the number of dipoles contained within the sphere of radius R_s:

$$\nu_D = (4\pi/3)NR_s^3 = \exp(3\varepsilon kT/\mu^2 N) \qquad (13)$$

which is shown in Fig. 4 for the same conditions as in Fig. 3. The significant point is that, for any given ε, T and l, ν_D rises rapidly below a critical density N_1. This is a consequence of the very steep rise of R_s in Fig. 3 and the conclusion is that dipoles are much less effective in screening other dipoles than are point charges, but dipolar screening is very effective at relatively high densities.

We somewhat arbitrarily define the critical density N_1 as that density for which $\nu_D = 2$, on the basis of the fact that $\nu_D = 1$ evidently corresponds to complete screening, while ν_D rises very rapidly for smaller values of N. With this definition we obtain

$$N_1 = \frac{3\varepsilon kT}{\mu^2 \ln 2} = 2.03 \times 10^{22} \frac{\varepsilon_r T}{l_{nm}^2} \qquad (14)$$

where l_{nm} denotes the value of dipolar length in nanometres and $\varepsilon_r = \varepsilon/\varepsilon_0$ is the relative permittivity. Numerical solutions are shown in Fig. 5 as logarithmic plots of N_1 versus $\varepsilon_r T$, for selected values of l_{nm}. $\varepsilon_r = 10$ may be regarded as typical of most dielectric materials, $\varepsilon_r = 100$ relates to high permittivity materials and ferroelectrics. $l_{nm} = 0.1 - 0.3$ is typical of most molecular dipoles, $l_{nm} = 1$ relates to larger molecules and $l_{nm} = 0.02$ is typical of induced atomic and molecular dipoles.

In our understanding of the phenomenon of screening, the situation in which $\nu_D \gg 1$ corresponds to an unscreened strongly interactive system, where dipoles "see each other" over large distances. Conversely, if $\nu_D \approx 1$ there is no interaction in a strongly screened system and each dipole behaves independently of all others.

We note that $N_1 \propto \varepsilon_r T\, l^{-2}$ so that N_1 falls with rising dipole moment and increases with rising permittivity. The immediate physical significance of this is as follows. The dipoles are going to behave like independent entities if their density N falls above the $N_1(\varepsilon_r T)$ contour, where screening is very effective and will behave as a strongly interacting set if N falls below this contour. The larger ε_r and the smaller l_{nm} the higher the density below which the dipoles behave in an interactive manner, and conversely. Moreover, the interactive behaviour becomes stronger with rising temperature, but it is necessary to bear in mind that in many dipolar systems the dipoles are thermally activated and therefore their effective density is rising with T faster than does $N_1(\varepsilon_r T)$, so that in a given system the effect of a rise of temperature may be to bring about independent behaviour. We shall discuss some examples in the following section.

4. Numerical relations

In the limit of dipolar density of $10^{28}\,m^3$ or higher, such as in polar liquids, any conceivable combination of ε_r and l_{nm} would give non-interacting dipoles,

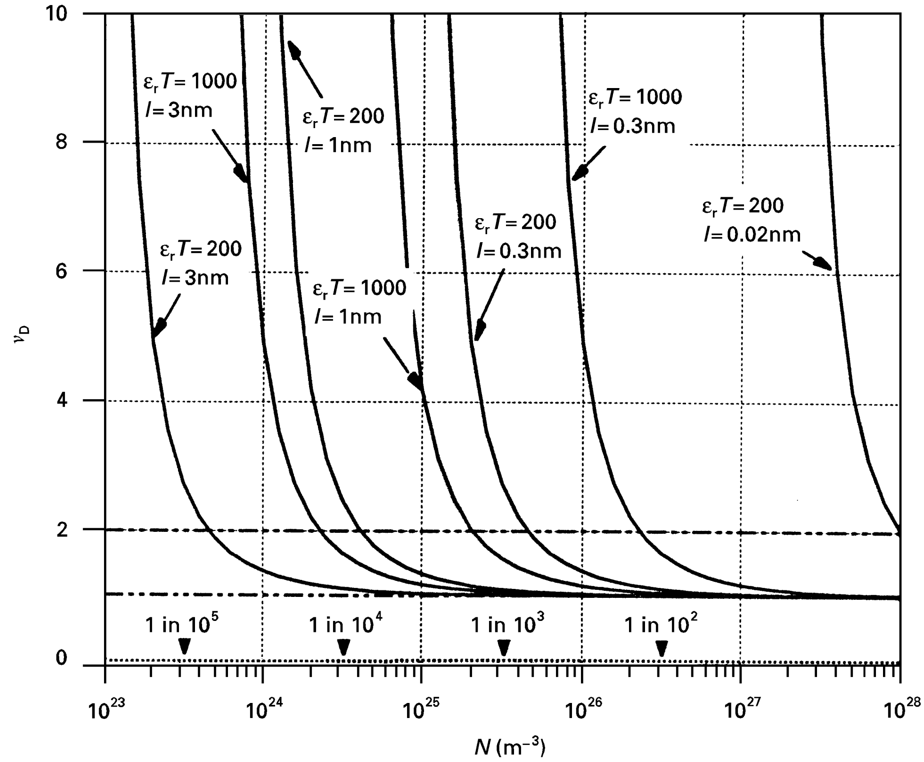

Figure 4 The number, ν_D, of dipoles within a screening sphere of any given dipole as function of dipole density, N. With increasing N, ν_D falls towards 1, implying that there is just one dipole within the screening range, in other words screening is very effective. Once ν_D exceeds the value 2, say, at a density N_1, it increases rapidly with falling N leading to a rapid increase of interactions among the dipoles within a screening distance.

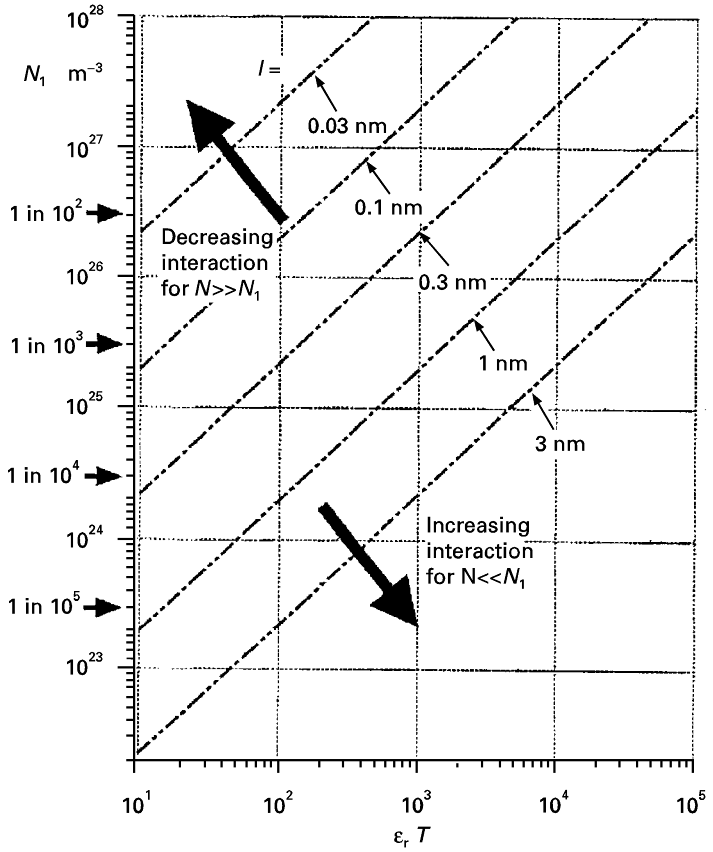

Figure 5 The critical density N_1 given by Equation 14, below which interactions between dipoles become strong and above which they are weak. The density N_1 is shown as function of the product of the temperature T and of the relative permittivity ε_r, with the "length" l_{nm} of the dipole in nanometres as parameter. Marked on the density axis are densities as fractions of the "molecular" density $3 \times 10^{28}\,m^{-3}$. For $N \ll N_1$ dipolar fields interact strongly, individual dipoles are unlikely to follow external fields, thereby reducing their influence on polarization 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 $l_{nm} \approx 0.1$–0.3 is typical of most molecular dipoles, $l_{nm} = 1$ relates to larger molecules and $l_{nm} = 0.03$ is typical of induced atomic and molecular dipoles.

explaining the observed fact that such liquids behave in a near-Debye manner, which might otherwise sound strange in view of the high density.

Even at "dilutions" of the order of 1 part in 10^5, screening is virtually complete except for dipolar lengths $l < 1$–3 nm, and especially so at higher temperatures. Here we recall the result quoted in Fig. 5.2 of Jonscher [6] referred to as DRS, where single-crystal CaF_2 doped with erbium to 1 part in 10^4 and 1 part in 10^5 shows an almost pure Debye response. There the dipole consists of the Er^{3+} ion substituting for a Ca^{2+} ion and an interstitial F^- ion on any one of the nearest vacant sites. Because the dipolar length may be assumed to be of the order of 1 nm, $\varepsilon_r = 6.6$ and the temperature is in excess of 170 K, the density of 1 part in 10^4 is likely to correspond to a non-interactive system, which is consistent with the near-Debye response, while the density of 1 part in 10^5 should correspond to an interactive system deviating from the Debye behaviour, which does not appear to agree with observations. It is possible, of course that the nominal densities are not correct.

There are other experimental results which have never been explained, shown in Fig. 5.40 of DRS and referring to single-crystal β-alumina measured *normal* to its planes of easy conduction where it is behaving as an insulator. In the temperature range 300 K down to 88 K there is a clear loss peak superimposed on a flat background, but between 20 and 50 K there remains only the flat background, while there is no trace of the peak. This would be consistent with the screening model if the reduction of temperature from 80 K to 50 K should take the density of available dipoles outside the screening range, as explained earlier.

One other interesting results may be found in the data of Hofmann *et al.* [7] reproduced also as Fig. 1.1 of Jonscher [8] showing the dielectric response of glycerol over a wide range of frequencies and temperatures. Well-defined, broadened asymmetric loss peaks give way progressively to much flatter response at temperatures below $-80\,^{\circ}$C eventually becoming at $-150\,^{\circ}$C virtually "flat" in the frequency range considered. This can be understood in terms of the numbers of available dipoles falling below N_1 with falling temperature. The same results also show the effect of the *rate of response* of dipoles – at higher frequencies the numbers of dipoles responding is smaller than at lower frequencies, as discussed in Jonscher [8]. We do not know of any other explanation of the observed behaviour.

5. Effect of screening on dipolar dynamics

We now consider the central point of the present discussion – the effect of screening on dipolar relaxation. It is evident that the case of complete screening must correspond to Debye relaxation, because there is no interaction between any of the dipoles and the only process determining the relaxation is the probability of a transition between the allowed orientations in Fig. 1. As this involves overcoming an energy barrier, the relaxation time $\tau = 1/\omega_p$ is constant for all dipoles with the same barrier and the result is a Debye relaxation.

Much more interesting is the behaviour of unscreened systems in which dipoles interact sufficiently strongly to assume lowest energy ordering over "domains" the size of which cannot be predicted in general, but the important point is that the dipole moment of the complete domain is much lower than the algebraic sum of the constituent dipoles. Now the application of an external field to the system causes orientation of *some* dipoles, typically for $E = 10^3\,\mathrm{V\,m^{-1}}$, $l = 1\,\mathrm{nm}$, $T = 300\,\mathrm{K}$, the fraction $qE\,l/kT = 4 \times 10^{-5}$. The result of dipole–dipole interactions with incomplete screening extending over many dipoles is that the system becomes "rigid" in the sense that the fields generated by the interacting dipoles are stronger than externally applied fields. Once the ordering sets in, the energy of individual domains becomes sufficiently low for most available dipoles to become involved. This means that the number of dipoles available for re-orientation in an external field is much smaller than would be the case in the absence of ordering and the polarizability of the system is correspondingly reduced, having been low to begin with in view of the low number of dipoles.

The conclusion of this analysis is that organized dipolar domains in a system with weak dipolar screening change drastically the manner of polarization by enabling reversals of polarization to take place with very low energy loss. This is the requirement for the occurrence of the ubiquitous "flat" loss [8–10]. We have to ask why a *finite*, albeit low loss is incurred with falling density of dipolar species – why the loss should not descend down to levels below the detection limit. Here we note that the falling level of N implies increasing organization into antiferroelectric domains, and these must constitute a finite and irreducible loss process.

Dipolar screening has a *dynamic* influence on dipolar orientations, by *delaying* the response of individual dipoles to external fields. Given a sufficiently long time of action of a field, the dipoles are bound to achieve a thermodynamic equilibrium according to Equations 7 and 8. Alternating fields are being screened more effectively at higher than at lower frequencies.

In conclusion, we believe that the mechanism of dipolar screening is capable of explaining a number of features of dielectric relaxation in low-loss systems which are not, at present, understandable in terms of existing theories. A further application of this process will be given in a separate publication on the so-called "trans-universal" loss [11].

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