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Low-frequency dispersion in volume and interfacial situations

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The ubiquitous and little-understood phenomenon of low-frequency dispersion (LFD) is described and the experimental evidence for it is summarized for a variety of dielectric and semiconducting systems. Both frequency- and time-domain behaviour are reviewed and it is pointed out that very high charge densities are being stored at low frequencies. The connection between LFD and electrochemical reactions is emphasized. The physical conditions under which LFD can be seen are discussed with particular emphasis on the distinction between interfacial and volume processes. Earlier interpretations of LFD-like phenomena in terms of Maxwell–Wagner processes and fractal geometry of contacts are briefly discussed and found to be insufficient to account for the observed facts. It is concluded that there is likely to be more than one physical or physico-chemical cause giving rise to the variety of LFD phenomena observed in nature but their common feature must be a frequency-independent ratio of loss to polarization. We define an "energy criterion" which gives a physical basis for the interpretation of power-law responses and on this basis we propose a new electrochemical model of very general applicability giving the correct dynamic response and having the advantage of not requiring enormous electric fields to account for the very high charge storage observed. Further critical experimental studies are required to elucidate the remaining questions.

1. Introduction

The purpose of the present paper is to bring together and review critically the experimental evidence for a widely occurring, though poorly recognized, form of dielectric behaviour which represents a natural limiting case of the "universal dielectric response" [1] and is referred to as *low-frequency dispersion* (LFD). These phenomena were discovered in the course of a wide-ranging study of dielectric responses of solids undertaken in the former Chelsea Dielectrics Group which is currently being continued in this laboratory. They are characterized by a strongly dispersive behaviour of the real and imaginary components of the effective complex susceptibility $\tilde{X}(\omega)$, expressed here in terms of the complex capacitance $\tilde{C}(\omega) = C'(\omega) - iC''(\omega)$ so as not to prejudge the question of whether one is dealing with interfacial or volume effects

$$\begin{aligned}\tilde{X}(\omega) &= \tilde{C}(\omega) - C_\infty = X'(\omega) - iX''(\omega)\\ &= A(i\omega)^{n-1}\end{aligned} \tag{1}$$

where C_∞ is the value of $C'(\omega)$ at a sufficiently high frequency for the loss processes in question to have become negligible. A is a constant and the exponent n is small compared with unity. The implication of this empirical relation is that the real and imaginary components of $\tilde{X}(\omega)$ *are the same functions of frequency*, i.e. they maintain a constant frequency-independent ratio

$$\begin{aligned}X''(\omega)/X'(\omega) &= C''(\omega)/[C'(\omega) - C_\infty]\\ &= \cot(n\pi/2)\end{aligned} \tag{2}$$

which is the general property of the so-called "universal dielectric relation" [1] and which, in the present case, implies that the loss is much larger than the real part, $X''(\omega) \gg X'(\omega)$, i.e. the system is highly lossy.

An immediate consequence of the power law of Equation 1 in the frequency domain (FD) is the time-domain (TD) response to a step-function voltage in the charging and discharging modes which is the Fourier transform of Equation 1 and represents another fractional power law in time:

$$i(t) \propto t^{-n} \tag{3}$$

which, in the case of small values of n arising in LFD, implies a *very slowly* time-varying current which may be described as "quasi-d.c." [2]. It is most important to note the fundamental difference between LFD and true direct current (d.c.) transport, which consists in the fact that d.c. does not involve any storage of charge in the system, while LFD does. The implication of this is that a d.c.-conducting system must give a truly time-independent step charging current in response to step-voltage excitation but it *cannot give any discharge current.* A corresponding illustration of this

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may also be seen in the frequency domain, where d.c. response gives a constant $X'(\omega)$ and $C'(\omega)$ towards low frequencies, while LFD shows a massive rise, sometimes by several orders of magnitude. The frequency- and time-domain behaviour of LFD systems is shown schematically in Fig. 1 which includes the highly lossy LFD response as well as the more normal low-loss high-frequency universal behaviour for which the exponent n lies closer to unity.

With the benefit of hindsight it is possible to conclude that LFD-like phenomena had been seen in the past, although they were evidently not recognized as a distinctive class in its own right. As a very characteristic example, we shall quote the well-known review of the dielectric properties of a wide range of materials by Westphal and Sils [3] in which data relating to higher temperatures and low frequencies clearly show a rise of $C'(\omega)$ and of $C''(\omega)$. The significant point here is that, in common with widely accepted custom, $C'(\omega)$ is plotted *linearly* against logarithm of frequency, while $C''(\omega)$ is plotted *logarithmically*. This method of presentation virtually ensures that the correct power law, Equation 1 with its vital consequence Equation 2, cannot be gleaned from experimental data and this is undoubtedly the reason why LFD behaviour had not been spotted sooner, simply for lack of convincing experimental information. This has led to the physically implausible interpretations in terms of Maxwell–Wagner phenomena which will be discussed in a later section.

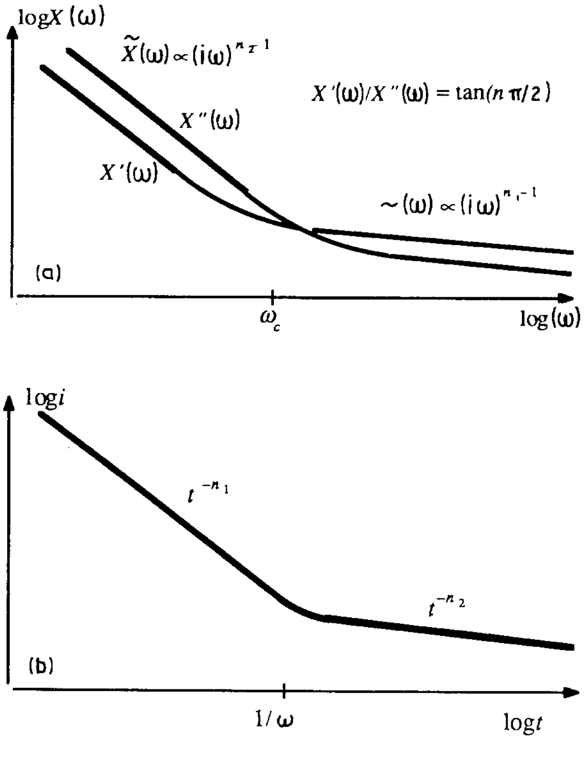


Figure 1 (a) A schematic presentation of the frequency-domain behaviour of a system showing LFD behaviour with the characteristic parallellism in the logarithmic plots of the real and imaginary components of the complex capacitance, $C'(\omega)$ and $C''(\omega)$, respectively. The high-frequency region corresponds to the normal low-loss behaviour of dielectrics; the low-frequency dispersive region is the LFD phenomenon. (b) The corresponding time–domain behaviour, with the long-time almost constant current corresponding to the low-frequency dispersive part of diagram (a).

One consequence of Equation 1 is that the alternating current (a.c.) conductance has a weak but discernible frequency dependence

$$G(\omega) \propto \omega^{n} \qquad (4)$$

which also underlines the close relationship with d.c. processes, for which $G = \text{const.}$

The importance of the slowly decaying charging and discharging currents, which are well documented experimentally, lies in the apparent divergence of the total charge given by the integral

$$Q = \int_0^\infty i(t)\,\mathrm{d}t \qquad (5)$$

This type of behaviour is very similar to that found in primary or secondary batteries, where large quantities of charge are stored with relatively low voltage and no need for a high electric field, in complete contrast with the conventional electrostatic mode. This aspect will be discussed below.

The experimental evidence for LFD comes primarily from FD measurements, although some TD data are also available. This raises the question of the validity of the Fourier transformation between FD and TD in rather non-linear systems, but our experience suggests that TD–FD transformation remains valid within reasonable limits even in cases of evident non-linearity.

Experimental evidence shows clearly that LFD phenomena are seen in three types of situations, shown schematically in Fig. 2:

(a) volume transport;
(b) transport *across* interfaces;
(c) transport *along* interfaces, e.g. on humid surfaces.

Our experience shows that the FD and TD characteristics of these three types are sufficiently similar to make it difficult to distinguish between the first two, while there is at least geometrically no doubt when the third one applies. Thus we may regard case (c) as not requiring further detailed comments, except that care should be taken to avoid volume conduction shunting the presumed surface behaviour by the use of samples as thin as possible.

Processes (a) and (b) have to be distinguished on the basis of further criteria to determine which of them applies in any given situation. One experimental test which could provide the answer is to vary the interface with the same bulk material. This is the test which we discuss below for the case of Schottky barriers *versus* p-n junctions, where the answer is unequivocal that it is the interface that gives the LFD behaviour. Another test is to actually measure the potential distribution along the thickness of the sample, something that is seldom easy to do and which we have applied in the case of the stack of filter papers described below where the answer was unequivocally that the behaviour was dominated by volume processes. One further test may be applied consisting in the variation of the thickness of the bulk material under study, but to be conclusive this variation would need to be over at least an order of magnitude or so, and this may not usually be feasible, since in many cases it would be difficult to

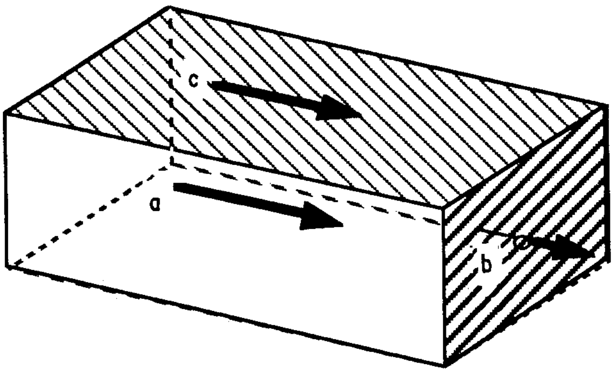


Figure 2 A schematic representation of the principal LFD processes, respectively, (a) in the volume, (b) across an interface and (c) in the plane of an interface or surface.

assert that the thickest and thinnest samples were of the same composition and structure. Thus, in many practical cases it is not easy to distinguish experimentally between cases (a) and (b) above.

It is important to stress that LFD processes involve enormous quantities of charge being stored at low frequencies at relatively very low voltages. The earlier "electrostatic" models such as Maxwell–Wagner involve therefore very high fields and this necessitates the introduction of the concept of capacitive structures of atomic thicknesses, while not being capable at all of explaining volume LFD responses. Likewise, the extremely long slowly time-dependent charging and discharging currents are compatible with electrochemical "battery action" and this is explored later in this paper.

We recall the elementary principle governing the series connections of "universal" lossy capacitors, as shown in Fig. 3a where we distinguish the "bulk" material, a "barrier" or space-charge region, and an interfacial sheet at a metal electrode. Any one of these may be strongly dispersive. The space-charge barrier region would clearly be applicable in an electronic semiconductor, Fig. 3b, while in ionic systems its presence is less likely and, in any case, its dimensions would be on the atomic scale in view of the very high ionic densities in such systems, leading to very short screening lengths.

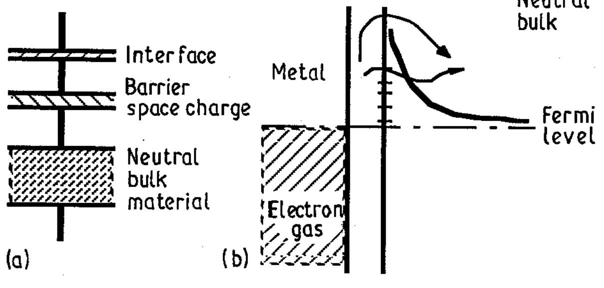


Figure 3 (a) A schematic representation of the series combination of a "bulk" region, a space-charge region and an "active" interfacial sheet region, each represented by a "universal" lossy capacitor. The magnitude of the bulk capacitor is small in comparison with the space-charge region capacitor, on account of their relative geometrical sizes. (b) The application of this principle to the case of a Schottky barrier on n-type semiconductor, showing the injection of electrons from the interfacial sheet into the space-charge barrier, effectively constituting a leakage current whose rate processes are determined by the interface.

If the entire system shows LFD behaviour, then there are the following possibilities:

(i) The volume itself is strongly dispersive, and its impedance dominates the series combination, i.e. its admittance is smaller than that of the other elements,

(ii) The volume is effectively conducting and does not possess any dielectric "signature" of its own, so that it may be represented by a d.c. conductance G_0. If this is sufficiently *large* then the contacts dominate the behaviour and two situations may arise:

(ii.1) The contacts *inject* and *remove* charge carriers, and the rates of injection and removal limit the response of the system as a whole. An example of this is the Schottky barrier with LFD.

(ii.2) The contacts are *blocking* and their frequency or time dependence is determined, for example, by their geometry or roughness.

2. Outline of the problem

In the past, strongly rising capacitance towards low frequencies has been loosely associated with the so-called Maxwell–Wagner behaviour, which was regarded as essentially a barrier capacitive effect in series with a resistance, the R–C model which should have an ideal Debye response in the frequency domain or its time-domain equivalent of exponential response to step-function excitation. More recently, the growing awareness of the ubiquity of the "universal" power-law Equations 1 and 3 has led some workers to seriously consider more sophisticated models.

We have proposed [4] that the unique slowly time-varying power law relationship in time and its frequency-domain equivalent are to be associated with electrochemical activity. At the present time, however, this proposition can only be regarded as reasonably well justified in the case of interfacial phenomena, while its extrapolation to volume situations remains conjectural. There are, moreover, alternative approaches to the interpretation of LFD, some of which are based on considerations of the effects of fractal contact geometries and will be reviewed later in this paper. The study of the time-domain response is fundamental to the understanding of systems showing LFD behaviour, since in many cases the response is non-linear in the amplitude of the applied bias and the applicability of the frequency-domain approach may be called into question [1].

3. Review of experimental evidence

3.1. Schottky barriers

The application of dielectric spectroscopic techniques to the study of delayed electronic transitions in semiconductors and semi-insulators has led to the recognition of a number of patterns of behaviour, some of which may be associated with the trapping and emission of electrons from deep levels in the forbidden gap

[5–8]. However, the general point has to be made that no LFD has ever been observed in any of the many p-n junctions investigated in our Chelsea Dielectrics Group, while Schottky barriers always show LFD at sufficiently low frequencies and high temperatures; an example of this is shown in Fig. 4. This is true regardless of whether we are dealing with elemental semiconductors such as silicon or compounds such as gallium arsenide. Furthermore, in the case of Schottky barriers there is evidence of LFD behaviour being strongly influenced by even relatively small external biases, with transitions from LFD to the closely related phenomenon of negative capacitance [9] on the application of a forward bias.

The inescapable conclusion from this well-established experimental evidence is that the cause of LFD in semiconductor systems is the presence of metal–semiconductor interfaces in Schottkys and their evident absence in p-n junctions. It is relevant to point out that although we are dealing here with evidently electronic semiconductors, the observed LFD phenomena need not necessarily be electronic in nature, since the interfacial layers in question are compound oxides of the metals and semiconductors involved and their condition may be influenced by the biasing of the system.

In terms of our model of Fig. 3b, the "bulk" region in a Schottky diode may be assumed to be purely resistive and the system consists, therefore, of the space-charge region proper, which is the same as in a p-n junction, and of the interfacial region which may be regarded as a two-dimensional "sheet" in series with the barrier. Now, according to the principles set out above, the only way in which the interfacial sheet can dominate the LFD behaviour is by sending charge carriers generated in it *across the space-charge region.* In this way, and in this way only, can the observed LFD behaviour in Schottky diodes be modelled, by assuming that the LFD action is dominated by the generation/recombination rate at the interface while the space-charge region transmits without constraint any carriers injected from the interface and therefore acts simply as a conductor or a very lossy capacitor in series with the interface. The effect of an external bias is then seen as being due to a change in the electrochemical nature of the interface bringing with it a variation of the rate of generation of electrons at the interface and their injection into the space-charge region.

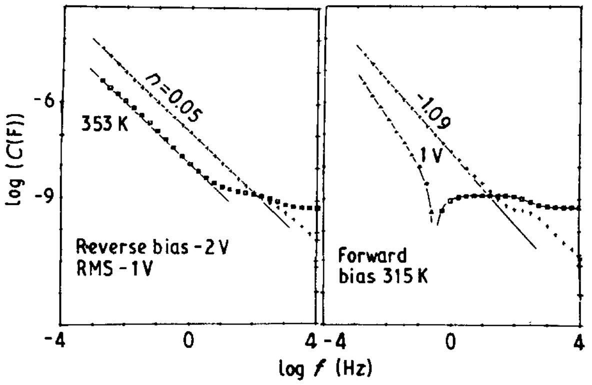


Figure 4 Examples of LFD and the closely related negative capacitance behaviour in GaAs Schottky diodes [7] at elevated temperatures under the action of small reverse and forward biases, respectively. Diagram (a) for 353 K, 0.2 V reverse bias, diagram (b) for 315 K, 1 V forward bias. Positive capacitance is plotted as squares, the absolute values of negative capacitance are plotted as triangles, and the imaginary (loss) component as crosses. Negative capacitance corresponds to small negative values of n in Equation 1 and the slope in (b) is steeper than -1.

3.2. Surface conduction on humid insulators [10]

While the subject of surface conduction on humid insulators has attracted a considerable amount of interest over many years, not least because of its evident technological significance in the context of outdoor electrical insulation, the emphasis appears to have been exclusively on the steady state, direct-current behaviour.

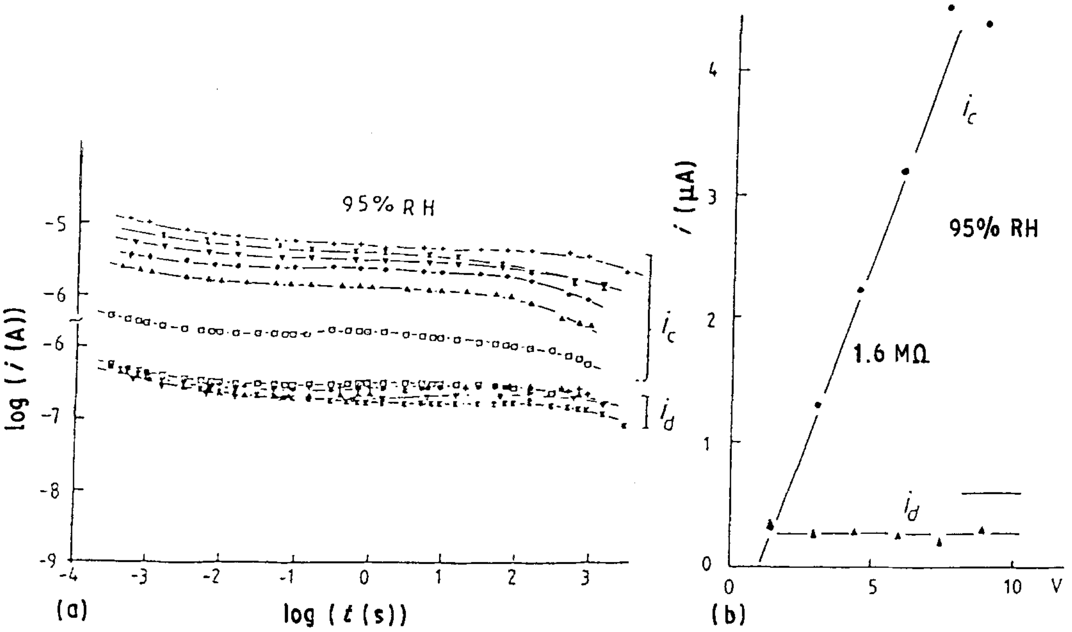
Our own extensive studies have explored for the first time the frequency- and time-domain response of surface conduction on humid insulators such as sand [1], mica [11], glass [12] and mica paper [13]. They have shown, among other features, that LFD is the dominant behaviour at sufficiently high humidities. The time-domain response is particularly instructive since, as is seen in Fig. 5, it shows clearly the difference between the dependence of the charging and discharging currents on the amplitude of the voltage step, showing that the system may be represented by a battery and a resistor in series, confirming the electrochemical nature of the processes in question. Certainly, the existence of the discharge current is totally inconsistent with any form of direct-current process.

It was also shown [12] that surface resistance $1/G$ does not scale linearly with the aspect ratio s/l of the inter-electrode spacing s and their length l, as would be the case with uniform sheet conduction, but goes exponentially with s/l, while its magnitude is *exponential* in the relative humidity, showing clearly that conduction occurs by some form of percolation along preferred paths on the humid surface.

A special case of humid dielectric medium is represented by soil and generally clays, sands, shales and other granular constituents of the top of the earth's crust. Their dielectric properties are being studied with the object of prospecting for water, oil and other minerals and we will quote one recent paper by Olhoeft [14] as representative of the type where a wide range of frequencies is being used to determine the processes in question. A particularly striking result quoted by Olhoeft is the independence of frequency of the specific resistivity of soils up to MHz frequencies. Expressing the resistivity in terms of the components of the complex capacitance this implies that

$$R(\omega) = \frac{\omega C''(\omega)}{[\omega C'(\omega)]^2 + [\omega C''(\omega)]^2} = \text{const} \qquad (6)$$

We note that this condition can only be satisfied if $\omega C'(\omega) = \text{const}$ and $\omega C''(\omega) = \text{const}$ and this implies that $C'(\omega) \propto C''(\omega) \propto 1/\omega$, which is approximately our condition for LFD. However, Olhoeft [15]



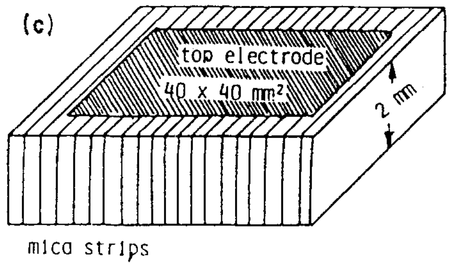


Figure 5 (a) Time-domain response of surface conduction on humid mica at 95% relative humidity (RH), showing the charging currents, i_c and discharging currents, i_d, for a range of step-voltage amplitudes as follows: □ 1.5, △ 3.0, ◇ 4.5, ▽ 6.0, × 7.5 and + 9.0 Volts. The individual sets of i_c and i_d data are displaced vertically for clarity, otherwise the lowest voltage data would overlap almost completely. (b) The values of i_c and i_d at 0.1 is plotted linearly against the corresponding voltage step amplitude for 95% RH showing the saturation of i_d and the voltage dependence of i_c corresponding to the resistance indicated and to an intercept V_0 on the voltage axis. (c) Schematic representation of the form of the sample, consisting of a "raft" of mica strips with evaporated aluminium electrodes at the opposite faces. (From reference [11])

points out that the behaviour of resistance, especially at low frequencies, is critically influenced by contaminants in the water permeating the materials in question, and particularly by the reactivity of these contaminants.

3.3. Biological materials

Biological materials, whether vegetable or animal, represent complex media with a very pronounced cellular structure, the interiors of the cells being filled with an ionically conducting liquid. Because of their high content of aqueous liquids, they represent a borderline case from our point of view as far as LFD processes in solids are concerned but a brief mention of them is indicated. Dielectric measurements on biological materials have been widely reported [16, 17] and they show the phenomena of LFD, where these have been correctly recognized as such and not mistaken for d.c. conduction or dismissed as Maxwell–Wagner processes. Recently, Hill *et al.* [18] have published measurements of the dielectric response of leaves covering the prodigious range of eleven decades 10^{-2}–10^9 Hz showing a general trend of slope -0.75 with some fine structure which is identified with separate processes in the interiors of the cells and in the membranes between them. In particular, the low-frequency part of the response is said to be "diffusion-like", while in fact it has a value of the exponent $n = 0.27$ which is within our LFD range.

3.4. Volume conduction in an LFD medium

There are very many examples of insulating materials showing LFD behaviour at sufficiently high temperatures; in fact, this appears to be the rule rather than an exception [1, 3]. For example, very clear LFD behaviour was reported in a semiconducting glass at sufficiently high temperatures [19] and also in mica normal to the cleavage planes [20]. We have pointed out [20] that in all cases in which a strong LFD region joins on to a higher-frequency low-dispersive and therefore low-loss range which is consistent with the geometrical dimensions of the volume of the sample, the only cause of LFD can be volume behaviour, since the contacts could not suddenly dominate the volume impedance. This is different from the classical case of a Schottky barrier in series with a highly conductive bulk region, since there the impedance of the bulk is low despite its having a low capacitance.

The behaviour of humid zeolites [21, 22] shows all the characteristic features of LFD in both time and frequency domains and the question may be raised whether they should be regarded as volume or surface media, given that on the molecular level zeolites consists of a regular array of interconnected cavities. We believe that on the macroscopic level they may be regarded as similar to other porous bulk materials such as humid cellulose or sand.

An experiment performed [23] to elucidate the interface-*versus*-volume nature of conduction in humid cellulose giving LFD, has shown clearly that the behaviour is distributed throughout the volume of the material, with the end electrode interfaces playing a negligible role in the determination of the response.

To the best of our present knowledge of the subject, we are not aware of any firmly established example of bulk *electronic* LFD in any context, although it is possible that the presence of incipient LFD in semi-insulating gallium arsenide [5] may be consistent with electronic processes.

4. Tentative interpretations

We conclude, first of all, that a remarkably wide range of physico-chemical situations, volume as well as interfacial, lead to similar frequency- and time-domain behaviour which we refer to as LFD. This feature alone implies that, however desirable it would be to have a very general model to explain LFD phenomena, it may be necessary to accept several more specialized models, since no single model is likely to be applicable across the entire spectrum of situations, interfacial ones as well as volume. In selecting the preferred model it is necessary to bear in mind its plausibility and, in the final analysis, its agreement with experimental data.

A special approach to the same question in the case of solid and liquid electrolytes considers the effect of the *roughness* of the interface between the material and the electrode. In these systems the "dielectric" is often a superionic conductor which may or may not have an inherent frequency dependence of its own, but which, for the present purpose involving low-frequency electrode-dominated behaviour, may be represented by a pure d.c. conductance.

The rate-limitation is assumed to take place at the metal interface which is taken to be blocking, so that no transfer of ions occurs there. There exists a rich literature on the analytical modelling of this type of system [24, 25], which amounts in effect to the calculation of the impedance of a fractal or non-fractal distributed network, of which the limiting example is the semi-infinite uniform distributed R–C line which is the archetype of the Warburg impedance with $n = \frac{1}{2}$. Depending on the choice of the geometry of the profile of the electrode/electrolyte interface, it is possible to generate at will any value of the exponent n, a freedom which may constitute an embarrassment since it increases the arbitrariness of the model. More significantly, however, critical experiments by Bates *et al.* [26] who have exposed metallic electrodes of carefully assessed roughness to liquid electrolytes do give a definite correlation between the roughness and the exponent. This confirms a wide body of "received widsom" that the exponent n is structure-sensitive, but in our opinion the question is still open and this is not necessarily *the entire answer* to the frequency dependence of the interfacial processes. It may be noted, of course, that the response quoted earlier of humid granular and porous media may also be affected by the same considerations.

The position becomes more complicated in the case where the "volume" is an insulating or semi-insulating ionic or molecular solid in which the concept of injection of ionic or other charge carriers is not easily envisaged on physical grounds. It is known that in some insulating materials certain ions, especially small ones such as protons, have a relatively high mobility, but these are exceptional situations which are not readily generalized. The most likely situation where the interface may become the rate-limiting process is therefore one in which the "volume" of the material possesses a sufficiently high conductivity that it does not represent any serious limitation to transport. Since, however, most examples of LFD in "insulating" materials refer to relatively high temperatures, it is difficult to be certain in any given case that the volume may have become sufficiently conducting for the interfacial process to become the dominant rate-limiting step.

On the basis of currently available evidence and of the present understanding of the subject, our conclusion must be that the observed LFD phenomena may be either bulk or interfacial and, in the latter case, may be influenced by the geometry of the interface or by its electrochemical behaviour.

This brings us to the question of the theoretical interpretation of the observed LFD characteristics, in all three cases (a), (b) and (c) enumerated above. We have already mentioned the Maxwell–Wagner model for the interfacial transport (b) and at this stage it will be sufficient to state that we regard this as a highly arbitrary model in which there is little evidence that the parameters that have to be introduced are compatible with the physical nature of the sample. Moreover, since the frequency dependence is not that of a Debye model, which is what a simple Maxwell–Wagner model is, but generally follows the fractional power law with small values of n, then one has to introduce a more or less arbitrary distribution of parallel R–C circuits which suffers from the common deficiency of all such "distributionist" interpretations that it does not *explain* the reasons for the general applicability of the fractional power laws [1].

True volume LFD has been treated theoretically by Dissado and Hill [2] and it is perhaps too early to be sure to what extent their theory is applicable in particular situations. However, this model implies that the charge stored in the system must result in a correspondingly high interfacial field and this is a common difficulty of all models based on electrostatic charge and energy storage. We do not know of any theoretical treatment capable of explaining the transport *in the plane* of the interface, case (c) above.

5. The energy criterion

We propose a simpler and intuitively more readily acceptable model which makes use of the physical significance of Equation 2 which is that [1]

$$\frac{\text{energy lost per radian}}{\text{energy stored in the system}} = \cot(n\pi/2) \quad (7)$$

We now propose that *if it were true* that for every reversal of *microscopic* polarization, be it a dipolar or a charge carrier process, the ratio

$$\frac{\text{energy lost in the reversal of every } \textit{microscopic} \text{ process}}{\text{energy stored in every } \textit{microscopic} \text{ process}} = \text{const} \qquad (8)$$

independently of the *rate* of this reversal, then the same would be true also of the *macroscopic* situation

$$\frac{\text{energy lost in the reversal of } \textit{macroscopic} \text{ polarization}}{\text{energy stored in } \textit{macroscopic} \text{ polarization}} = \text{const} \qquad (9)$$

again independently of the rate of reversals. We refer to this relationship as the energy criterion.

Now it is evident [1] that any physical mechanism which gives this rate-independent loss per reversal necessarily fulfils the conditions for the applicability of the universal relation of Equation 1 in view of the Kramers–Kronig relations. One specific model proposed [1] is the so-called "screened hopping model" which is very likely to be applicable in relatively low-loss materials, but there may be other possible models satisfying the same condition. Here we may suggest one such alternative model which may be applicable to LFD situations with their undoubted relation to electrochemical processes, as exemplified by the very slowly time-dependent charging and discharging currents and the massive charge accumulation implicit in the frequency-domain LFD behaviour.

5.1. The electrochemical model

We have suggested [3] that the electrochemical nature of the LFD phenomena may be approached in terms of charge storage by electrochemical as distinct from electrostatic means, which may be expressed schematically by the symbolic chemical reaction

$$A^+ + B^- \leftrightarrow AB \qquad (10)$$

where either the formation or the dissociation of the neutral compound AB dissipates energy irreversibly. Assume that we have a system in which the A ions are moving past the B ions and in the process are undergoing the reaction 10 as represented schematically in Fig. 6 which also shows the directions of the resultant ionic dipoles. Assuming that the relative positions of the two ions are reversed in every cycle, it is evident that every reversal is accompanied by the dissipation of the same amount of energy. While a more detailed analysis remains to be performed, it is intuitively evident that the energy loss arising from the formation of the compound AB may be much larger than the dipolar energy stored in the dissociated system, and this would explain the LFD nature of the process. In this respect the position is quite different from the process of screened hopping which applies to lower loss materials.

It is possible to envisage this process taking place uniformly throughout a given volume, or on a conducting surface, but its efficiency would be enhanced by the constriction of current flow to discrete filaments in the volume or on the surface. We have quoted experimental evidence that the process of conduction on humid surfaces proceeds on just such filamentary paths [12]. While we have no firm theory of such behaviour in two dimensions, the Dissado–Hill theory of volume LFD [2] may be said to involve the concept of filamentary transport, since it refers to preferred paths along which charge carriers are moving. It is a simple extension of this argument to propose that all volume and surface interfacial processes are filamentary in nature and that such situations *necessarily* lead to fractional power laws in frequency and in time. In addition, surface transport also shows the breakdown of ordinary geometrical scaling laws, which may suggest spatial *fractal* properties [24], but our understanding of this aspect is insufficiently advanced for a more detailed analysis to be developed at the present time.

Whatever may be said of the volume and surface LFD processes, the question of interfacial LFD poses a similarly difficult problem for which we do not have at present any definitive theoretical explanation. It is possible to envisage an extension of the argument given above to this case, since electrochemical phenomena are certainly involved. Intuitively, one would approach the time-domain response in terms of an *almost* time-independent current, suggesting a gradual production of a counter-electromotive force, which is compatible with the concept of an electrochemical cell

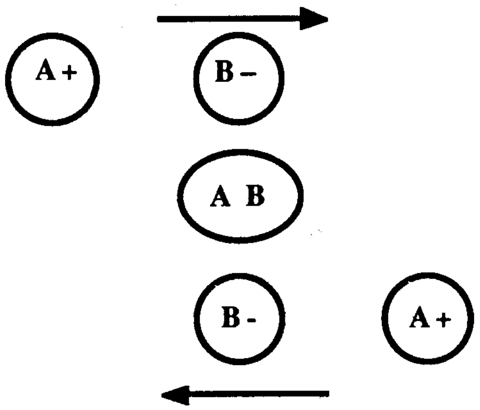


Figure 6 Schematic representation of an electrochemical reaction $A^+ + B^- \Leftrightarrow AB$ resulting in the formation of a neutral compound from two oppositely charged ions. This reaction stores charge and also leads to the dissipation of energy on either the dissociation or the formation of the compound. Either way, there is a constant energy loss per reversal of the microscopic dipole, with the proviso that this energy loss may be appreciable in comparison with the polarization energy, leading to strongly dispersive LFD with small exponent *n*.

reaching its fully charged state. We note, moreover, that in order to explain LFD behaviour in the time domain it is not necessary to establish the *precise* form of time dependence, so long as it is sufficiently slowly decreasing with time; the frequency domain transform is not very sensitive to the exact form of this time-dependence.

5.2. LFD and negative capacitance phenomena

We have mentioned in connection with the Schottky diode behaviour that the negative capacitance observed there is closely related to the LFD processes in that both correspond in the time domain to slowly time-varying polarization currents. We have also seen negative capacitances in surface conductance on humid insulator samples of relatively long and narrow geometry [12]. The principal difference, as pointed out in [9] is that LFD corresponds to a slowly *falling* charging current, while negative capacitance is the consequence of a slowly *rising* current over an interval of time. This statement simply spells out the mathematical requirement for obtaining a negative capacitance in the frequency domain; it does not necessarily provide an explanation of the physical processes leading to this behaviour. However, it may help to focus attention on the relevant aspects of the problem and it may be easier to think of the nature of the time-domain phenomena than of the frequency-domain response.

The important element is the recognition of the fact that the phenomenon of negative capacitance requires a period of rising polarization current which follows on a period of falling current, implying that there is a temporal evolution of some processes which are not dominant in the early stages of the charging operation and become dominant only later. Thus, whatever theory may be developed for this purpose must necessarily involve some such temporal evolution of properties, e.g. changing transparency of some barrier region or conductivity of a volume region or the variation of some relevant reaction rate.

6. Conclusions

We have presented a broad outline of the experimental features of the little-understood phenomenon of LFD as seen in various contexts, showing both frequency-domain and time-domain results, where the latter are available. We stress the fact that LFD constitutes a well-defined limiting form of the "universal" dielectric relation, with very small values of the exponent n and correspondingly high losses and massively large capacitances at low frequencies.

A broad division of LFD phenomena is established into (a) volume transport, (b) transport *across* interfaces and (c) transport *parallel* to interfaces and it is shown that all three obey substantially similar laws of frequency and time dependence. Criteria are established for the dominance of any one of the three categories in any particular situation. It may be difficult, however, to reach definitive conclusions between (a) and (b) without further experimental evidence such as potential probing along the distance between the electrodes, which may not always be easily accomplished.

We have proposed a novel approach to the interpretation involving the concept of a frequency-independent energy loss per reversal of the microscopic dipole moment. We propose a model which answers the $X''(\omega)/X'(\omega)$ ratios found in LFD as well as taking account of the evident electrochemical character of at least some of the observed phenomena. This model may be of very general applicability in volume and interfacial transport, and in the latter case parallel as well as normal to the interface.

Further work is necessary under well-designed experimental conditions to resolve the various remaining questions in particular cases. We have to admit the possibility that other mechanisms may be responsible but the far-reaching similarities in the behaviour of apparently very different systems suggest that the fundamental physical "energy criterion" model of constant-loss-per-reversal is applicable to all LFD phenomena. Any model which may be shown to satisfy this energy criterion necessarily gives the correct dynamic laws of behaviour without it being necessary to derive these laws explicitly.

In the intervening time since the submission of the manuscript certain new developments have occurred. Detailed information has been obtained on the behaviour of humid surfaces showing that the "contact" impedance has no visible effect on the behaviour and that the LFD processes dominating at low frequencies are little dependent on the nature of the metallic contact to the surface. This means that the surface LFD is dominated by the surface *between* the electrodes and not the electrodes themselves (N. Bano and A. K. Jonscher, to be published).

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