

An electrochemical model of low-frequency dispersion

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The widely observed phenomenon of low-frequency dispersion is interpreted in terms of an electrochemical process in which ionic charge carriers migrating under the action of an external field combine to form neutral molecules, thereby eliminating charges which would be necessary to sustain the very high capacitances at low frequencies. Both charging and discharging currents are almost independent of time with the discharge currents consistently lower than the charging currents. The neutral molecules provide a reservoir of charge and of energy which become released on discharging the system after step-function charging, most of the charge and energy being dissipated in what is a highly lossy system. The frequency-domain response is then interpreted using the new concept of “energy criterion” which is particularly suited to the analysis of fractional power-law dependence on frequency. This provides a self-consistent and realistic theory of low-frequency dispersion and enables the connection to be made between time and frequency-domain responses, despite the fact that the strong non-linearity of the response makes the Fourier transformation of limited usefulness.

1. Introduction

Low frequency dispersion (LFD) is a form of dielectric response found widely at low frequencies in materials in which the polarization response is dominated by slowly mobile electronic or ionic charge carriers [1, 2]. Extensive experimental evidence has become available recently covering a wide range of materials such as humid zeolites in the frequency domain [3] and in the time domain [4], humid mica [5] and dry mica at high temperatures [6] humid ceramics [7], surface conduction on humid insulators [8, 9], conduction in humid cellulose paper [10] and the response of humid sand and soil [11]. There is good evidence of this type of behaviour in biological systems [12–16], ionic conductors [17] and also in electronic semiconductors [18, 19].

Most experimental evidence on LFD is available in frequency domain (FD) spectra in which the complex dielectric susceptance $X'(\omega) = C'(\omega) - C_\infty$ and $X''(\omega) = C''(\omega)$, may be described [1, 2] in terms of two fractional power laws of the type

$$\tilde{X}(\omega) = \tilde{C}(\omega) - C_\infty = A_l(i\omega)^{n_l - 1} + A_h(i\omega)^{n_h - 1} \quad (1)$$

where the low-frequency exponent n_l is close to zero corresponding to the highly lossy LFD, while the low-loss high-frequency component is characterized by $n_h \rightarrow 1$. An immediate consequence of the power-law relation, Equation 1, is the independence of frequency of the ratio

$$X''(\omega)/X'(\omega) = \cot(n\pi/2) \quad (2)$$

which is less than one for $n > 0.5$ in low-loss materials and larger than one, i.e. highly lossy for $n < 0.5$ which corresponds to LFD.

The response given by Equation 1 corresponds to $\log X'$ and $\log X''$ against $\log \omega$ plots rising steeply towards low frequencies, hence the name “low frequency dispersion”. The general appearance of this relationship is shown in Fig. 1 and the physical significance is that there coexist in the system two independent parallel processes of which the one dominating at high frequencies is due to the normal dielectric response of the material, while the strongly dispersive one dominating at low frequencies is due to the “transport-like” processes which are normally associated with LFD. In this sense, the parallel existence of these two makes eminent sense physically – the two types of processes evidently coexist in the same medium. We note that there are many situations in which the shape of the FD spectrum departs significantly from the “simple” LFD pattern for example by showing a “bulge” at the transition between the low- and high-loss regions which may be associated with a less dispersive process dominating at the lowest frequencies, as shown in Fig. 2. We stress that this is purely a *modelling exercise* and there is no question of the series resistance, in particular, representing any physical resistance any more than does the equivalent circuit of a Debye response correspond to a series combination of a resistance and a capacitor. The physical significance of R lies in the representation of a *delaying process*, while the series combination of C_1 and $C_{1/2}$ signifies the predominance at very low

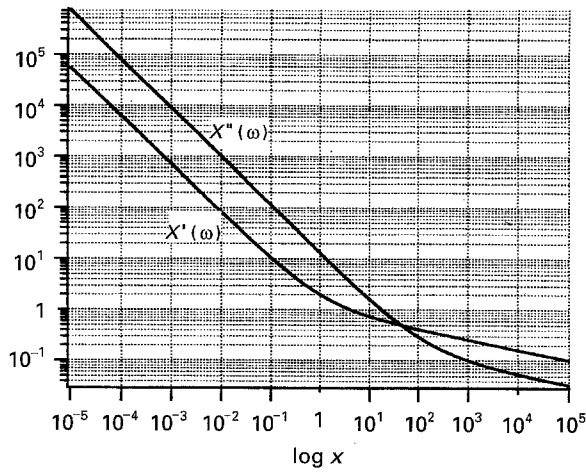


Figure 1 The functional form of the response of an LFD system with a low-loss “tail” to the characteristic. The exponents chosen in this instance are $n_1 = 0.05$ and $n_h = 0.8$. x is the frequency variable.

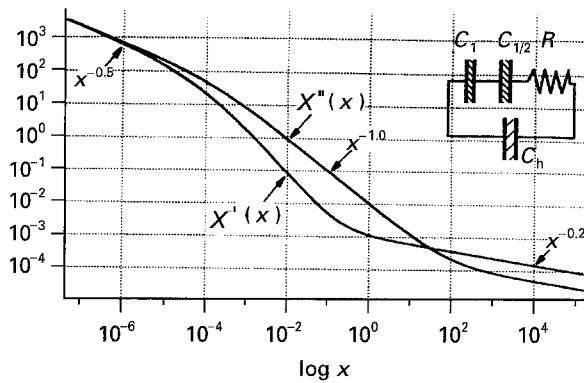


Figure 2 The functional form of the response of an LFD system consisting of a series combination of a capacitor C_1 with $n_{11} = 0.2$ and $C_{1/2}$ with $n_{12} = 0.5$, the latter dominating at lowest frequencies. The “bulge” arises from a resistance R in series with the two capacitors. The high-frequency low-loss component C_h with $n_h = 0.8$ dominates at high frequencies. The equivalent circuit is shown in the inset. x is the notional frequency variable.

frequencies of a less rapidly dispersive process than the LFD element C_1 .

The only earlier serious attempt to treat the theory of LFD that has come to our notice is that by Dissado and Hill [20] who also quote several examples of experimental data, most of them included in the present treatment. Their theory is an extension of their general theory of cluster vibrations [21] which formed the first serious attempt to interpret the “universal” fractional power law response on the basis of many-body interactions through their concept of “cluster vibrations”. The approach considers the modifications to the vibrational spectrum of a perfect lattice arising as a result of imperfections such as dipoles and charge carriers leading to the appearance of long “tails” to the spectrum which follow the fractional power laws. The derivation, which appears to be rigorous, shows these power laws to be natural consequences of interactions, rather than some accidental combinations of relaxation times. The Dissado and Hill theory defines clusters as local groupings of interacting defects and distinguishes intra-cluster and inter-cluster transitions. The former are responsible for the high-fre-

quency branch of the spectra, n_h in our notation, the latter determine the low-frequency branch which results in a loss peak for dipolar polarization, while in carrier-dominated systems they lead to LFD.

A more recent theory by Weron [22, 23] invoking a very general theory of stochastic processes and obtaining the complete range of power law exponents covering both loss peak and LFD situations has yet to be applied specifically to the carrier-dominated systems in which LFD is being seen. We shall return to comments about the Dissado and Hill and Weron theories after the discussion of time-domain responses. Further discussion and source literature of these problems will be found in a forthcoming monograph [24].

2. Empirical features of time-domain evidence

Compared with the FD responses, the time-domain (TD) response, obtained by applying a step-function voltage is less “dramatic” since the nearly time-independent charging current $i_c(t)$ and discharging currents $i_d(t)$ appear to give less information about the extent of charge storage in the system. On the other hand, the TD data contain the essential information about the differences between $i_c(t)$ and $i_d(t)$ without which our understanding of the processes involved would be completely insufficient. It therefore appears important to extend the analysis of the theoretical interpretation to the TD and not to rely solely on the FD. In fact, we should say that the only acceptable interpretation of LFD must be in the TD, since only a TD model can give a realistic basis for the analysis.

The Fourier transform of the fractional power laws (Equation 1) in FD gives another fractional power law time dependence

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

which corresponds to an almost time-independent current for LFD with its small values of n . Strictly speaking, no information can be obtained from the Fourier transformation on the magnitudes of $i_c(t)$ and $i_d(t)$ – the classical argument being that the difference between them is the “direct current” (d.c.) which is characterized by the absence of any delay with respect to the driving voltage. Closer examination of many experimental data shows that this simple reasoning is not true and this is particularly not so in most LFD systems.

On the face of it, the evident non-linearity of LFD response in the TD makes any attempt to Fourier-transform the data into the FD questionable, and yet the observed consistency of the data between FD and TD mentioned above suggests that it is desirable to extend the discussion of our model to the FD.

Fig. 3 presents the TD response for two somewhat idealized examples which sum up the principal features of experimental observations. The charging currents $i_c(t)$ and the discharging currents $i_d(t)$ are characterized by a very slow decay with time up to times of 10^3 – 10^4 s, consistent with the FD spectra of LFD in which the exponent n_1 is close to zero. The nearly constant $i_c(t)$ would be consistent with d.c.

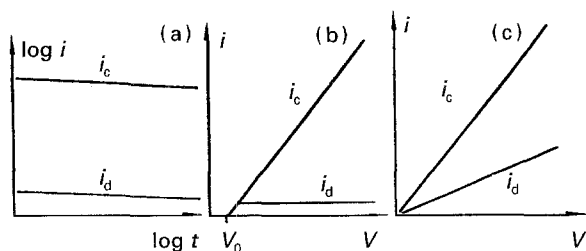


Figure 3 The basic features of TD LFD responses: (a) The time dependence of $i_c(t)$ and $i_d(t)$ showing their very slow variation and the difference in their magnitudes; (b) shows the dependence of i_c and i_d at a particular time on the charging voltage V , with the nearly saturated i_d and with $i_c \propto V - V_0$; (c) corresponds to the situation in which both i_c and i_d depend on V although i_d remains smaller than i_c .

conduction, but the presence of a finite $i_d(t)$ rules out this form of transport – no d.c. process could result in charge storage leading to a discharge current.

The dependence of $i_c(t)$ and $i_d(t)$ on the charging voltage V may follow the patterns shown in Fig. 3(b) where i_d is independent of V or that in Fig. 3(c) where both i_c and i_d are proportional to V . At all times, however, i_c is higher than i_d . Fig. 3(a) does not show the long-time decrease of both i_c and i_d , which is particularly observed for the latter as the stored charge becomes exhausted.

The TD behaviour of many LFD systems shows complicating features in the form of i_c and i_d failing to maintain the steady power-law trend and decaying more rapidly at shorter times, or even falling and rising again later [4], but this will not be discussed here.

We are now able to return to our earlier discussion of the theoretical models of Dissado and Hill and of Weron. Neither of these appears to take into account explicitly the specific TD behaviour of LFD systems and it appears to us that in failing to do this they miss an essential element of the physical situation. For this reason we proposed to develop our alternative model.

3. The electrochemical model

Our proposed model of electrochemical interactions involves the unique feature of “battery-like” action without which it is difficult to understand the TD response and which is capable of explaining the very high values of effective $C''(\omega)$ and $C''(\omega)$ being reached at low frequencies, often with no sign of saturation down to the lowest available frequencies. The electric fields that would otherwise be required in the interfacial region are difficult to envisage on physical grounds.

The electrochemical mechanism [25] proposed here relies on the formation of neutral compound molecules AB out of slowly mobile ions A^+ and B^- following the symbolic equation



where the corresponding densities v_A , v_B and v_{AB} are determined by the external conditions such as the impurity content in bulk materials or relative humidity in the ambient for surface conduction. They may

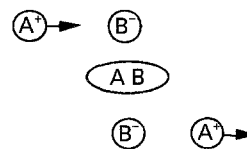


Figure 4 Top row: a mobile A^+ ion moving under the action of an external field in the direction shown by the arrow towards an immobile ion B^- . Middle row: a neutral molecule AB is formed by the reaction $A^+ + B^- \leftrightarrow AB$ resulting in the removal of charge from the system. Bottom row: dissociation of the molecule and ion A^+ continues on its path.

vary by several orders of magnitude, thereby enabling a study to be made of LFD behaviour as a function of the density of species.

With reference to Fig. 4 consider an ion A^+ situated in the vicinity of an ion B^- and moving under the action of an external field in the direction of the arrow. For simplicity let ion B^- be immobile, although this does not affect the substance of our discussion. Now if the individual A^+ ions were allowed to drift indefinitely in a steady field and they were being removed at one electrode and supplied at the other this would result in the classical d.c. conduction with no charge and no dipole moment in the system. If, on the other hand, the electrodes were blocking then space charges would develop and would lead to a Maxwell–Wagner situation with a very large dipole moment across the system.

The nature of the molecules AB and of the ions A^+ and B^- remains to be determined in any particular case, but taking the situation obtaining in humid insulators it is natural to expect the protons H^+ , hydroxyl ions OH^- and hydronium ions H_3O^+ to be involved. It is not clear at present what determines the range traversed by any particular ion before it forms a neutral molecule and, moreover, whether a molecule once formed may then undergo a subsequent dissociation, thus extending the range of the ions. The effective dipole moment associated with any particular ion is determined by the distance traversed by that ion before forming a neutral molecule, with any intermediate association/dissociation processes acting purely as delays in the transport process, somewhat by analogy to electron trapping/detrapping in semiconductors. It is reasonable to expect the distance traversed in any given time to be proportional to the driving electric field E , while the number of ions is determined by the supply from whatever source, such as ambient humidity or the density of impurity centres in bulk LFD.

3.1. Energy criterion formalism

Our experimental evidence suggests strongly that the LFD action is distributed throughout the inter-electrode space instead of being confined to some barrier regions near the electrodes. Therefore in our approach to LFD which we propose here, the A^+ ions meet the B^- ions and form neutral molecules AB. This is a situation analogous to the charging of a secondary battery, where a large amount of charge can be accommodated in the form of a neutral compound at one electrode. If the B^- ions are distributed in the system

then the individual A^+ ions migrate until they “meet” their B^- ions which stops their further displacement and freezes further increase of the resulting dipole moment. The result is an accumulation of AB molecules in the system with no charge and a dipole moment corresponding to the last position of the ions. These AB molecules now constitute the “memory” in the systems of the prior charging operation and they would eventually dissociate in the reversible reaction giving the characteristic $i_d(t)$.

Without going into detail, the formation of AB molecules might be expected to depend on the total charge passed in the “charging” operation, which may be expressed as the integral of the charging current over the charging time. For the case in Fig. 1(b) we postulate, in accordance with some experimental data

$$i_c = (V - V_0)/R \quad (4)$$

where V_0 is a “standing voltage” and R is an internal resistance, and

$$i_d = V_0/R \quad (5)$$

Experimentally we know that both $i_c(t)$ and $i_d(t)$ are only very weakly dependent on time, so the total charge in the charging operation (Q_c) until time t may be expressed in the form

$$Q_c(t) = \int_0^t i_c(t) dt = \frac{Vt}{R} \quad (6)$$

while the charge in the discharge process is

$$Q_d(t) = \int_0^t i_d(t) dt = \frac{V_0 t}{R} \quad (7)$$

The last equality in Equations 6 and 7 makes use of the model relations (Equations 4 and 5) but the integral expressions are valid quite generally and they would be applicable to situations where $i_c(t)$ and $i_d(t)$ fall rapidly at longer times. In particular, the ratio $Q_c(t)/Q_d(t)$ is the ratio of $i_c(t)/i_d(t)$ so long as they do not change with time.

The discharge process consists of the ions released by dissociation of the molecules AB drifting back towards the places “from which they came” in the first instance. However, it is clear that some ions so released will not “remember” whence they came – their original sites may have been occupied by other ions, or they may become “stuck” in some intermediate position. It is clear, therefore, that the charge Q_c is not recoverable fully in the discharge process, except at very low driving voltages where experiments show that $i_c(t)$ and $i_d(t)$ are very similar in magnitude and their time dependence is also similar, giving similar total charges.

The energy involved in the charging process (W_c) is

$$W_c(t) = VQ_c/2 = (V - V_0)Vt/2R \approx V^2t/2R \quad (8)$$

and that in the discharge process is

$$W_d(t) = V_0Q_d/2 = V_0^2t/2R = (V_0/V)^2W_c(t) \quad (9)$$

and it is evident that $W_c(t) \gg W_d(t)$.

Consider now the situation in the presence of a sinusoidally time varying signal voltage $V = V_m \sin(2\pi t/T)$ of period $T = 2\pi/\omega$. The current flowing under the influence of V is very approximately

$$i_c(t) = (V_m/R)\sin(2\pi t/T) \quad (10)$$

in view of the fact that the current response is almost in phase with the voltage since there are no significant delaying processes. This is shown schematically in Fig. 5. We now have the energy spent in $1/2\pi$ of the full cycle

$$\begin{aligned} W_1 &= \frac{V^2}{4\pi R} \int_0^T \sin^2(2\pi t/T) dt = \frac{V^2}{4\pi R} \int_0^{2\pi} \sin^2 z dz \\ &= \frac{V^2}{2R\omega} \end{aligned} \quad (11)$$

and we refer to this as the energy lost in the process per radian, since none of that energy can be recovered from the system. Now the process of charging an LFD system entails some storage of energy which at the peak of the sinewave would give a stored energy W_s which would be in the ratio to W_1 given by Equation 7 so that

$$W_s/W_1 = i_d V_0 / i_c V \quad (12)$$

So long as the currents $i_c(t)$ and $i_d(t)$ remain in a time-invariant ratio during a half-period $T/2$ of the sinewave this provides a more realistic evaluation of the ratio of energy lost per radian to energy stored at the peak than a reliance on Equations 4 and 5. The ratio W_s/W_1 given by Equation 12 then leads to the determination of the exponent n in the power law using Equation 2 and this may be related to the observed FD behaviour.

3.2. Some orders of magnitude

Consider now some magnitudes of the energies involved. Typical dissociation energies of diatomic and polyatomic molecules are between 10^2 and 10^3 J mol^{-1} which is equivalent to between 1 and $10 \text{ eV molecule}^{-1}$. Some energies for dissociation at surfaces may be significantly lower, but the general order of magnitude should be similar. In transport

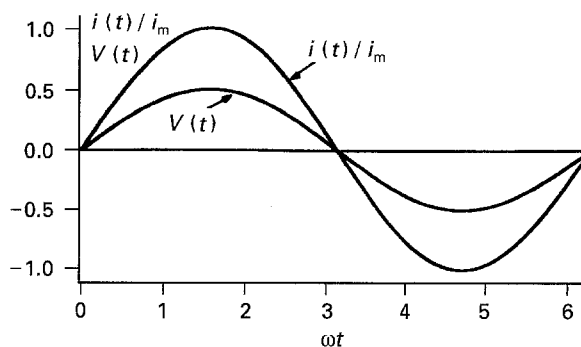


Figure 5 The driving sinusoidal voltage $V(t)$ and the resulting charging current $i(t)$ shown effectively in phase with one another on account of the near-d.c. character of this current and of the relatively small charge recovery involved. The $V(t)$ is not to any particular scale.

terms this is equivalent to deep or moderately deep trapping and it may be considered to be the dominant source of energy loss in our LFD mechanism, as was to be expected.

4. Discussion

The analysis given above provides guidance to the FD behaviour of LFD systems, even though a strict analysis is not possible because of non-linearity of the response with respect to the applied voltage. Allowing for the lack of precision in the definition of the standing voltage V_0 , it remains evident that the ratio (Equation 12) is very small in most conditions, so that the exponent n is close to zero. Likewise, the ratio of these currents is itself a function of the charging voltage V and this is one of the limitations of the present analysis. Part of the problem lies in the fact that we are stretching the concept of the Kramers–Kronig relations when the ratio (Equation 12) is not a constant. However, the expectation is that provided the ratio remains small, the deviations from constancy of this small number are not likely to result in a serious departure from the ideal analysis.

Equations 9 and 10 include the frequency dependence on ω^{-1} which is close to the LFD expression $\omega^n - 1$ for small values of n and the reason for the discrepancy may be found in the replacement of the slightly falling current by a constant value. This is the penalty of carrying out an approximate analysis. It would be more interesting to extend the analysis to include the sharply falling currents at long times, which might bear a relation to the rising n values (falling slopes) of the LFD response at the lowest frequencies.

The present analysis does not follow the usual pattern of “energy criterion” argument [26], since it is not concerned directly with reversals of microscopic polarizations, as is typically the situation in other contexts. The conclusion from this analysis is that the electrochemical model is consistent with the energy criterion argument in the FD and that it can account for the observed large dispersion observed in carrier-dominated dielectrics at low frequencies. The electrochemical model is thus established as a very realistic model of LFD relaxation.

The present theoretical approach cannot claim to be complete and much further work remains to be done in order to fill in the details and to obtain a better understanding of the LFD processes. In particular, it will be necessary to carry out more TD measurements under carefully controlled conditions, so as to ascertain the respective roles of the density of available charges and of the amplitude of the applied signal, both in TD and FD experiments. Interaction between surface and bulk transport has to be elucidated, as exemplified by the different behaviours of humid sand without and with a finite bulk conductivity [27]. It will be necessary to devote more attention to the development of specific electrochemical reac-

tions and to the elaboration of the energy considerations applicable in them. The significance of the present approach in the context of electronic conduction has to be better understood with particular emphasis on the development of the relevant models.

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