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1994 J. Phys.: Condens. Matter 6 8087

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Universal scaling of the dielectric relaxation in dipole liquids and glasses

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Received 31 March 1994, in final form 21 June 1994

Abstract. A long-standing puzzle in the relaxation of glasses has been the upward curvature of the imaginary part of the dielectric constant on the high-frequency side of the primary relaxation peak. Similarly, a puzzle of several years' standing has been the 'universal scaling' of the dielectric constant observed in dipole glasses; what has been difficult to explain is the fact that the departure from the apparent Kohlrausch–Williams–Watts (KWW) form for the relaxation follows the same general scaling function as the KWW portion near the relaxation peak. This is shown to be easily interpretable in terms of a crossover from independent 'hopping' transitions at high frequencies to correlated hopping transitions near the peak, provided the crossover frequency and high-frequency approximate power are *both* related to the peak frequency and KWW exponent respectively. Such a specific derivation has already been accomplished in electronic and ionic hopping conduction systems; its analogue for dipole glasses is consistent with the observed scaling behaviour.

1. Introduction

Probably as many different theoretical treatments of dielectric relaxation in glasses exist as there are phenomenologies to report the data†. While many arguments can be made in favour of one or other of the many theories, such a discussion will not be attempted in this paper in any depth. The same applies to the various phenomenologies. The purpose of this paper is to establish whether the results [1–5] from percolation-theoretical treatments of the AC conductivity of glasses are compatible with the particular scaling representation reported by Dixon and co-workers [6] (and also more recently [7]), and described as universal. The general percolation-theoretical treatment will be seen to reproduce Dixon scaling very well, including the upward curvature at higher frequencies, which results in a deviation from the Kohlrausch–Williams–Watts (KWW) [8–10] phenomenology. It is a fundamental property of percolation-based theories that (provided the distribution of elementary relaxation times has only one width parameter, i.e. provided the distribution is composed of only one

† Instead of offering a list of approaches considered, some theories that are related to the present work will be mentioned in the course of the paper. Some mention of the various phenomenologies is appropriate right at the onset, because controversies over the actual form of the conductivity are reported by referring to the different phenomenologies to which the data are supposed to conform. These include KWW, 'stretched exponential' relaxation functions, and in the conductivity, various approximate power laws which involve logarithmic deviations from linearity, true power laws, *sums of power laws*, and so on. In fact, however, no phenomenology represents the data over the entire frequency range. It is an interesting fact that some people assume that such an event means that different portions of the response curve are due to completely different mechanisms, a conclusion which by no means follows (as the data of Dixon and co-workers [6] considered here reveals).

peak) the frequency marking the onset of the importance of correlation effects is universally related to the frequency defining percolation. The former frequency will be seen here to be connected with the high-frequency deviation from response functions generated from KWW relaxation functions, while the latter frequency defines the loss peak. This universal relationship is reflected in the result of Dixon and co-workers [6], that a scaling form of the dielectric constant based on *the peak frequency* also encompasses the high-frequency wing of the relaxation, although this wing may seem to be simply added on, i.e. an independent relaxation (and has, in fact, been interpreted thus [11–13]).

The question of the high-frequency departure from typical KWW phenomenology is of fundamental importance to dielectric and other relaxation functions. Similar behaviour in the dielectric constant is observed in ionic [12] and electronic [14] glasses, and even cluster compounds [15] as well. The corresponding increase in the approximate power of the AC conductivity with frequency has been noted as a general tendency in amorphous systems [16]. In ionic glasses attempts have been made to identify multiple relaxation processes [11, 12], but the type of scaling relationship which is discussed here (as well as the Barton–Nakajima–Namikawa (BNN) [17–19] relation, and the scaling [15] of the approximate power of the AC conductivity with the DC conductivity) point to a fundamental framework which unites the description of the relaxation in all these systems, and at all frequencies from DC up almost to vibrational frequencies. When vibrational frequencies are approached, however, a conduction regime may be encountered with a quadratic frequency dependence [20]. The physical basis for the conduction in this regime appears not to be in the hopping type of relaxation considered here; it is noteworthy that this regime also does not appear in the Dixon [6] scaling formulation, in which it would appear as a region with zero slope.

2. Model

The present model (essentially a somewhat extended version of a previous model [21]) of a viscous fluid whose molecular units have a dipolar moment allows each molecule a limited number of orientations that are accessible to each other by classical excitations over a barrier (hopping). Relaxation times [16, 21] of such processes are

$$\tau_{ij} = \nu_{\text{ph}} \exp\left(\frac{E_{ij}}{kT}\right). \quad (1)$$

In this equation the barrier height is denoted by E_{ij} , ν_{ph} is a vibrational frequency and kT is the product of the Boltzmann constant and the temperature. A continuum of orientations is accessible from each state without a hopping transition. The continuum of states is considered accessible over short times of order ν_{ph}^{-1} , and to contribute to the real part of the dielectric constant, $\text{Re } \varepsilon(\omega)$, at $\omega \approx \nu_{\text{ph}}$. At lower frequencies, hopping transitions make an additional contribution to the dielectric constant. While some number of orientations are also possible, the requirement that a significant contribution to $\varepsilon(\omega)$ results (with the usual additional requirement that the relaxation time is on the order of the inverse of the frequency of the applied field) allows one to select two (or at most a very small number) of the possible orientations of a given molecule for consideration. One should keep in mind, however, that a more exact treatment may require explicit consideration of several distinct hopping transitions for each molecule. In the context of the present derivation, such a consideration could change primarily the normalization factor of the assumed distribution

of barrier heights (discussed later in this section), but would also affect the values of the dipole moments. The latter modification would show up only in the prefactor of the conductivity, and will not be further discussed.

At high frequencies, relaxation of the individual molecules is assumed to be independent while at lower frequencies the possibility of correlations is considered. The previous calculation [19] for dipole glasses/viscous liquids did not treat correlations; incorporation of this additional physics into the dielectric response is the objective of this work.

The correlations assumed here are analogous to those [1,2] considered for ionic conducting glasses and are treated within an analogous framework. Thus if ω_c is associated with critical (volume) percolation of the participating dipole relaxations, and the separation of the critical transitions (with rates $w_{ij} \approx \omega_c$) is l , then the number of dipoles between the critical transitions that may be blocked from adjusting to the electric field is proportional to the ratio l/r_0 of the distance l , between the critical transitions and the size of the molecules, r_0 . This factor represents an approximate enhancement of the conductivity at the peak frequency, since an additional number of molecules proportional to this number may reorient themselves at this frequency of the applied field. Choosing an enhancement factor proportional to l/r_0 implies that the interaction effects are dominant along approximately 1D paths connecting 'critically' slow transitions. Such tenuous paths are made important (in a self-consistent way) through the assumption of the relevance [21] of percolation theory [22] to the conductivity. The critical transition rate, w_c , is found by requiring the set of all independent *microscopic* transitions with $w_{ij} = \tau_{ij}^{-1} \geq w_c$ to just percolate. It has been asserted that, under certain conditions, the relaxation peak frequency corresponds to this rate w_c . What conditions define percolative transport?

Percolative transport implies that on the time scale required to establish steady state response, the number of environments seen by each molecule participating in the response is very small [23]. In other words, the molecules that respond more slowly are so much slower that the environments of those which *can* respond sufficiently rapidly may be regarded as approximately static. Of course this is only an approximation, but it is an approximation that gets better as the temperature is lowered. Since general features of percolative transport appear to be observed consistently below the so-called mode-coupling temperature, T_c (such as decouplings of various relaxation properties, a crossover from time-temperature superposition to T -dependent peak widths with reduction in T and so on) the crossover for relevance of percolative transport has been presumed to be given by T_c . Moreover, computer simulations [24,25] suggest that such a crossover should occur when transport properties have slowed by about four orders of magnitude, often noted [26] in the vicinity of T_c .

Consistent with percolation theory, the condition that defines the onset of correlations is also geometric in origin; when the average cluster size of dipoles with relaxation times smaller than or equal to the inverse of the applied field is, say, two, then one may expect these dipoles to be unable to relax independently. In other words when, on the average, an arbitrary dipole with principal relaxation time $\tau < \omega^{-1}$ is a nearest neighbour of one other dipole, which satisfies the same rate condition, then it is not possible to treat (on the average) relaxations of such dipoles independently. At higher frequencies, the number of dipoles with $\tau \leq \omega^{-1}$ is sufficiently small that the individual dipoles satisfying the rate condition are unlikely to be close to each other, allowing their relaxations to be treated independently. Finally, when the clusters of dipoles with microscopic relaxation times $\tau_{ij} \leq \omega_c^{-1}$ just reach infinite size, critical percolation is reached, and $w_c \approx \omega_c$ the relaxation peak frequency.

First, assume that the differential probability, dF , of a given barrier height being within dE of E is

$$dF = f\left(\frac{E}{E_0}\right) \frac{dE}{E_0}. \quad (2)$$

This probability is normalized, i.e.

$$\int_0^\infty f\left(\frac{E}{E_0}\right) \frac{dE}{E_0} = 1. \quad (3)$$

The condition yielding the critical frequency, $\omega_c = \nu_{\text{ph}} \exp(-E_p/kT)$, has been given [19] as

$$\int_0^{E_p} f\left(\frac{E}{E_0}\right) \frac{dE}{E_0} = \alpha_c \equiv \frac{Z_c}{Z} \quad (4)$$

where α_c is a fraction for which the total volume associated with the transitions with barrier heights $E \leq E_p$ percolates. This number can be written as the quotient Z_c/Z , where Z is the number of volumes (of comparable size to r_0^3 , the dipolar volume) neighbouring a given dipole that are accessible by hopping transitions, and Z_c is the critical number of such volumes. An equation such as (4) implies a random association of microscopic transitions, at least on length scales smaller than the separation, l , of the critical transitions, with relaxation times $\tau_c = \omega_c^{-1} = \nu_{\text{ph}}^{-1} \exp(E_p/kT)$. There is evidence [27] that dipolar liquids are *inhomogeneous*, at least over small length scales, so using notions from percolation theory will in principle yield transport properties in accord with experiment for $\omega > \omega_c$. (The fact that not all the volumes are completely independent of each other, or of the original dipolar position, means that the critical number of such volumes, Z_c , will not be the same as in an uncorrelated problem, e.g. [25]).

The most important correlations are assumed to be related to 'hard-core' repulsion, and to arise from the restriction of orientations available to a given molecule through the orientations of its nearest neighbours. In frequency-dependent response, the onset of these correlations is assumed to correspond to a frequency, ω , for which exactly $1/Z = 1/6$ of all the transitions have $w_{ij} \geq \omega$. Then, on the average, an individual volume will 'connect' with *one* other similar volume when a fraction $1/Z$ of the total microscopic transitions encounter barrier heights less than E_c . In analogy with the previous equation, E_c is defined using $Z_0 \equiv 1$, i.e.

$$\int_0^{E_c} f\left(\frac{E}{E_0}\right) \frac{dE}{E_0} = \frac{Z_0}{Z} \equiv \frac{1}{Z}. \quad (5)$$

This energy value, E_c , defines through $\omega_0 = \nu_{\text{ph}} \exp(-E_c/kT)$, the onset of correlated hopping (as the frequency is reduced) or, as the frequency is raised, the deviation from KWW phenomenology.

Z_0 and Z_c may not be treated as independent parameters. Since the exact numerical values for this problem are unknown, values from other related problems [4, 28] are employed ($Z_0 = 1$; $Z_c = 2.7$). Although subsequent research may demonstrate that different values are appropriate, the results of this calculation depend on $\log Z_c$, and the exact value chosen is relatively unimportant. Moreover, although numerical values of the frequencies ω_0 and ω_c are affected by the choice of Z_c , the existence of the sort of scaling relationship that encompasses the deviation from KWW phenomenology depends only on the fact that the respective energies E_c and E_p are both proportional to the same energy, E_0 , (as long as the distribution of barrier heights has just a single peak).

3. Calculations

The contribution to the current from a dipole that jumps back and forth over a barrier of height E_{ij} involving a change in dipole moment proportional to er_0 (r_0 the linear size) is [21, 29]

$$j(\omega) = \frac{F_0 e^2 r_0^2}{kT} \left(\frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \right) \quad (6)$$

where F_0 is the *magnitude* of the applied (harmonic) field and e is the electronic charge.

The conductivity of an independent set of molecules that can rotate between two discrete states is given (in the pair approximation, e.g. [21, 29]) by

$$\sigma(\omega) = \frac{e^2 \omega}{E_0 r_0} f\{kT[\ln(\nu_{ph}/\omega)]\} \quad (7)$$

where the normalization (proportional to r_0^{-3}) involves the molecular volume, r_0^3 , because the function f is a probability. Such an equation is derived from assuming a superposition of independent Debye relaxations and involves the approximation that only those processes with relaxation times $\tau \approx \omega^{-1}$ contribute importantly to the real part of the conductivity. It is very important to keep in mind that this type of treatment traces the dominant relaxations at any frequency to well defined relaxations (associated with given molecules in specific environments). The approximation is accurate [30] as long as $kT/E_0 < 1/10$. Thus the ratio kT/E_0 may be treated in a self-consistent way as an expansion parameter. In the following an exponential [31–33] distribution of barrier heights is assumed; such a distribution leads to an exact power law behaviour (at high frequencies where the individual relaxations that contribute to $\sigma(\omega)$ are on the average widely separated, and may be considered independent of one another). It is, however, not assumed that an exponential distribution should be generally valid. This distribution is chosen for the convenience of further calculations, for which analytical results of the conductivity are indispensable:

$$f(E) = \exp\left(\frac{E}{E_0}\right) \left[\exp\left(\frac{E_m}{E_0} - 1\right) \right]^{-1}. \quad (8)$$

For the above distribution of barrier heights, the following result for $\sigma(\omega)$ is obtained in the pair approximation (7):

$$\sigma(\omega) = \frac{e^2 \nu_{ph}}{E_0 r_0} \left(\frac{\omega}{\nu_{ph}} \right)^{1-kT/E_0} \propto (\omega)^{s'} \quad (9)$$

with

$$s' = 1 - \frac{kT}{E_0}. \quad (10)$$

The absolute lower boundary of applicability of such a result, from the considerations of the previous section, is given by

$$\omega_0 = \nu_{ph} \exp\left(\frac{E_c}{kT}\right)$$

where

$$E_c = E_m - E_0 \ln Z. \quad (11)$$

In the regime of frequencies between ω_0 and ω_c , at which the relevant volume percolates, the conductivity must be modified by a factor that describes the number of molecules whose reorientations are blocked until the molecule *considered* is able to reorient itself. Thus the pair conductivity that would describe $\sigma(\omega)$ *in the absence of correlations* is enhanced by the rearrangement of additional molecules, for which other reorientations become possible after the molecule considered which had $\tau \approx \omega^{-1}$ could respond. The number of *additional* such molecules per critical transition is determined by the association of molecules into clusters (taken here from percolation theory), and rises from near 0 at ω_0 to roughly l/r_0 at ω_c . The net response is given by the pair response *multiplied* by the number of such 'blocked' dipoles, since each makes a similar response.

The lower limit of the correlated hopping regime is then given by

$$\omega_c = \nu_{ph} \exp\left(\frac{E_p}{kT}\right)$$

where

$$E_p = E_m - E_0 \ln \frac{Z}{Z_c}. \quad (12)$$

At the lower limit of this regime the conductivity is modified by the factor l/r_0 mentioned in the previous section; within this regime the exact calculation of the frequency dependence of $\sigma(\omega)$ is very difficult, even in more concrete electronic and ionic hopping models. However, since the observed conductivity very closely resembles a power law within this range of frequencies, and since it is relatively easy to calculate an average power for $\sigma(\omega)$, this course of action is chosen here. To calculate an average power we must know ω_0 , ω_c and the values of the conductivity at these two frequencies; $\langle s \rangle$ is then found by

$$\langle s \rangle = \ln\left(\frac{\sigma(\omega_0)}{\sigma(\omega_c)}\right) \left[\ln\left(\frac{\omega_0}{\omega_c}\right) \right]^{-1}. \quad (13)$$

In this equation the ratios of ω_0/ω_c and $\sigma(\omega_0)/\sigma(\omega_c)$ appear. The former ratio is given by

$$\frac{\omega_0}{\omega_c} = \exp\left(\frac{E_p - E_c}{kT}\right) = Z_c^{E_0/kT}. \quad (14)$$

To write the ratio of the conductivities we need

$$\sigma(\omega_0) = \frac{e^2 \omega_0}{r_0 E_0 Z} \exp\left(\frac{E_m}{E_0}\right) \quad (15)$$

and the enhancement factor [2, 27] for $\sigma(\omega_c)$, assumed to be

$$\frac{l}{r_0} = \left(\frac{\int_{E_p - kT \ln(\nu_{ph}/\omega)}^{E_p + kT \ln(\nu_{ph}/\omega)} \frac{dE}{E_0} f(E)}{\int_0^{E_p} \frac{dE}{E_0} f(E)} \right)^{-1/3} = [2 \sinh(kT/E_0)]^{-1/3} \approx \left(\frac{E_0}{kT}\right)^{1/3}. \quad (16)$$

The form of this equation is general; it gives the ratio of the separations of all processes with $\tau \leq \omega^{-1}$ to those with $\tau \approx \omega^{-1}$. Now the value of the conductivity at ω_c is

$$\sigma(\omega_c) = \frac{e^2 \omega_c Z_c l}{r_0 E_0 Z r_0} \exp\left(\frac{E_m}{E_0}\right) = \frac{e^2 \omega_c Z_c}{r_0 E_0 Z} \left(\frac{E_0}{kT}\right)^{1/3} \exp\left(\frac{E_m}{E_0}\right). \quad (17)$$

In contrast to (ionic and electronic) systems with an intrinsic DC conductivity, and which therefore have no obvious constraints on the zero-frequency dielectric constant, $\text{Re } \epsilon(0)$, dipole glasses/viscous liquids do have a constraint on $\text{Re } \epsilon(0)$. Thus, dipoles that are blocked from reorienting themselves at a given frequency must reorient themselves at some lower frequency (corresponding to a later time, i.e. when the 'blocking' transition has proceeded), and the enhancement of the conductivity at low frequencies is associated with a reduction of the conductivity at some other frequency. The constraint is determined through application of Kramers-Kronig relations to $\sigma(\omega)$, because it is expressed on the condition on the static dielectric constant. The distribution chosen is assumed to be compatible with this constraint; this can be self-consistently incorporated into the values Z and Z_c , but is not attempted here. The purpose here is only a direct demonstration of the geometric nature of the condition defining the onset of correlated hopping at ω_0 ; unfortunately, it is not possible to describe an exact calculation of $\sigma(\omega)$. The result for $\langle s \rangle$ may now be written

$$s \equiv \langle s \rangle = 1 - \frac{kT}{E_0} - \frac{kT}{3E_0} \frac{\ln E_0/kT}{\ln Z_c}. \quad (18)$$

In the previous treatment [21] of this problem, in which correlations in the relaxation were ignored, the low-frequency conductivity could be represented as

$$\sigma(\omega) = \sigma(\omega_c) \left(\frac{\omega}{\omega_c}\right)^2. \quad (19)$$

Invoking the (somewhat sparse) evidence that dipolar liquids are homogeneous on length scales greater than about 3–5 intermolecular separations allows us to neglect the effects of correlations on greater length scales. Thus, the low-frequency conductivity may still be represented as quadratic in the frequency (subject to the condition on homogeneity), and (19) is adopted here as well.

With regard to the low-frequency conductivity, however, it must be said that some systems [34] appear to follow the law $\sigma(\omega) \propto \omega^m$, with $m < 2$. Whether such a result for the conductivity truly requires inhomogeneity on length scales larger than the separation of processes with critical rates, as claimed above, or whether collective relaxations (for example, Goldstone modes) can generate such a dependence without inhomogeneities is still unresolved and (to my knowledge) unaddressed. Since considerable controversy exists regarding the experimental results in this range of frequencies even in the systems considered by Dixon and co-workers [6], this question is not further addressed here. In summary, neither theory nor experiment can resolve the situation at low frequencies. But the present state of percolation theoretical approaches is that stretching of the relaxation peak at low frequencies requires inhomogeneities over distances larger than those marking the separation of critical processes, while specific calculations of such effects have only been made in conducting glasses.

In summary, one can represent the conductivity in the three separate frequency regimes as

$$\sigma(\omega) = \sigma(\omega_c) \left(\frac{\omega}{\omega_c}\right)^2 \quad \omega < \omega_c. \quad (20)$$

In general, however, the following relationship may be valid:

$$\sigma(\omega) = \sigma(\omega_c) \left(\frac{\omega}{\omega_c} \right)^p \quad p \leq 2 \quad \omega < \omega_c$$

$$\sigma(\omega) = \sigma(\omega_c) \left(\frac{\omega}{\omega_c} \right)^s \quad \omega_c < \omega < \omega_0 \quad (21)$$

$$\sigma(\omega) = \sigma(\omega_0) \left(\frac{\omega}{\omega_0} \right)^{s'} \quad \omega_0 < \omega \quad (22)$$

where s' and s are given in (10) and (18) respectively.

4. Comparison with scaling

The 'universal' scaling function is given in terms of the ratio of the width of the observed relaxation peak to the width of an ideal Debye relaxation peak. This width has been calculated to be [21]

$$w = \frac{\log(\omega_>/\omega_<)}{\log(\omega_>/\omega_<)_D} = \frac{2-s}{2(1-s)} \quad (23)$$

(with $\log \equiv \log_{10}$) assuming that the low-frequency conductivity is quadratic in the frequency. Here $\omega_<$ and $\omega_>$ are defined such that $\varepsilon(\omega_<) = \varepsilon(\omega_>) = \frac{1}{2}\varepsilon(\omega_c)$, and the subscript D means the Debye case. Generalization to values of the power $p \neq 2$ is elementary, but will not be considered here. The factor that actually appears in the scaling formulation is the inverse of w , i.e.

$$w^{-1} = 2 \left(\frac{kT}{E_0} + \frac{kT \ln E_0/kT}{3E_0 \ln Z_c} \right) \left[1 + \frac{kT}{E_0} + \frac{kT \ln E_0/kT}{3E_0 \ln Z_c} \right]^{-1} \quad (24)$$

It will be useful to represent w^{-1} in the following rather complicated form for the purpose of calculating the slope of $g(x)$. The ratios required will involve fractions with identical denominators (also, a ratio of natural logarithms may be represented as a ratio of logarithms to the base 10):

$$w^{-1} = 2 \left[\frac{kT}{E_0} + \frac{1}{3} \frac{kT \log(E_0/kT)}{E_0 \log Z_c} + \left(\frac{kT}{E_0} \right)^2 + \frac{2}{3} \left(\frac{kT}{E_0} \right)^2 \frac{\log E_0}{\log kT} + \frac{1}{9} \left(\frac{kT}{E_0} \right)^2 \left(\frac{\log E_0}{\log kT} \right)^2 \right] \times \left(1 + \frac{kT}{E_0} + \frac{1}{3} \frac{\log(E_0/kT)}{\log Z_c} \right)^{-2} \quad (25)$$

The product $w^{-1}[1+w^{-1}]$ also appears:

$$w^{-1}[1+w^{-1}] = 2 \left[\frac{kT}{E_0} + 3 \left(\frac{kT}{E_0} \right)^2 + 2 \left(\frac{kT}{E_0} \right)^2 \frac{\log E_0/kT}{\log Z_c} + \frac{1}{3} \frac{kT \log E_0/kT}{E_0 \log Z_c} + \left(\frac{kT}{E_0} \right)^2 \left(\frac{\log E_0/kT}{\log Z_c} \right)^2 \right] \left(1 + \frac{kT}{E_0} + \frac{1}{3} \frac{\log(E_0/kT)}{\log Z_c} \right)^{-2} \quad (26)$$

It is also useful to write $w^{-1}(1 + w^{-1})$ in this apparently complicated representation for the purpose of calculating slopes (which require taking quotients). In particular, the same denominator, D , will appear in both w^{-1} and $w^{-1}(1 + w^{-1})$:

$$D = \left(1 + \frac{kT}{E_0} + \frac{1}{3} \frac{\log(E_0/kT)}{\log Z_c} \right)^2. \quad (27)$$

In [6] it was found that in all of the systems considered (which had no secondary relaxation peaks), and at all temperatures, the following scaling form of the imaginary part of the dielectric constant as a function of frequency, $\text{Im } \varepsilon(\omega)$, resulted in the collapse of all the experimental data onto a single curve:

$$y = w^{-1} \log \left(\frac{\text{Im } \varepsilon(\omega) \omega_c}{\Delta \varepsilon(0) \omega} \right) = g \left[w^{-1}(1 + w^{-1}) \log \left(\frac{\omega}{\omega_c} \right) \right] \equiv g(x). \quad (28)$$

This scaling function can obviously only be correct [21, 35] if the conductivity at frequencies below the peak frequency (at ω_c) is quadratic in the frequency. While this point is quite controversial (see, for example, [7, 35]), this is not the frequency range considered here. The present calculations are modifications of a calculation that predicted such a frequency dependence, but a different result can be obtained if (i) the system is inhomogeneous [36] on a scale larger than l , and (ii) dynamic interaction effects [37, 38] (i.e. correlated hopping) continue to be of importance at such low frequencies. It is not the purpose here to suggest that either of the two results for the low-frequency conductivity must necessarily follow. It is considerably safer to turn the argument around and say that one may use experimental results to determine the physics of a particular system, i.e. whether the above two conditions are met or not. In case the low-frequency conductivity of a given system is not quadratic, it is obvious that the scaling function of [6] must be generalized to include the broadening of the peak on the low-frequency side as well. Again, however, such a condition on the low-frequency side of the peak is a property of larger-scale inhomogeneities; the presence, or lack of same, has no effect on the conductivity at higher frequencies, nor does it pertain to the geometric relationship defining the two frequencies ω_0 and ω_c , which is the focus of this work.

Using (26) for $w^{-1}(1 + w^{-1})$ yields

$$x(\omega_0) = w^{-1}(1 + w^{-1}) \log \left(\frac{\omega_0}{\omega_c} \right) = \frac{2 \log E_0/kT}{3 \log Z_c} \left(1 + 3 \frac{\log Z_c}{\log E_0/kT} + \frac{kT \log E_0/kT}{E_0 \log Z_c} + 6 \frac{kT}{E_0} \right) \frac{\log(Z_c)}{D} \quad (29)$$

for the right-hand side of (27) describing the Dixon scaling function [6]. Clearly, $x(\omega_c) = 0$ because of the ratio ω_c/ω_c in the logarithm. To calculate the left-hand side, we need first the hopping contribution to the static dielectric constant (from frequencies, ω , such that $0 \leq \omega \leq \nu_{\text{ph}}$). This result is found from

$$\Delta \varepsilon(0) = \int_0^{\nu_{\text{ph}}} \sigma(\omega) \frac{d\omega}{\omega^2} = \int_0^{\omega_c} \sigma(\omega_c) \left(\frac{\omega}{\omega_c} \right)^2 \frac{d\omega}{\omega^2} + \int_{\omega_c}^{\omega_0} \sigma(\omega_c) \left(\frac{\omega}{\omega_c} \right)^s \frac{d\omega}{\omega^2} + \int_{\omega_0}^{\nu_{\text{ph}}} \sigma(\omega_0) \left(\frac{\omega}{\omega_0} \right)^s \frac{d\omega}{\omega^2}. \quad (30)$$

Equation (29) may be simplified as follows:

$$\Delta\varepsilon(0) = \frac{\sigma(\omega_c)}{\omega_c} \left(1 + \frac{1}{1-s}\right) + \frac{\sigma(\omega_0)}{\omega_0} \left(\frac{1}{1-s'} - \frac{1}{1-s}\right). \quad (31)$$

Now the result for $w^{-1} \log[\text{Im}(\varepsilon(\omega)\omega_c)/\omega\Delta\varepsilon(0)]$ can be written:

$$y(\omega) = \frac{1}{w} \log \left(\frac{\text{Im}(\varepsilon(\omega)\omega_c)}{\Delta\varepsilon(0)\omega} \right) \\ = \frac{1}{w} \log \left\{ \left(\frac{\omega}{\omega_c} \right)^{s-2} \left[\left(1 + \frac{1}{1-s}\right) + \left(\frac{kT}{E_0}\right)^{1/3} \left(\frac{1}{1-s} - \frac{1}{1-s'}\right) \right]^{-1} \right\}. \quad (32)$$

Equation (32) may be evaluated as follows (approximating the denominator in the logarithm by its largest term, $1/(1-s)$):

$$y(\omega_0) = -\frac{2}{3} \frac{\log E_0/kT}{\log Z_c} \left(1 + 3 \frac{\log Z_c}{\log E_0/kT} + \frac{4}{3} \frac{kT \log E_0/kT}{E_0 \log Z_c} + 6 \frac{kT}{E_0}\right) \frac{\log Z_c}{D}. \quad (33)$$

From (17), (24) and (30), $y(\omega_c)$ is given by

$$y(\omega_c) = -\frac{2}{3} \frac{\log E_0/kT}{\log Z_c} \left(\frac{2}{3} \frac{kT \log E_0/kT}{E_0 \log Z_c} + 2 \frac{kT}{E_0}\right) \frac{\log Z_c}{D} \quad (34)$$

(with the same approximation for the denominator in the logarithm).

The slope of $g(x)$ between ω_c and ω_0 is found easily:

$$m = \frac{y(\omega_0) - y(\omega_c)}{x(\omega_0) - x(\omega_c)} = -\left(1 + 3 \frac{\log Z_c}{\log E_0/kT} + \frac{2}{3} \frac{kT \log E_0/kT}{E_0 \log Z_c} + 4 \frac{kT}{E_0}\right) \\ \times \left(1 + 3 \frac{\log Z_c}{\log E_0/kT} + \frac{kT \log E_0/kT}{E_0 \log Z_c} + 6 \frac{kT}{E_0}\right)^{-1} \\ \approx -\left(1 - \frac{1}{3} \frac{kT \log E_0/kT}{E_0 \log Z_c} - 2 \frac{kT}{E_0}\right). \quad (35)$$

To a good approximation the scaling function $g(x) = -x$ for $\omega_c \leq \omega \leq \omega_0$. This is observed experimentally [6]. However, the above formula shows a slight (positive) deviation from a slope of -1 . In fact, this comes about because the Dixon scaling function is not represented by two straight lines that intersect at $(0, 0)$. Rather, the experimental results [6] and calculations both yield $y(\omega_c)$ somewhat less than zero. However, because of the curvature of $g(x)$ near $x = 0$, the slope of the (KWW) straight-line fit (over 2–4 decades in frequency above the loss peak) is determined by extrapolating back through approximately the point $(0, 0)$. If we use $y(\omega_c) = 0$, we find for the slope, m :

$$m = -\left(1 + 3 \frac{\log Z_c}{\log E_0/kT} + \frac{4}{3} \frac{kT \log E_0/kT}{E_0 \log Z_c} + 6 \frac{kT}{E_0}\right) \\ \times \left(1 + 3 \frac{\log Z_c}{\log E_0/kT} + \frac{kT \log E_0/kT}{E_0 \log Z_c} + 6 \frac{kT}{E_0}\right)^{-1} \\ \approx -\left(1 + \frac{1}{3} \frac{kT \log E_0/kT}{E_0 \log Z_c}\right). \quad (36)$$

This value of m also shows a slight deviation from a slope of -1 , but in this case the deviation is negative (to third order in the expansion). Although we take the average value here, this demonstrates that a noticeable uncertainty in the calculation of the slope exists. The average value is given by

$$\langle m \rangle = -\left(1 - \frac{kT}{E_0}\right). \quad (37)$$

A slight positive deviation from the value $m = -1$ results; the difference, however, is smaller than the uncertainty in the method to determine m .

In the vicinity of ω_0 the slope of $\log \varepsilon(\omega)$ against $\log \omega$ increases gradually:

$$-\frac{kT}{E_0} \left(1 + \frac{1}{3} \frac{\log E_0/kT}{\log Z_c}\right) \rightarrow -\frac{kT}{E_0}.$$

How does this appear on the scaled axes? One might assume that the scaling procedure, which in practice amounted to subtracting $1 - \frac{1}{3}(kT/E_0) \log(E_0/kT)/\log(Z_c)$ from the slope at lower frequencies, would have the same effect at higher frequencies, leading to

$$m' = -\left(1 - \frac{1}{3} \frac{kT}{E_0} \frac{\log E_0/kT}{\log Z_c}\right).$$

In fact, this is approximately true. This will be demonstrated later, but is important for the following discussion.

From (29) and (33) it is seen that ω_0 slides upward in x and downward in y , the dependence on the temperature being logarithmic, i.e. a slow variation (a decrease in T of *one half* only changes the value of ω_0 on the scaled axes by about 10%). To fourth order in the expansion, the downward 'sliding' of the left-hand side of the equation evaluated at ω_0 is identical.

The upward curvature of the relaxation is due to the increase in the power of the conductivity in the neighbourhood of ω_0 (through the gradual crossover to independent hopping). The 'sliding' out to higher frequencies on the scaled plot of ω_0 would be consistent with a greater departure from $m = -1$, observed at lower frequencies. However, the calculated deviation from $m = -1$ seems to diminish as the temperature drops ((43) below). This is because in the region around ω_0 , the crossover to pair hopping produces a gradual change in slope, in contrast to the simplification considered here. Thus, what is calculated here cannot describe the curvature of $g(x)$ very well in the neighbourhood of its deviation from the KWW fit. It is therefore important to check whether the experimental values for $x(\omega)$ and $y(\omega)$ at *much higher frequencies* are consistent with the theoretical results obtained. Note, however, that since both the change in slope and the position of the crossover depend on the ratio of the same energy (E_0) to kT , the two effects are generally compatible with each other, and with the universal tendency for scaling.

For $\omega > \omega_0$ the approximate slope of the scaling function is calculated as follows:

$$x(\omega) = w^{-1}(1 + w^{-1}) \left[\log\left(\frac{\omega_0}{\omega_c}\right) + \log\left(\frac{\omega}{\omega_0}\right) \right]. \quad (38)$$

This may be rewritten as

$$x(\omega) = x(\omega_0) + x(\omega_0) \left(\frac{1}{\log Z_c} \frac{kT}{E_0} \right) \log\left(\frac{\omega}{\omega_0}\right). \quad (39)$$

Similarly

$$y(\omega) = \frac{1}{w} \log \left(\frac{\text{Im}\varepsilon(\omega)\omega_c}{\Delta\varepsilon(0)\omega} \right) = \frac{1}{w} \log \left[\frac{\text{Im}\varepsilon(\omega_0)\omega_c}{\Delta\varepsilon(0)\omega} \left(\frac{\omega}{\omega_0} \right)^{-1-kT/E} \right]. \quad (40)$$

Substituting:

$$y(\omega) = \frac{1}{w} \log \left\{ \left(\frac{\omega_0}{\omega_c} \right)^{-1-kT/E_0} \left[1 + \frac{1}{1-s} + \left(\frac{kT}{E_0} \right)^{1/3} \left(\frac{1}{1-s'} - \frac{1}{1-s} \right) \right] \right. \\ \left. \times \left(\frac{\omega}{\omega_0} \right)^{-1-kT/E_0} \right\}. \quad (41)$$

This result may now be simplified:

$$y(\omega) \approx y(\omega_0) + y(\omega_0) \left(\frac{kT \log \omega/\omega_0}{E_0 \log Z_c} \right) \left(1 + \frac{4}{3} \frac{kT \log E_0/kT}{E_0 \log Z_c} \right)^{-1}. \quad (42)$$

After some algebra:

$$m' = -1 \left(1 - \frac{kT \log E_0/kT}{E_0 \log Z_c} \right). \quad (43)$$

This result should be compared with (37), from whence it can be seen that the slope is less negative at higher frequencies.

Two specific points, (x, y) , are now estimated. For the purpose of this calculation, Z_c is chosen to be 2.7 (the same value used in electronic and ionic glasses) and E_0/kT is taken to be 10 (the minimum ratio for accuracy of percolation-based theories). Substitution yields

$$x(\omega_0) = 1.7 \quad y(\omega_0) = -1.8 \quad (44)$$

in approximate accord with the scaling function (which has $m = -1$ for $0 < x < 2$, and in which $y(\omega_c) < 0$). The second point chosen is $x = 8$ (at the upper frequency limit of the data reported). Using (39), one can solve for

$$\frac{kT \log \omega/\omega_0}{E_0 \log Z_c} = \frac{8 - 1.7}{1.7} \quad (45)$$

and find

$$y(\omega) = -1.8 - 6.3 \frac{1.8}{1.7} \frac{1}{1 + 1/3} = -6.7 \quad (46)$$

in very close agreement with the 'universal' scaling function [6]. Although these last two examples do not constitute a proof that the theoretical approach yields the scaling function (since only one value of kT/E_0 , and only one form of a barrier height distribution, has been investigated), they provide further evidence that percolation theoretical treatments are consistent with the Dixon scaling function [6].

Finally, the approximate power of the frequency in $\sigma(\omega)$ obviously depends on the energy scale of the distribution that is relevant at ω ; if the frequency is high enough (and the system complex enough) so that another relaxation peak is involved, one should not

expect the scaling form to still hold, since the energy scale that appears in w is that of the portion of the distribution which involves the primary relaxation peak. Nevertheless, even in such situations, the scaling function of Dixon and co-workers [6] appears to be consistent with an envelope of curves in the vicinity of the secondary relaxation peak. While such a geometrical relationship between two of the relevant frequencies (excluding the secondary relaxation peak) will still hold, and will still provide some constraints, an actual test of the validity of the present framework must be postponed until it is possible to perform numerical calculations. These will necessarily involve the conservation principle on the static dielectric constant referred to, and should probably also be compared with computer simulations of the relaxation using a combination of molecular dynamics (for short times, or large frequencies) and Monte Carlo methods (for long times, or small frequencies). The depth of such an investigation is well beyond the scope of the present paper.

5. Discussion

The relevance of the derivation here is primarily in the description of the high-frequency side of the primary dielectric relaxation peak. At low frequencies, the actual form of the relaxation is still in dispute [6, 35]. The controversy revolves around the frequency dependence of the conductivity at frequencies below the primary relaxation peak frequency, ω_c . But this controversy is relevant to the applicability *even above the peak frequency* of the 'universal' scaling function for dielectric relaxation investigated here. Clearly, the Dixon [6] scaling result requires a quadratic frequency dependence at low frequencies. Experimental evidence to the contrary exists [39] (even for the *same* systems investigated by Dixon and co-workers [6]), but has been subsequently disputed (and counter disputed) [35]. Compilations [34, 37] of data from different systems suggest that many systems have a non-integral power dependence on the frequency at low frequencies, a behaviour also noted in electronic systems [14] (where non-local relaxation is clearly relevant). But theoretical explanations of such behaviour seem to require spatial inhomogeneities on length scales larger than the separation of rate determining processes (here, roughly $(E_0/kT)^{1/3}r_0$, or for typical experimental conditions roughly $3r_0$). And some evidence exists [27] to suggest that dipolar liquids are homogeneous on such length scales (local dielectric probes, which average over 3–5 intermolecular distances yield the same relaxation functions as investigations on a macroscopic scale).

In the approach of applying concepts from percolation theory to the dielectric relaxation of viscous dipolar liquids, the identification of the relaxation peak frequency, ω_c , as corresponding to percolation of the volume associated with microscopic transitions whose rates are faster than the peak frequency, and that of the departure from KWW phenomenology at ω_0 as a crossover to independent relaxation, seems to be in accord with the 'universal' scaling noted in [6]. The slope of the scaling function in the neighbourhood of the peak, the crossover to a smaller (negative) slope at ω_0 , the relationship of ω_0 to ω_c , as well as values of the scaling function at ω_c , ω_0 and in the high-frequency limit, are all in close accord with results from experiment. However, the effect on the scaling function due to a reduction in temperature is not precisely reproduced in the approximation of calculating slopes in two regions, and connecting the points with straight lines. Apart from the obvious problem of not representing the curvature of the scaling function $g(x)$, there is an additional problem of slightly overestimating the peak width (because of the slight curvature between ω_c and ω_0). While this problem in itself is not of great importance, the overestimation is accentuated with a drop in temperature because the frequency ω_0 is found at slightly

higher values of x in the scaled plot. So a greater portion of the curvature is included in the approximation finding the slope near the peak. This difficulty certainly contributes to the problem that the departure from KWW is reduced with a decrease in T , instead of remaining constant, as required for exact scaling. Unfortunately, without a precise analytical expression for the curvature of $g(x)$, a better approximation is not possible. But even in 'traditional' systems [4] with percolative transport, in which it is possible to write an expression combining cluster statistics with cluster relaxation times, the resulting equation defining the dominant *cluster* processes is a complex transcendental equation that cannot be analytically solved, and which could not be used to obtain an analytical expression for the width of the relaxation peak. Without such an analytical expression, it will only be possible to make an exact comparison with experiment through numerical results.

Although only an exponential distribution has been tested directly in this calculation, the relationship between the slope of the frequency-dependent dielectric constant near the peak, and that at higher frequencies, is still determined through the enhancement of the conductivity near the peak from correlations in the microscopic transitions. These correlations have a universal relationship to the relaxation function, which is expressed through the cluster statistics of percolation theory. That the high-frequency portion of the relaxation also scales with the peak region is evidence that the fundamental magnitude of the relaxation in both the high-frequency (independent-relaxation) regime and the low-frequency (collective-relaxation) regime is defined by the statistics of the individual microscopic processes. Thus the effects of correlations represent a 'universal' *modification* of the independent relaxations, a modification that can be expressed as a renormalization.

A very interesting aspect of the Dixon scaling function [6] is that it is able to isolate different factors influencing the peak width, in particular, by showing that *for any energy scale*, i.e. distribution parameters, the relaxation data is collapsed onto a single curve. This apparent verification of the relationships between the peak width and the peak value will allow us to isolate any additional temperature dependence of the peak width as due to a *temperature dependence of the energy scale*.

If the treatment given here is valid, it is easy to generalize to powers of the low-frequency conductivity other than two and, in view of the concrete representation of $\varepsilon(\omega)$ in the various frequency regimes, a generalization of the Dixon scaling [6] could probably be proposed. However, even further care would be required in the selection of a distribution of macroscopic rates in order that the condition on the conservation of the static dielectric constant be maintained (in view of the continued relevance of correlations in the relaxation at frequencies *below* ω_c). Such a development would be beyond the scope of this work.

Here we wished only to examine the consequences and implications of the scaling properties of $\text{Im}\varepsilon(\omega)$ at frequencies where the results typically deviate from KWW phenomenology. The method applied to analyse the conductivity, and hence $\text{Im}\varepsilon(\omega)$, was percolation-theoretical in nature, and was adopted in part because of the experimental similarities of dielectric relaxation in a variety of systems, ranging from electronic glassy systems through ionic conducting and dipole glasses to polymers and solutions. In some of these systems the relevance of percolation theory to transport has been clearly established, while in others considerable evidence already exists to suggest its relevance. The upward curvature of $\text{Im}\varepsilon(\omega)$ studied here is common to all these systems, and is proposed to have the same origin in a crossover from pair hopping to multiple hopping (in highly correlated systems, sequentially correlated hopping). While the actual derivation of $\sigma(\omega)$ in this regime is not complete when the enhancement of $\sigma(\omega)$ compared with pair hopping is due to correlations, a comprehensive treatment is available [28], even for this regime, in certain electronic conducting systems. If the analogy noted here turns out to be quantitative *and*

universal, then a general framework for the calculation of dielectric relaxation in amorphous systems has been found.

6. Conclusions

The model of relaxation assumes that the individual dipolar molecules relax independently at high frequencies, and that correlations set in at a frequency, ω_0 , when the average number of dipoles responding as rapidly, or more rapidly than ω_0 , is high enough so that the typical 'responding' dipole is the nearest neighbour to one other such dipole. The peak frequency, ω_c , is then defined by the condition that all dipolar transitions with individual transition rates faster than or equal to ω_c occupy a percolating volume. The conditions defining ω_0 and ω_c relate these two frequencies to each other, and hence the departure from apparent KWW relaxation (at high frequencies) is related to the relaxation in the vicinity of the peak (as long as the distribution of individual barrier heights as only one fundamental energy scale).

The scaling form for the imaginary part of the dielectric constant as a function of frequency, $\text{Im}\epsilon(\omega)$, which has been found to be consistent with a number of experiments by the University of Chicago group [6, 7, 35], has been shown to be consistent with a theoretical treatment of the dielectric relaxation in dipole liquids which is analogous to percolation treatments of electronic and ionic conducting glasses. Some details remain to be checked, but the slight deviation from the point $(x, y) = (0, 0)$, the slope of approximately -1 between $(0, 0)$ and $(2, -2)$, as well as the slight increase in slope at higher values of the ordinate, are all obtained from the same theoretically derived form for the conductivity, $\sigma(\omega)$.

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