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# Inhomogeneities as a result of non-exponential relaxation in disordered systems

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## Abstract

In many disordered systems such as supercooled liquids the relaxation function does not decay exponentially with time. In this paper, it is shown from a consideration of the initial conditions that a system of identical molecules, each of which has the same non-exponential relaxation function, must be inhomogeneous. As a result, the relaxation function for the system is not the same as that of an individual molecule, contrary to what is often assumed. As an example, the general formulae are applied to a simple model system in which the dielectric relaxation function of the individual molecules is of the stretched exponential form. It is found that while the dielectric relaxation of the system can be well approximated by a function of this form, its stretching parameter and relaxation time differ from those for the individual molecules.

## 1. Introduction

Since an understanding of the physics of supercooled liquids and glasses is a major unresolved problem in the theory of condensed matter [1], the relationship between the microscopic and macroscopic properties of such systems is of considerable interest. In recent years a growing body of experimental evidence has accumulated that supercooled liquids are not microscopically homogeneous [2], e.g. from multi-dimensional nuclear magnetic resonance (NMR) [3] and dielectric hole burning [4] experiments. This evidence has led many authors to assume that these systems consist of entities, which for convenience we will call molecules, for each of which the property of interest decays exponentially with time but with a distribution of relaxation times (DRT) [5,6]. For instance, such a distribution in the relaxation times of the dipole–dipole correlation functions of the individual molecules will lead to non-exponential decay of the dipole–dipole correlation function of the whole system, and so of its dielectric relaxation [7], as is observed experimentally [1]. One major problem with such an approach is to account for the somewhat arbitrary DRT required to describe the results, and in particular to relate it to the known structure and molecular properties of the system. Another problem

is that the correlation functions of the individual molecules may also not decay exponentially with time, as is indicated by the NMR experiments, a point that was recognized by Richert and Richert [8], who considered the effect on the dielectric relaxation of the system of a distribution of molecules for which the dipole–dipole correlation function showed stretched exponential relaxation. However, a point that has usually been overlooked is that any system in which the individual molecules relax in a non-exponential manner will generally be microscopically inhomogeneous as a result of this non-exponential relaxation. This is to be contrasted with the assumption that inhomogeneities are the cause of the non-exponential relaxation, as is implicit in the DRT approach and also in that of a distribution of waiting times used in theories involving continuous time random walks (CTRWs) [9]. One important consequence of such inhomogeneities, which we consider in this paper, is that it leads to a difference between the relaxation behaviour of the system and that of the individual molecules in it. In particular, we find for a simple model system that if the dielectric relaxation of each of the individual molecules can be described by the same stretched exponential function of the time, then that of the whole system can also be described to a good approximation by a function of this form, but with different values of the stretching exponent and relaxation time.

The key to proving the above results lies in an examination of the initial state of the system. While this problem was discussed to some extent many years ago for the CTRW theories of electrical conductivity [10–12], it has generally been ignored in considerations of the relaxation of systems such as supercooled liquids and glasses. The usual assumption, implicit in most theoretical derivations of a non-exponential relaxation function from a microscopic physical model, is that at the moment which is chosen as the origin of time,  $t = 0$ , the system consists of identical particles or molecules in identical states. Such an assumption is made in many theories of dielectric relaxation, ranging from the physically simple picture of Ngai's coupling model [13] to the highly sophisticated quantum mechanical theory of Dissado and Hill [14]. For instance, in Ngai's model all the molecules are assumed to be free at time  $t = 0$ , while as time proceeds they become more and more entangled with neighbouring molecules, as a result of which their relaxation rate slows down, leading to stretched exponential relaxation of the dipole–dipole correlation functions of the individual molecules. Similarly, in the theory of Dissado and Hill, it is assumed that each particle initially shows a fast relaxation, which gradually slows down as time proceeds and the size of the cluster of particles interacting with the original one increases. In each of these theories, as well as in many others, the development in time of the dielectric relaxation of the individual molecules, starting at time  $t = 0$  in a specific state, is found to lead to a relaxation function similar to that observed experimentally for the whole system. However, as is well known in statistical mechanics, at any instant there will be an ensemble distribution of molecules over all the available states, with important consequences for the relaxation behaviour of the system. For instance, even in an ideal monotonic gas in thermal equilibrium at a finite temperature, while the individual atoms are identical they all have different velocities, so that they exhibit inhomogeneity in any property associated with their velocity, which leads to Doppler broadening of the system's spectral lines. In a more complicated system, such as a liquid, not only will the orientations and velocities of the molecules differ, but also their neighbourhoods and hence their interactions with the surrounding molecules. In that case, the meaning of identical molecules is only that on average, over a long time interval, each molecule experiences the same behaviour, but certainly not that they are at any instant all in identical states. For calculations of how a property such as the system's dipole–dipole correlation function relaxes with time, the effects of such differences in the initial states of the different molecules can be extremely important. As a result, as we show in this paper, there can be appreciable differences between the relaxation function of the individual molecules and that of the whole system.

In section 2 of this paper, we show why non-exponential relaxation of the individual molecules leads to inhomogeneities in the system, and derive formulae for the effect of these inhomogeneities on the relaxation of a simple system of identical molecules. In order to clarify the meaning of a DRT, we also present a formula for the relaxation function that would be obtained with the same DRT as in the actual system but with simple exponential relaxers. In section 3 we apply these formulae to a simple type of system in which the dipole–dipole correlation function of the individual molecules decays with time as a stretched exponential function, for reasons that are explained there, and present the results of calculations for this system. In section 4 we discuss the main features of our results, namely that the dipole–dipole correlation function of a system decays more slowly than that of the individual molecules, and that the relaxation function derived from the system’s actual DRT differs considerably from the DRT that would be derived from the system’s relaxation function. These features are not specific to the model system that we considered, but should be of quite general validity. Finally, we summarize our conclusions in section 5.

## 2. Non-exponential relaxation and inhomogeneities

The first point that we consider is how non-exponential relaxation for a set of identical molecules must lead to microscopic inhomogeneities in the system. In order to do this, let us consider a system of identical molecules, and (for convenience in the terminology) examine their dipole–dipole correlation function, which determines the dielectric response of the system [7]. For each of the identical molecules, let this function have the value  $m(t)$  at time  $t$  after it was in a specified state, which we call the reference state, and let  $\tau(t)$  denote its instantaneous relaxation time. Then, by definition, the relaxation function  $h(t)$  of the property  $m(t)$ , which is defined by  $m(t) = h(t)m(0)$ , satisfies the rate equation

$$dh/dt = -h(t)/\tau(t) = -w(t)h(t), \quad (1)$$

where the initial or reference state  $m(0)$  can often be chosen so that the relaxation rate  $w(t) = 1/\tau(t)$  is a non-increasing function of the time  $t$  so long as the relaxation proceeds without any disturbance, as in the models mentioned in the introduction [13,14]. This empirical equation only assumes that identical molecules experience on average the same sequence of such relaxation rates when starting from their uniquely defined reference state. Since by definition  $h(0) = 1$ , the solution of this equation can be written in the form

$$h(t) = \exp \left[ - \int_0^t w(y) dy \right]. \quad (2)$$

If  $\tau(t)$  has the constant value  $\tau_0$ , so that  $w(t) = 1/\tau_0$ , corresponding to a simple exponential decay of  $h(t)$ , then  $w(t) = 1/\tau_0$  and  $h(t) = \exp[-t/\tau_0]$ , so that equation (2) is the same whatever instant is chosen as the origin of time,  $t = 0$ . In this case the system is homogeneous, i.e. all the molecules have the same relaxation rate  $1/\tau_0$  or relaxation time  $\tau_0$ . For any non-constant value of  $\tau(t)$ , or in other words for any non-exponential relaxation, this is not the case. If the molecules started relaxing from their reference state at different times  $t_j$  before the moment chosen as the origin of time, then at any given time  $t$  they will have a distribution of instantaneous relaxation times  $\tau_j = 1/w(t + t_j)$ . Thus, at any instant the system as a whole will be inhomogeneous, with some molecules apparently having short relaxation times  $\tau_j$  and others having long ones, even though the molecules comprising the system are identical. This is why non-exponential relaxation of the molecules will always lead to inhomogeneities in the system, a result that is completely independent of the form of  $w(t)$  and so of the relaxation function  $h(t)$ . As mentioned in the introduction, this inhomogeneity is in the properties of the individual molecules, rather than in mesoscopic properties of the system such as density

fluctuations. Incidentally, the analysis by Richert and Richert [8] of a system's relaxation in terms of a distribution of stretched exponential functions with a DRT only considered functions that started relaxing at time  $t = 0$ , and so completely ignored this point.

Another important requirement that is often ignored is that for experiments such as dielectric relaxation one is usually interested in systems that are macroscopically in a steady state at a given temperature. For instance, the frequency-dependent dielectric constant  $\varepsilon(\omega)$  of a supercooled liquid at a given temperature is well defined experimentally, even though the system is not in thermal equilibrium. On the other hand, if all the molecules have transition rates that are gradually slowing down, the system's average dynamics will become more sluggish as time proceeds. In order to avoid this, there must be a possibility for a molecule to return it to its reference state, so that its relaxation rate jumps from  $w(t)$  to  $w(0)$ , and there are various ways in which this can affect the system's relaxation function. One simple case, which is the only one that we consider here, is that such a jump is associated with a complete loss of memory of the system's initial state, so that the molecule's relaxation function  $h(t)$  becomes zero when such a jump occurs. The opposite extreme case, which we do not consider here since its analysis is more complicated, is where the jump from one state to another is not accompanied by any change in  $h(t)$  but only by a change in the rate at which it relaxes. One simple example of this, which we have discussed elsewhere [15], is where a molecule jumps without any change in its orientation, and so in  $h(t)$ , between two states, associated with different environments, in one of which it relaxes much faster than in the other.

The probability density  $f(t')$  that the system's relaxation rate at time  $t = 0$  is  $w(t')$  is just the probability density that a molecule does not return to its reference state for time  $t'$  after entering it. The relaxation function at time  $t$  for a molecule that was in its reference state at time  $-t_j$  and has not experienced a sudden jump in its transition rate is

$$h_j(t) = [h(t + t_j)/h(t_j)], \quad (3)$$

where the factor  $1/h(t_j)$  ensures that  $h_j(0) = 1$ , as is required for a relaxation function. It follows that for a system containing a large number of molecules whose relaxation started at arbitrary times the total relaxation function of the system  $H(t)$  will be given by

$$H(t) = \int_0^\infty [h(t + t')/h(t')] f(t') dt'. \quad (4)$$

The main point that we wish to emphasize in this paper is that this relaxation function differs from that,  $h(t)$ , of the individual molecules unless  $h(t)$  is a simple exponential function of the time  $t$ . In order to demonstrate this, we consider in what follows only the simplest model system, in which the flip of a molecule's dipole leads to a total loss of memory of its previous orientation, so that  $h(t)$  is proportional to the probability that the molecule has not made a jump up to time  $t$ , and to a sudden change in the molecule's environment occurring then and only then, as a result of which the molecule returns to its reference state. In that case,

$$f(t) = -dh/dt \equiv -h'(t), \quad (5)$$

so that the relaxation function for the system is

$$H(t) = - \int_0^\infty [h(t + s)/h(s)] h'(s) ds = \int_0^\infty h(t + s) w(s) ds. \quad (6)$$

One other function that is of interest, as discussed in section 4, is the relaxation function that would be produced by a system of independent exponentially relaxing molecules with the same DRT as in our system, namely relaxation times  $1/w(t)$  with the probability density  $f(t)$ , which we denote by  $H_{DRT}(t)$ . This function is given by

$$H_{DRT}(t) = \int_0^\infty f(t') \exp[-w(t')t] dt', \quad (7)$$

and in general differs from  $H(t)$ .

### 3. Calculations for systems with stretched exponential relaxation

We now consider a system of molecules each of which exhibits, on average, stretched exponential relaxation, i.e. decays with time as  $\exp[-(t/\tau)^{1-n}]$ . There are a number of reasons for choosing this function. Firstly, it is a very flexible two-parameter function, to which experimental results are often fitted. Secondly, such a relaxation function is also often derived from a specific model, as in Ngai's coupling model [13] and various other types of model [16]. Finally, its most important property for the purpose of this paper is that it clearly and simply shows the importance of the choice of the origin of time, since if  $\beta \neq 1$  there is no simple relationship between  $h(t)$  and  $h(t+t')$ , i.e. between the relaxation function of a molecule that started relaxing at time  $t = 0$  and of one that started relaxing at time  $t = -t'$ .

A problem with the use of such a relaxation function from the time  $t = 0$  is that it requires  $w(0)$  to be infinite, which does not make sense physically. One way of overcoming this difficulty, as proposed by Ngai [13], is to choose  $w(t)$  to be constant up to time  $t_c$ , corresponding to simple exponential relaxation up to that time. Accordingly we choose

$$\begin{aligned} w(t) &= w_0, & t \leq t_c \\ &= [(1-n)/\tau_0](t/\tau_0)^{-n} & t > t_c \end{aligned} \quad (8)$$

where the form of  $w(t)$  for  $t > t_c$  is the one required to produce for  $h(t)$  the stretched exponential form

$$h(t) = A \exp[-(t/\tau_0)^{1-n}], \quad t > t_c. \quad (9)$$

The requirements that  $h(0) = 1$ , and that  $w(t)$  and  $h(t)$  be continuous at time  $t = t_c$ , lead after simple calculations to the result that

$$\begin{aligned} h(t) &= \exp[-(1-n)(t_c/\tau_0)^{1-n}t], & 0 < t < t_c; \\ &= \exp[n(t_c/\tau_0)^{1-n} - (t/\tau_0)^{1-n}], & t > t_c. \end{aligned} \quad (10)$$

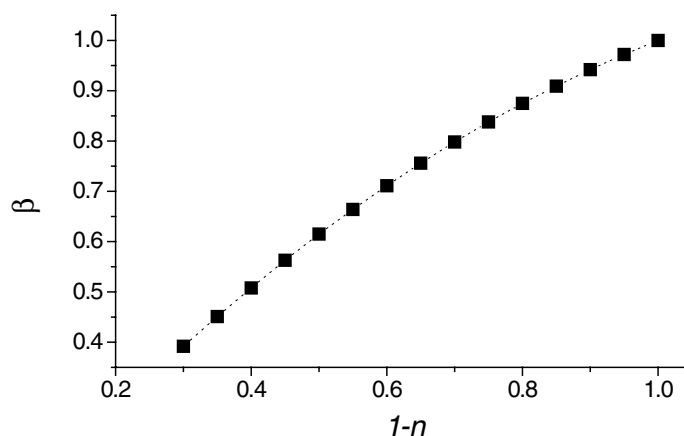
We found that the results of numerical calculations using equations (6) and (10) can usually be well approximated by a stretched exponential function,

$$H(t) \simeq C \exp[-(t/\tau_s)^\beta]. \quad (11)$$

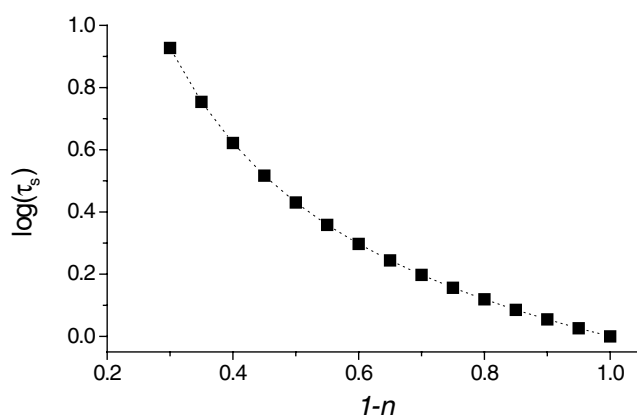
A brief discussion is required of how we determined the values of  $\beta$  and  $\tau_s$  that provide the best fit to the numerical results. A plot of  $\ln(-\ln[H(t)])$  as a function of  $\ln(t)$  will only be a straight line if  $C = 1$ , which is essential if equation (11) applies at time  $t = 0$  but not if it only applies after some finite time, as is the case for the relaxation function  $h(t)$  of equation (10) and as is usually observed experimentally. Moreover, it is well known that such a plot is not a very sensitive test of the quality of the fit of equation (11). Accordingly, we wrote equation (11) in the form

$$\ln[H(t)/H(t_0)] \simeq \exp[\beta \ln(t_0) - \beta \ln(\tau_s)] - \exp[\beta \ln(t) - \beta \ln(\tau_s)], \quad (12)$$

with  $H(t_0) \simeq 0.99H(0)$  and found the values of  $\beta$  and  $\tau_s$  that gave the best fit, using the standard Levenberg–Marquandt algorithm, for  $H(t)$  evaluated at equal intervals of  $\ln(t)$ . These optimal values were not very sensitive to the range of values of  $H(t)$  for which the fit was performed, and for the sake of consistency we performed the fit for the different values of  $1-n$  up to times  $t$  such that  $H(t) \simeq 0.01H(0)$ . In order to compare the results for different values of  $1-n$ , we chose  $t_c$  such that  $w_0 t_c = \delta$  and so  $h(t_c) = \exp(-\delta)$ , i.e. so that the relaxation function had decreased from unity by a fixed small amount when the simple exponential relaxation changes over to stretched exponential relaxation. The results were virtually independent of  $\delta$  for values of  $\delta$  between  $10^{-2}$  and  $10^{-4}$ , and so we chose  $\delta = 10^{-3}$  in our calculations.

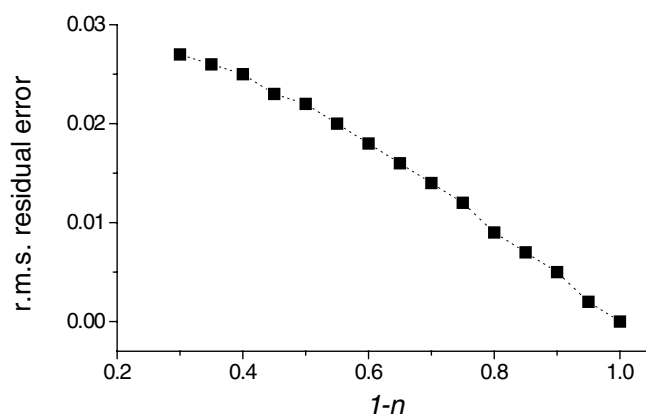


**Figure 1.** The stretching exponent  $\beta$  for the best fit of  $H(t)$  to a stretched exponential function as a function of the stretching exponent  $1 - n$  of the molecular relaxation function  $h(t)$ . The broken curve is only to guide the eye.



**Figure 2.** The relaxation time  $\tau_s$  of the best fit of  $H(t)$  to a stretched exponential function as a function of the stretching exponent  $1 - n$  of the molecular relaxation function  $h(t)$ , for which  $\tau_0 = 1$ . The broken curve is only to guide the eye.

The results of our calculations, for values of  $1 - n$  between 0.3 and 1, are shown in figures 1 and 2. As is to be expected for simple exponential relaxation, the fit to equation (12) was perfect for  $n = 0$ , with  $\beta = 1 - n = 1$  and  $\tau_s/\tau_0 = 1$ . As the stretching exponent  $1 - n$  of the elementary function decreases, that of the best fit,  $\beta$ , also decreases but more slowly, as can be seen from figure 1. In figure 2, we present  $\tau_s$  as a function of  $1 - n$ , and we see that the value of  $\tau_s$  increases steadily as  $1 - n$  decreases. In all our calculations, we measured time in units of  $\tau_0$ , i.e. we set  $\tau_0 = 1$ . The quality of the fit of  $H(t)$  to the stretched exponential function became progressively worse as  $1 - n$  decreased and in figure 3 we show the rms residual error in the fit of  $\ln[H(t)/H(t_0)]$  to  $[(t_0/\tau_s)^\beta - (t/\tau_s)^\beta]$  as a measure of the accuracy of the fit of the actual  $H(t)$  to the stretched exponential form. As can be seen from this figure, even for  $1 - n = 0.3$ , this error is less than 0.03, which corresponds to a 3% difference between the fitted and actual values of  $H(t)$ .



**Figure 3.** The rms residual error in the fit of  $\ln[H(t)/H(t_0)]$  to  $[(t_0/\tau_s)^\beta - (t/\tau_s)^\beta]$  as a function of the stretching exponent  $1 - n$  of the molecular relaxation function  $h(t)$ . The broken curve is only to guide the eye.

Finally we consider the relationship between our results and those of the DRT approaches. If  $H(t)$  were due to a set of simple relaxers with a distribution  $g(\tau)$  of relaxation times  $\tau$ ,

$$H(t) = \int_0^\infty g(\tau) \exp(-t/\tau) d\tau, \quad (13)$$

then the mean relaxation time  $\langle\tau\rangle$  for  $H(t)$  would be  $\int_0^\infty H(t) dt$ . For the stretched exponential form of equation (11), it is given by

$$\langle\tau\rangle = \Gamma(1/\beta)\tau_s/\beta. \quad (14)$$

The main reason for using  $\langle\tau\rangle$  as an indication of the timescale of the rate of decrease of the relaxation functions is that it can readily be compared with the corresponding quantity for  $H_{DRT}(t)$ , which we denote by  $\langle\tau_{DRT}\rangle$ . In view of equations (5) and (7),  $\langle\tau_{DRT}\rangle$  is given for our system by

$$\langle\tau_{DRT}\rangle = \int_0^\infty h(t) dt, \quad (15)$$

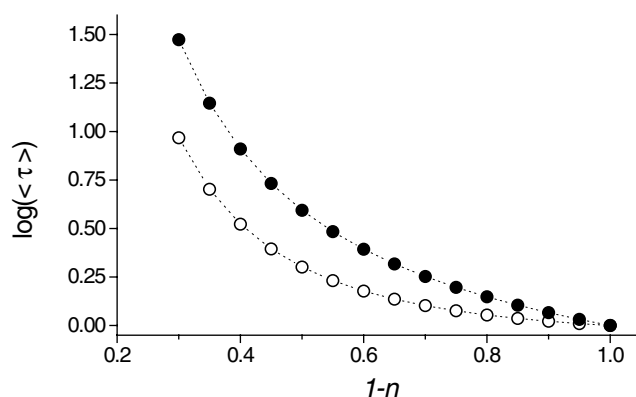
and so to a very good approximation by equation (14) with  $1 - n$  in place of  $\beta$  and  $\tau_0$  in place of  $\tau_s$ . Incidentally, in view of equation (15), for our model system  $\langle\tau_{DRT}\rangle$  is equal to  $\langle\tau\rangle$  for the relaxation function of the individual molecules  $h(t)$ , but this result will not be true in general.

#### 4. Discussion

We now turn to a brief discussion of the physical reasons for the results presented above, in addition to the basic result that the relaxation function of the system differs from that of the individual molecules, and why they can be expected to be valid quite generally.

The first key feature of our results is that when the molecular relaxation function is non-exponential, with a transition rate  $w(t)$  that does not increase with time, then the relaxation function of the system decays more slowly than the molecular one, and at a rate which increases as the stretching exponent  $1 - n$  decreases, as can be seen from figures 2 and 4. The reason for this is that at any given time  $t$  the system's relaxation function contains contributions from a distribution of molecules with instantaneous relaxation times  $1/w(t + t')$ , where  $t' > 0$ , and at least some of these are longer than that of the molecular relaxation function,  $1/w(t)$ , so





**Figure 4.** The mean relaxation times  $\langle \tau \rangle$  for  $H(t)$  of the system (filled circles) and for  $H_{DRT}(t)$  (empty circles), which for our model system is the same as that for  $h(t)$ . The broken curves are only to guide the eye.

the average relaxation time of the system at any instant is longer than that of the molecular relaxation function. This effect should become more pronounced as the rate of decrease of  $w(t)$  becomes more rapid, and so for the stretched exponential relaxation as  $n$  increases and so as the stretching exponent  $1 - n$  decreases, in view of equation (9), and the results shown in figures 2 and 4 agree with this.

The other point that we wish to consider is the difference between the system's actual relaxation function  $H(t)$  and that  $H_{DRT}(t)$  of a system of particles having simple exponential relaxation functions with the same DRT as that of the molecules in the actual system. As can be seen from figure 4  $H_{DRT}(t)$  has a smaller value of  $\langle \tau \rangle$  than does  $H(t)$ , i.e. it decays more rapidly with time than does  $H(t)$ . This is to be expected, since in  $H_{DRT}(t)$  an exponential relaxation is associated with each transition time, whereas in  $H(t)$  the much slower molecular relaxation function (in our case, a stretched exponential function) is associated with it. The important point about this result, and the reason for performing the associated calculations, is that it shows that if a DRT is used to describe the system's actual relaxation function  $H(t)$  then the distribution of relaxation times  $g(\tau)$  appearing there have no direct connection with that of the actual instantaneous relaxation times of the molecules in the system, as used in  $H_{DRT}(t)$ . Thus while the DRT approach has some formal value [5], it does not necessarily provide reliable information about the microscopic properties of the system, such as the degree of microscopic inhomogeneity in it.

## 5. Conclusions

We conclude that a critical consideration of the initial conditions for the system is of vital importance for predicting from any specific microscopic model the behaviour of the relaxation function of a system. Our analysis shows that any system in which the individual molecules exhibit non-exponential relaxation will be inhomogeneous at any instant of time. As a result, the relaxation function of the whole system is not the same as that of the individual molecules, and the difference between them increases with increasing non-exponentiality of the molecular relaxation function. As an example of the application of our approach, we found that, for a simple model system in which the relaxation function of the individual molecules is described by a stretched exponential function, the relaxation function of the system as a whole can often

be well approximated by a function of this form, but with a different stretching exponent and mean relaxation time. In addition, we showed that the analysis of a system's relaxation function in terms of a DRT does not necessarily provide reliable information about the system's microscopic properties.

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