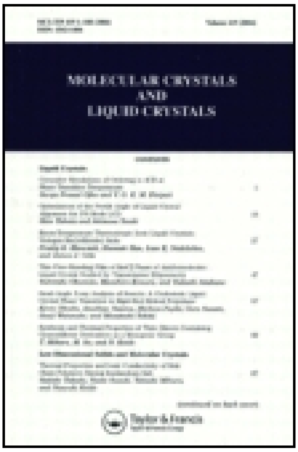

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Scalable Non-exponential Dielectric Response in Lecithin-Water Multilayers

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Data on the non-Debye dielectric relaxation of hydrated lecithin is analyzed. The fit to Cole-Cole and stretched exponential functions is poor, while the Cole-Davidson function gives a good fit to the data. This is consistent with the Dissado and Hill IR divergence theory of the dielectric response which implies that relaxation is due to proton hopping on finite connected hydrogen-bonded clusters. Alternatively it is possible that the non-Debye response is due to cooperative rotation of the head-groups and water dipoles.

INTRODUCTION

Many materials that contain adsorbed water and flexible molecules exhibit a maximum in the imaginary part of the dielectric function, ε''. For fully hydrated systems this peak occurs at about 100 MHz. In lecithin-water multilayers the dielectric dispersion in this frequency range has been attributed to the phospholipid head-groups.[1] Similar effects have been observed for biological tissue, hydrated proteins and DNA and are claimed to be due to bound water.[2] It seems likely that a cooperative response of the hydrogen-bonded water and head-group network is involved. We have studied the dielectric properties of lecithin-water multilayer dispersions as a function of water content.[3] The dielectric response in the viscinity of the peak was found to depend only on amplitude and the frequency of the maximum loss, f_0.[4] The peak frequency decreased by five orders of magnitude when lecithin samples were dehydrated to 5 weight percent water. It occurs at frequencies that vary from 10 kHz in samples containing 5 weight percent water to a few 100 MHz in fully hydrated samples.[1] The shape of the curves is independent of both temperature and concentration and was found to satisfy a time-temperature-concentration scaling principle. Low frequency loss peaks whose characteristic frequencies scale with water content have also been observed in protein samples.[5]

Although a Debye response has been obtained in some biological materials, the scalable response that we observed for lecithin multilayers is highly non-Debye. A dielectric response that is described by a single exponential decay in the time domain, $e^{-t/\tau}$, gives a dielectric function of the form $(\varepsilon_0 - \varepsilon_\infty)/(1 + i\omega\tau) + \varepsilon_\infty$ in the frequency domain. Here $i \equiv \sqrt{-1}$, $\tau \equiv 2\pi/f_0$, ω is angular frequency and ε_0

and ε_∞ are the low and high frequency limits of ε. The imaginary part of this Debye dielectric function goes as ω^{-1} for frequencies large compared to τ^{-1}, whereas we obtained a high frequency exponent of -0.37 ± 0.02 for phospholipid-water multilayers, and exponents close to $-1/2$ have been observed for water adsorbed on protein molecules. Thus the form of the dielectric function that we obtained indicates a response quite different from what would correspond to a single exponential decay in the time domain. However, the fact that the peak shifts in frequency by five orders of magnitude without any significant change in shape argues that the non-exponential decay is not the result of several independent relaxation processes. This type of non-Debye scalable dielectric behaviour has been identified in many heterogeneous and disordered solids and is referred to as the "universal dielectric response."[6]

In the remainder of this paper we will discuss a number of empirical functions and theories that describe non-exponential dielectric response. We will also present the results of curve fits to our lecithin-water data. Possible physical mechanisms responsible for the observed scalable non-exponential dielectric response in materials containing adsorbed water will then be discussed.

ANALYSIS AND DISCUSSION

Non-exponential dielectric response functions are obtained almost universally in polymeric and inhomogeneous materials and a number of different explanations of this phenomenon have been proposed. In Table I the mathematical form of the dielectric increment function and the low and high frequency exponents have been tabulated for some of the alternative theories and empirical functions.

The first four entries in Table I give the relatively simple functions that are often used to analyze dielectric data. The Debye function represents a system of dipoles rotating independently and subject to viscous resistance. The Cole-Cole, Cole-Davidson, and Havriliak-Negami functions are empirical and cannot in general be given a physical interpretation. They are included because it is often convenient for computational purposes to represent the results of theories associated with a definite physical model in terms of these functions.

A number of theories that use self-similarity arguments predict a stretched exponential dielectric response in the time domain. The defect diffusion model as proposed by Glarum and later clarified by Bordewijk[7] seems attractive in the context of a system of dipoles with restricted mobility such as is the case for the water and phospholipid head-group dipoles. In this model a dipole cannot relax until a mobile defect such as a broken hydrogen bond reaches it. For a three dimensional model the high frequency exponent is always -1, that is the Debye function is obtained, and in two dimensions the magnitude of this exponent is $-1/2$. The hierachial model of Palmer and co-workers[8] is based on the premise that there is a hierarchy of cluster sizes and a cluster cannot relax until an appropriate configuration of the next smaller group of clusters is reached. For stretched exponential solutions the number of clusters of a particular size scales as λ^{-n} after n iterations, and the relaxation time scales as a^n where λ and a are constants. The

TABLE I

Summary of functions and theories used in the analysis of our dielectric data

FUNCTION	EXPRESSION	exponent, p, in $\varepsilon'' \sim \omega^p$	
		LOW f	HIGH f
Debye	$\frac{1}{1 + i\omega\tau}$	+1	-1
Cole-Cole (CC)	$\frac{1}{1 + (i\omega\tau)^{\alpha}}$	$+\alpha$	$-\alpha$
Cole-Davidson (CD)	$\frac{1}{(1 + i\omega\tau)^{\beta}}$	+1	$-\beta$
Havriliak-Negami (NH)	$\frac{1}{(1 + (i\omega\tau)^{\alpha})^{\beta}}$	$+\alpha$	$-\alpha\beta$
Sum of exponentials	$\sum \frac{\Delta\varepsilon_n}{1 + i\omega\tau_n}$	+1	-1
stretched exponential	$\int \frac{d}{dt}\left(e^{-(t/\tau)^{\alpha}}\right) e^{i\omega t}\, dt$	+1	$-\alpha$
Bordewijk[7]	defect diffusion	+1	-1 in 3D -1/2 in 2D
Palmer et al[8]	hierarchy of cluster sizes	+1	$-\left(1 - \frac{\ln\lambda}{\ln a}\right)$, $\tau \sim a^n$ $N \sim \lambda^{-n}$
Schlesinger[11]	fractal time	+1	$-\left(1 - \frac{\ln\lambda}{\ln a}\right)$
Niklasson[10]	clusters, fractal time, D_t	$\pm D_t$	$\frac{D}{D_w + \frac{D(1-D_t)}{D_t}}$
Dissado & Hill[9]	$\left(1+i\omega\tau\right)^{1-n} {}_2F_1\left(1-n, 1-m; 2-n; \frac{1}{1+i\omega\tau}\right)$	m (inter) cluster distribution	-(1-n) (intra)
Nee & Zwanzig[12]	dielectric friction ≈CD	+1	-0.6
Bagchi & Chandra[13]	diel. fr., no diffusion ≈CC	+0.6	-0.6
our data[3,4]			-0.37

high frequency exponent referred to in Table I is also the exponent α in the stretched exponential function, $e^{-(\omega\tau)^{\alpha}}$, and is given by $-(1 - \ln(\lambda)/\ln(a))$.

Dissado and Hill[9] have developed a model based on the relaxation of clusters which interact so that both intra- and inter-cluster relaxation processes occur. They propose that water clusters are polarized by a succession of proton transfers within a hydrogen bonded network. Effective proton transfer over distances greater than the cluster correlation length requires an intercluster exchange process. In the limit where the intercluster exponent equals unity, the Cole-Davidson function is obtained. However, their physical mechanism involves clusters being polarized by mobile ions and does not imply dipole rotation.

Niklasson[10] has proposed a fractal model for the dielectric properties of disordered materials that incorporates polarization of finite and infinite clusters as well as fractal time processes. Fractal time processes can arise from multiple trapping and trap controlled hopping. (Schlesinger[11] has reviewed fractal time processes and discussed university of the stretched exponential function.) The power law at low frequencies is due to fractal time processes, while the high frequency power law depends on fractal time and conduction on a fractal structure. The crossover between these two power laws regions corresponds to the correlation length of the material. A peak in ε'' implies the existence of finite clusters. This model of the physics of the process is compatible with Dissado and Hill's theory, although the form of the crossover function is not given by Niklasson.

If dielectric friction is included, the response of a system of identical dipoles is non-Debye, that is non-exponential in the time domain. Nee and Zwanzig[12] studied rotational diffusion in two dimensions and concluded that the dielectric properties of such a system of dipoles can be approximated by a Cole-Davidson function with $\beta = 0.6$. It has recently been concluded by Bagchi and Chandra[13] that the exponential response observed for liquids arises because these molecules can diffuse as well as rotate. Thus the reduced diffusion rate of the lipid and water molecular in lecithin-water dispersions of low water content could account for their non-Debye dielectric response. Bagchi and Chandra solved hydrodynamic equations numerically and found that, for a three dimensional system of dipoles with no diffusion, the dielectric response can be approximated by a Cole-Cole function with $\alpha = 0.63$.

In Figures 1(a) to (c) the results of curve fits to the lecithin-water data are plotted for Cole-Cole, stretched exponential, and Cole-Davidson functions. A term proportional to $(i\omega\tau)^{-p}$ has been included to account for the rise in ε'' at low frequency. The magnitude of the exponent, p is close to 0.9 as discussed in Reference 3. The functions used to fit the data were of the form

$$\varepsilon(\omega)/\varepsilon_0 = A(i\omega)^{-p} + (\Delta\varepsilon/\varepsilon_0)\,F(\omega\tau, q) + \varepsilon_\infty/\varepsilon_0.$$

Here $F(\omega\tau, q)$ is one of the functions in the second column of Table I and q is the high frequency exponent given in the last column of Table I. The real part of ε was also used in the curve fits, but deviations were small and ε' is not shown in the plots in Figure 1. The shape of the ε'' versus frequency curve has been shown to be universal[4] and only data representative of the master curve in Reference 4

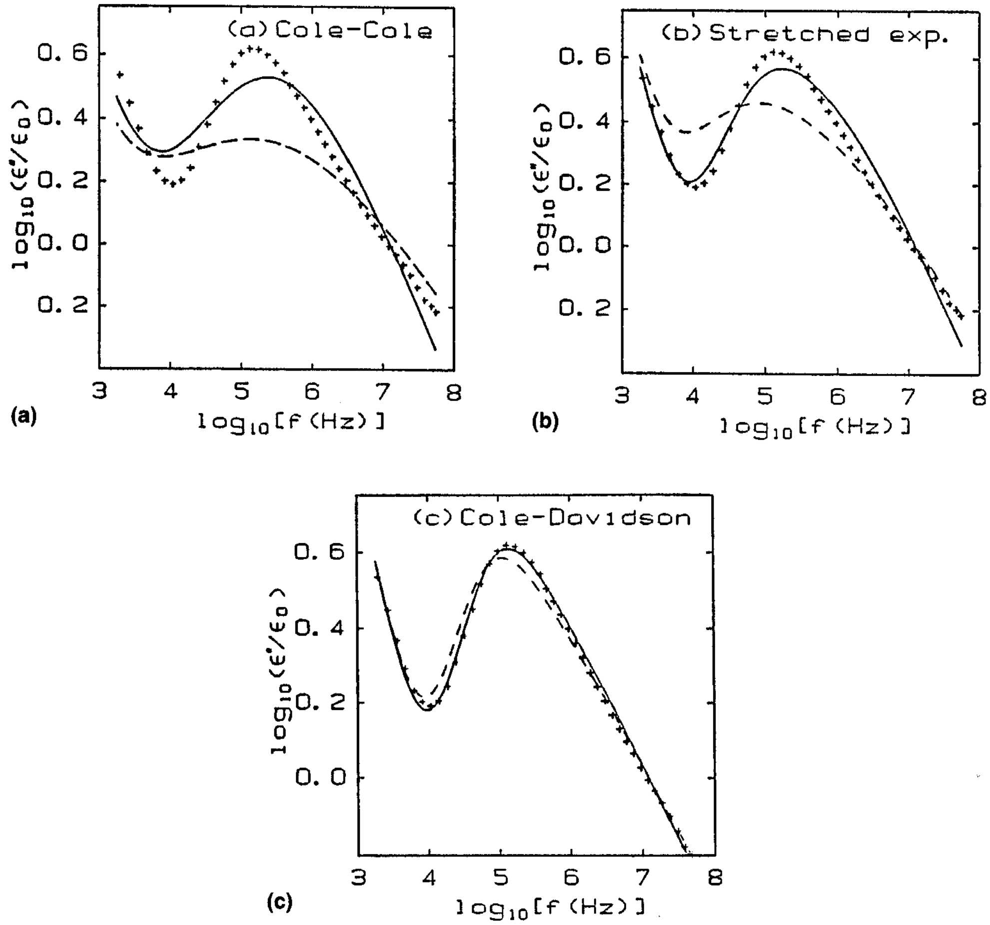

FIGURE 1 Fits to ε″ versus frequency data for lecithin-water multilayers presented as log-log plots. The functions used as given in Table I are (a) the Cole-Cole, (b) the stretched exponential and (c) the Cole-Davidson functions as indicated. The crosses are a representative set of the data points given in Reference 4, and the solid lines are the best fit obtained using the Simplex algorithm. The dashed lines are calculated using the same functions as for the solid lines, but with the additional constraint that the curve should asymptotically fit the data at high frequency.

is shown. The crosses represent the data and, for clarity, only enough points to define the curve have been included. The solid curve represents the best fit to the data obtained using the Simplex algorithm for non-linear curve fitting. The parameters corresponding to the best fit are given in Table II. For the dashed curve it was required that high frequency slope fit the data. This is probably a necessary condition if the correct physical interpretation is to be identified. The above functions were chosen for computational convenience, since they have been used to describe the results of various theories, as discussed above. Numerical values of the stretched exponential in the frequency domain were obtained by the method of Macdonald and Hunt.[14]

It is clear from Figure 1 that the symmetric Cole-Cole function and the stretched

TABLE II

Parameters obtained from the Simplex algorithm as the best fit to our lecithin data

FUNCTION	p	A	q	$\Delta\varepsilon/\varepsilon_0$	$\tau(10^4 s)$	$\varepsilon_\infty/\varepsilon_0$
Cole-Cole	0.90	1150	0.571	13.9	15	5.78
Cole-Davidson	0.925	3760	0.384	13.1	5	5.26
stretched exponential	0.946	4250	0.504	13.1	15	5.64

exponential function do not describe our lecithin-water multilayer data very well. We have also tried a sum of exponentials with little success. However, the Cole-Davidson function is a good, though not perfect, match to our data. This seems to eliminate all but two of the possible explanations presented here. Relaxation of a two dimensional system of dipoles, subject to dielectric friction but unable to diffuse would give qualitative agreement, although the magnitude of the high frequency exponent predicted by this model is too large by a factor of almost two. Dissado and Hill's theory appears to be in the best agreement with our data, even without the introduction of an extra parameter to describe the low frequency slope. Introduction of this as an adjustable exponent should produce a fit to within the uncertainty of our experiment.

CONCLUSION

Our dielectric data for lecithin-water multilayer dispersions are *not* consistent with models based on (i) a sum of independent or loosely coupled exponential relaxation processes, (ii) a symmetric dielectric response function such as the Cole-Cole function which is predicted for a three dimension system of dipoles in the absence of diffusion, or (iii) a stretched exponential dielectric response. A two dimensional dipole rotation model including dielectric friction seems to be a plausible explanation. Fractal time process could be introduced to reduce the magnitude of the high frequency exponent. The non-Debye nature of the relaxation process may be due in part to the low diffusion rates of the head-groups and water dipoles. In this case dielectric friction give a high frequency exponent of about -0.6.[12,13]

The best match to our data is obtained with Dissado and Hill's cluster model where the low frequency exponent is close to unity, implying highly irregular clusters. In this limit the Dissado and Hill result reduces to the Cole-Davidson function and all the mathematical forms that we used for curve fitting contain the same number of adjustable parameters. However, if this is the correct model, the apparent dielectric relaxation in lecithin-water multilayers is not due to rotation of phospholipid head-groups or water molecules, but rather to proton hopping that polarizes connected clusters of hydrogen bonded groups. Niklasson's fractal model is also compatible with our results, though less specific, and presents a similar physical picture of polarization of clusters. These cluster models suggest that the process responsible for the peaks in ε'' peak is connected to the critical effects studied by Careri and co-workers,[15] and implies the existence of a percolation threshold.

References

1. J. C. W. Shepherd and G. Büldt, *Biochim. Biophys. Acta*, **83**, 514 (1978).
2. S. Mashimo, S. Kuwabara, S. Yagihara and K. Higasi, *J. Phys. Chem.*, **91**, 6337 (1987).
3. M. H. Hawton and W. J. Keeler, *J. Appl. Phys.*, **64**, 5088 (1988).
4. M. H. Hawton and W. J. Keeler, *Phys. Rev. A*, **41**, 2218 (1990).
5. J. Eden, P. R. C. Gascoyne and R. Pethig, *J. Chem. Soc.*, Faraday Trans. 1, **76**, 426 (1980).
6. A. K. Jonscher, *Dielectric Relaxation in Solids* (Chelsea Dielectrics Press, London, 1983).
7. J. Bordewijk, *Chem. Phys. Lett.*, **32**, 592 (1975).
8. R. G. Palmer, D. L. Stein, E. Abrahams and P. W. Anderson, *Phys. Rev. Lett.*, **53**, 958, 958 (1984).
9. L. A. Dissado and R. M. Hill, *J. Chem. Soc.*, Faraday Trans. 2, **80**, 291 (1984), *Chem. Phys.* **111**, 193 (1987).
10. G. A. Niklasson, *J. Appl. Phys.*, **62**, R1 (1987).
11. M. F. Schlesinger, *J. Stat. Phys.* **36**, 639 (1984).
12. T.-W. Nee and R. Zwanzig, *J. Chem. Phys.*, **52**, 6353 (1970).
13. B. Bagchi and A. Chandra, *Phys. Rev. Lett.*, **64**, 455 (1990).
14. J. R. Macdonald and R. L. Hunt, *J. Appl. Phys.*, **84**, 496 (1986).
15. G. Careri, A. Giansanti, and J. A. Rupley, *Phys. Rev. A*, **37**, 2703 (1988).