

Comment on "Scaling in the Relaxation of Supercooled Liquids"

In a recent Letter Dixon, Wu, Nagel, Williams, and Carini¹ report dielectric-susceptibility measurements of several glass-forming liquids over 13 orders of magnitude in frequency. They introduce a scaling procedure by which all data, from all samples at all temperatures, collapse onto a single master curve. This curve unequivocally differs from all previously published relaxation functions. We have recently developed a model for the relaxation of dispersive excitations (magnons, phonons, polaritons, etc.) on a random distribution of finite clusters. We have shown that this model provides excellent agreement with the observed magnetic relaxation of random magnetic systems² and stress relaxation of ionic glasses.³ Here we show that this model may also explain the universal scaling reported in Ref. 1.

For our model we assume that a given particle belongs to a finite cluster containing s particles with probability sn_s , and that each cluster relaxes independently with a size-dependent rate w_s . For uniform initial polarization P_0 , the net relaxation is the sum over all possible cluster sizes $P(t) = P_0 \sum_s s (sn_s) e^{-w_s t}$ (note the second moment of n_s is used assuming a variable number of participating particles). The Fourier transform of $-dP(t)/dt$ gives the complex susceptibility:

$$\epsilon(\omega) = P_0 \sum_s s (sn_s) (1 + i\omega/w_s) / [1 + (\omega/w_s)^2]. \quad (1)$$

The principal result of Ref. 2 is that excellent agreement with observed behavior is obtained for relaxation rates which vary exponentially with inverse cluster size ($w_s = w_0 e^{C/s}$), characteristic of finite-size quantized dispersive excitations. Here w_0 is the relaxation rate of an infinite cluster, and C is a function of the average cluster size times the average interaction between particles divided by $k_B T$. In Ref. 2 we use the distribution of cluster sizes from percolation theory: $n_s \sim s^{-\theta} \exp(-s^\delta)$, where the scaling exponents for concentrated three-dimensional systems on a fixed lattice are $\theta = -\frac{1}{9}$ and $\delta = \frac{2}{3}$. Assuming a similar distribution, the extraordinary quality and range of data from Ref. 1 allow experimental determination of these exponents for cluster sizes in supercooled liquids. We find $\theta = -1.6 \pm 0.5$ and $\delta = 3.0 \pm 0.5$ for salol at the six temperatures reported in Ref. 1. Once these exponents have been determined (θ and δ must be similar for systems which scale as reported in Ref. 1), all data can be fitted using Eq. (1) with three adjustable parameters: P_0 , w_0 , and C . The single parameter C controls the width and shape of the entire dynamic response. For $C \approx 0$ (weakly interacting particles or high temperatures) Eq. (1) yields single-relaxation-rate Debye-like behavior, whereas for $C \gg 1$ the spectrum is extremely broad.

Using Eq. (1), least-squares fits to the dielectric susceptibility of salol at 219, 225, 233, 243, 255, and 290 K yield $C = 4.7, 4.5, 4.3, 4.0, 3.3,$ and 1.5 , respectively. Figure 1 shows the data (dots) and fitting functions

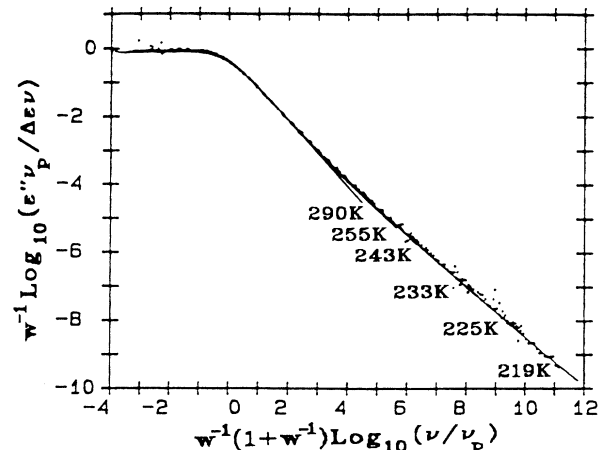


FIG. 1. Scaling plot for the imaginary part (ϵ'') of the dielectric susceptibility of salol (dots) and fitting functions (solid curves). The fitting functions for the five temperatures 219–255 K show excellent agreement with the master curve reported in Ref. 1. Deviation of the 290-K fitting function (which has been extrapolated to 100 GHz) is indicative of the approach to Debye behavior.

(solid curves) scaled as prescribed in Ref. 1. For 219–255 K the fitting functions qualitatively and quantitatively reproduce the master curve, demonstrating that the scaling procedure accurately compensates for changes in width and shape as C varies from 4.7 to 3.3. For 290 K, the fitting function (which has been extrapolated to 100 GHz) shows deviations indicative of the approach to Debye behavior.

Our model for relaxation of finite-size quantized dispersive excitations is not a microscopic theory. Nevertheless, it does provide a general mechanism linking fundamental excitations to observed behavior. Using our model, the universal dynamic response reported in Ref. 1 may be explained by scaling of finite cluster sizes in supercooled liquids.

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Ralph V. Chamberlin

Department of Physics, Arizona State University
Tempe, Arizona 85287-1504

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¹P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams, and J. P. Carini, *Phys. Rev. Lett.* **65**, 1108 (1990).

²R. V. Chamberlin and D. N. Haines, *Phys. Rev. Lett.* **65**, 2197 (1990).

³R. V. Chamberlin, D. N. Haines, and D. W. Kingsbury, in *Proceedings of the International Discussion Meeting on Relaxation in Complex Systems, Crete, Greece, 1990* [J. Non-Cryst. Solids (to be published)].