

## Universal Scaling of the Relaxation near a Model Glass Transition

Diandra L. Leslie-Pelecky and Norman O. Birge

*Department of Physics and Astronomy and Center for Fundamental Materials Research, Michigan State University,  
East Lansing, Michigan 48824-1116*

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We report dielectric measurements of the orientationally disordered crystalline phase of cyclo-octanol over the frequency range 1.3 mHz–5.5 kHz. The data show that cyclo-octanol exhibits a slow relaxation that is indistinguishable in every respect from that exhibited by a supercooled liquid near its glass transition. In particular, the data obey a scaling relationship reported by Nagel and co-workers for a variety of structural glasses. These results show that cyclo-octanol is an ideal model system for studies of the glass transition, and suggest that the scaling relationship is far more universal than expected.

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A structural glass is formed by supercooling a liquid past its liquid-to-crystal phase transition, and continuing to cool until the viscosity is immeasurably large. A wide variety of measurement techniques, including dielectric and mechanical relaxation, specific heat and others, have been used to study the approach to the glass transition [1]. These techniques reveal the presence of two features common to all glass-forming liquids: a nonexponential relaxation toward (metastable) equilibrium, and a rapidly increasing relaxation time as the temperature is lowered. Although these general features are similar for all materials, the details of the behavior vary. The observed relaxational behavior does not obey a simple dependence on time or frequency, and the shape of the relaxation varies with temperature, material, and even in measurements of the same material using different experimental probes.

Despite the observation of these two signature features in numerous materials and much theoretical work, there is still no accepted fundamental theory of the glass transition. In this paper, we focus on two experimental approaches aimed at providing a greater understanding of the glass transition. The first approach is a search for “universal” laws characterizing a wide variety of glass-forming materials [2,3]. Böhmer *et al.* [2], in categorizing over 70 glasses and glasslike materials, have demonstrated that there exists a strong correlation between the “fragility” [4] of the material, defined by the temperature dependence of the relaxation time, and the departure from exponential behavior of the relaxation near the glass transition. This correlation is useful for classifying types of materials, and more importantly for determining which materials deviate from “typical” glass-forming behavior; however, it does have limitations. Not only do the details of the two general properties observed in glass formers cover a wide range of behaviors, but the degree of nonexponentiality can depend on the choice of experimental probe, even when measuring a single material. A stronger form of universality was discovered recently by Dixon, Wu, Nagel, Williams, and Carini [5], who found that relaxational data from several organic glass formers over a very wide range of temperature and frequency could be collapsed onto a scaling curve parametrized by the peak position and width of the relaxation. Although

the form of the scaling relationship does not yet have a theoretical underpinning, it suggests a degree of universality not anticipated by any previous work.

The second experimental approach toward understanding the glass transition is based on studying model systems—materials that exhibit a glasslike transition but lack the complexity of true (structural) glasses. Examples of such materials are the orientationally disordered crystals [6,7] such as cyclohexanol [8]. [There are also classes of orientationally disordered crystals, such as  $(\text{KBr})_{1-x}(\text{KCN})_x$ , that have quenched randomness. Experimental [2] and theoretical [9] evidence suggests that such materials fall in a different “universality class” than homogeneous systems, which include most structural glass formers.] In orientationally disordered crystals, the molecules are translationally ordered, limiting the dynamical behavior to the rotational and conformational degrees of freedom. Restriction of the relevant degrees of freedom should, in principle, facilitate theoretical modeling of the material and the accompanying transition. Detailed studies of model glasses may lead to an understanding of which aspects of the glass transition behavior are the most “universal,” and which depend on the microscopic particulars of the material being studied.

We have measured the complex dielectric susceptibility,  $\varepsilon = \varepsilon' - i\varepsilon''$ , of the orientationally disordered phase of cyclo-octanol ( $\text{C}_8\text{H}_{15}\text{OH}$ ) near its glasslike transition [10]. Our data show that this material exhibits all of the characteristics of a typical structural glass former near the glass transition. The dielectric relaxation is nonexponential, and can be approximated by standard [e.g., Cole-Davidson [11] or Kohlrausch-Williams-Watts [12] (KWW)] phenomenological fitting forms, with the width of the relaxation increasing slightly with decreasing temperature. The rapid decrease of the peak frequency of the relaxation with decreasing temperature is described by the Vogel-Tamman-Fulcher [13] (VTF) expression. The width parameter of the KWW form,  $\beta$ , and the fragility index derived from the VTF expression obey the correlation observed by Böhmer *et al.* [2] for structural glasses. Our most striking result is that the dielectric data obey the scaling relationship developed by Nagel and co-workers [5], and furthermore, that the precise

form of the scaling curve is remarkably similar to that found for organic structure glass formers. Our results show not only that cyclo-octanol is an ideal model system for glass transition studies, but more importantly that the scaling form reported by Dixon *et al.* [5] may be far more universal than they imagined.

Cyclo-octanol has three solid phases. As the sample is cooled below the freezing temperature, the centers of mass of the cyclo-octanol molecules order on an fcc lattice; however, the molecules retain their ability to reorientate via rotations about the center of mass. This orientationally disordered phase  $S_I$  is the subject of our measurements. If the sample is allowed to cool slowly from  $S_I$ , a transition to a second orientationally disordered phase,  $S_{II}$ , is observed. In  $S_{II}$ , the allowed reorientations of the molecules are restricted to those about an axis with zero dipole moment [14]. A transition to  $S_{III}$ , the state in which the dipoles are fully ordered, is observed on continued slow cooling. The transitions to  $S_{II}$  and  $S_{III}$  may be bypassed by supercooling. As the temperature of the supercooled orientationally disordered phase,  $S_I$ , is decreased, the molecular reorientation degrees of freedom gradually slow down, eventually undergoing a glasslike transition. Further detailed information on the phase diagram and cooling protocols will be reported elsewhere [15].

We measure the dielectric susceptibility of cyclo-octanol using a cylindrical capacitor in a sample cell similar to that of Adachi *et al.* [16]. Measurements of the orientationally disordered phase span a frequency range from 1.3 mHz to 5.5 kHz and temperatures from 166 to 205 K. Figures 1(a) and 1(b) show the real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the dielectric susceptibility as a function of frequency for temperatures of 170, 175, 180, 190, and 205 K. The solid lines are fits to the Kohlrausch-Williams-Watts (KWW) function, which is the Fourier transform of the time-domain response  $\phi(t) \propto \exp[-(t/\tau)^\beta]$ . Although a reasonable fit to  $\epsilon''$  is obtained near the peak, the KWW function disagrees with the data in the high-frequency tails. [The inability of the KWW form to adequately represent the data over the entire frequency range will become more apparent when the data are plotted on the scaling plot of Fig. 4(a).] Although dc conductivity is observed in cyclo-octanol, contributions from this effect are negligible in the temperature and frequency range over which the data are analyzed.

The dielectric response curves of Fig. 1 are characterized by three temperature-dependent quantities: the peak frequency,  $f_p$ , the width  $w$ , and the relaxation strength,  $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$ . ( $\epsilon'$  also depends on  $\epsilon_\infty$ .) The width  $w$  is normalized by the width of a Debye relaxation (1.14 decades), and can be accurately estimated from the value of  $\beta$  obtained from the KWW fit:  $1 - \beta = 1.047(1 - w^{-1})$  [17]. Figures 2(a) and 2(b) show the dependence of the peak frequency and width on inverse temperature. Figure 2(a) demonstrates the rapid increase of the

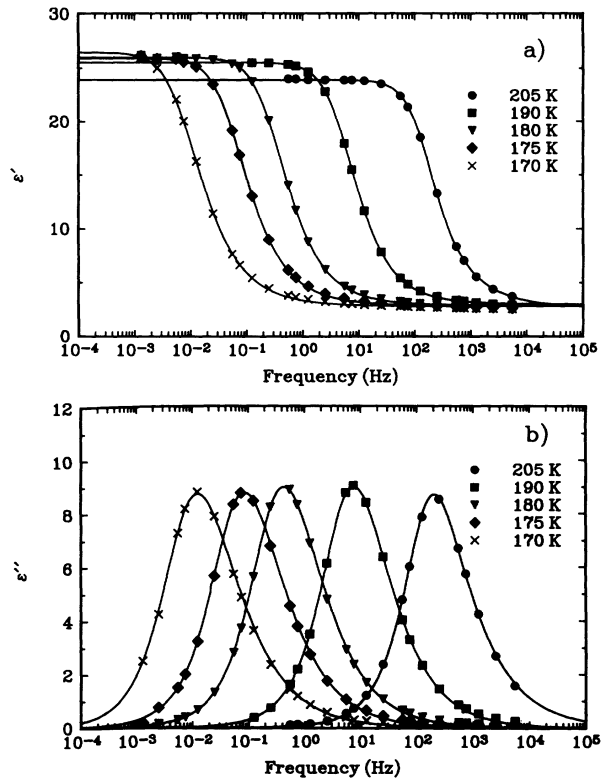


FIG. 1. (a)  $\epsilon'$  and (b)  $\epsilon''$  versus frequency for temperatures of 170, 175, 180, 190, and 205 K. Solid lines represent fits to the KWW function.

mean relaxation time as the glass transition temperature is approached. The solid line represents a fit to the Vogel-Tamman-Fulcher form  $f_p = f_0 \exp[A/(T - T_0)]$  with  $T_0 = 95$  K. This corresponds to an intermediate fragility, with fragility parameter  $m = 33$  [18]. Figure 2(b) shows that the width of the relaxation increases with decreasing temperature. The values of  $m$  and  $\beta$  satisfy the relationship [19] found by Böhmer *et al.* [2] for a wide variety of glass and glasslike materials. These results confirm that the glasslike transition in cyclo-octanol displays the same general behavior as that found near the transition in structural glasses.

Although the KWW form is useful for extracting values for the width and peak frequency, this form does not accurately describe the data at high frequencies. A variety of forms describing the shape of the dielectric relaxation have been proposed [3,20]. Rather than search for the "correct" fitting function, an alternative approach toward understanding the relaxation is to search for universality in the shape of the relaxation over a broad range of temperature, frequency, and possibly different materials. A natural starting point is to check whether the data obey "time-temperature superposition"—i.e., if the relaxation curves are shifted so that their peaks line up, the data for all temperatures and frequencies would lie on a single curve. The variation of the width param-

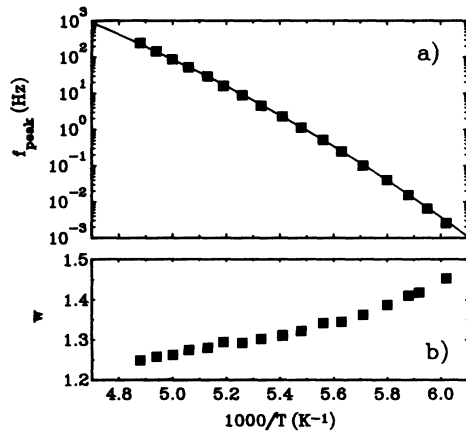


FIG. 2. (a) The peak frequency,  $f_p$ , and (b) the width,  $w$ , of the dielectric relaxation as functions of  $1000/T$ . The solid line in (a) is a fit to the VTF form, with  $f_p = 2.2 \times 10^{11}$  Hz,  $A = 2286$  K, and  $T_0 = 95$  K.

ter,  $w$ , with temperature indicates that our data do not obey this relation. To attempt to compensate for the temperature-dependent width, we can divide the abscissa by the width and simultaneously normalize the ordinate by the relaxation strength. Figure 3, a plot of  $\log_{10}(w\epsilon''/\Delta\epsilon)$  vs  $(w^{-1})\log_{10}(f/f_p)$ , shows that although the peaks and widths of the relaxation curves coincide, there is systematic scatter at high frequencies.

Dixon *et al.* [5] showed that a plot of  $w^{-1}\log_{10}(\epsilon''f_p/\Delta\epsilon f)$  vs  $w^{-1}(1+w^{-1})\log_{10}(f/f_p)$  collapses dielectric relaxation data from 6 different glass formers onto a single scaling plot valid over 13 decades of frequency. There is disagreement as to whether the same scaling form is valid for low-molecular-weight glass-forming polymers [21]. Figure 4(a), a scaling plot of our cyclo-octanol data after Ref. [5], shows that this scaling form successfully collapses the dielectric susceptibility data from all temperatures and frequencies onto a single line. The disagreement of the solid line, which represents the KWW fit with  $\beta = 0.70$  [22], and the scaled data confirm that the KWW form does not adequately describe the relaxation in cyclo-octanol. The success of this scaling form indicates that the glasslike transition in cyclo-octanol exhibits the same characteristics as the glass transition in structural glasses. We suggest that cyclo-octanol is therefore a strong candidate as a model system for studies of the glass transition.

Having demonstrated that this scaling form produces self-consistent results within data for one material, we compare the shape of the scaling plot of cyclo-octanol with that found for organic structural glass formers. Figure 4(b) plots a subset of the data in Fig. 4(a) as circles, along with the analogous data for glycerol (from Ref. [5]), which are shown as squares. Figure 4(b) shows that not only do the dielectric data of cyclo-octanol obey the scaling relationship of Dixon *et al.* [5], but that the precise forms of the scaling plots for the two materials are

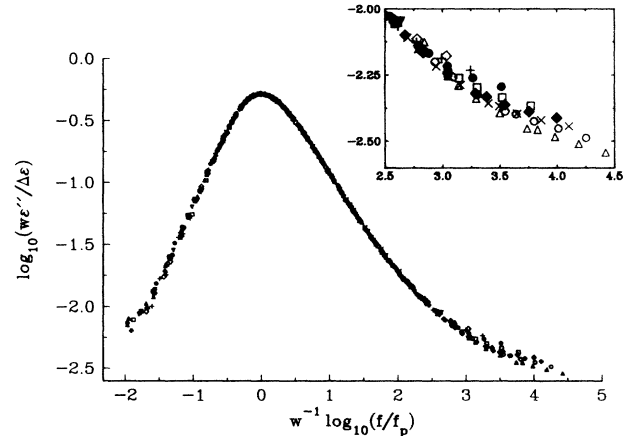


FIG. 3. Scaling plot of  $\log_{10}(w\epsilon''/\Delta\epsilon)$  vs  $w^{-1}\log_{10}(f/f_p)$ . This simple scaling form forces the peaks and widths of the data sets taken at different temperatures to coincide, however, there are systematic deviations from scaling in the high-frequency tails. The inset expands the data for large abscissa values, demonstrating systematic deviations with temperature. The symbols correspond to 166 K ( $\Delta$ ), 168 K ( $\circ$ ), 169 K ( $\times$ ), 170 K ( $\blacklozenge$ ), 172.5 K ( $\square$ ), 175 K ( $\bullet$ ), 177.5 K ( $+$ ), and 180 K ( $\diamond$ ).

remarkably similar. At large values of the abscissa variable the cyclo-octanol data lie slightly above the glycerol data. This difference is most likely due to the shifting of the peak frequency to the lower limits of our measuring apparatus. The lack of data on both sides of the peak in  $\epsilon''$  causes an uncertainty in determining the width of the relaxation, which may account for the small discrepancy. The success of the scaling form in representing data for systems as different as cyclo-octanol and glycerol suggests that the scaling form proposed by Dixon *et al.* [5] is much more universal than originally thought.

In structural glasses, the slow degrees of freedom include both translational and rotational motions of the constituent molecules. Considering the multitude of molecular motions involved, it is surprising that the primary relaxation of many structural glass formers is relatively narrow. The coincidence of the peak frequencies measured by disparate probes shows that the translational diffusion is governed by the same relaxation time as the molecular reorientations in many glass formers [23]. In contrast to structural glasses, the slow degrees of freedom in the orientationally disordered phase of cyclo-octanol include only rotational and conformational modes. We find it remarkable that the detailed shape of the relaxation function in these two disparate classes of materials is so similar.

In conclusion, dielectric measurements have demonstrated that the glasslike transition in orientationally disordered cyclo-octanol exhibits all of the characteristics observed in structural glass-forming liquids, despite the presence of translational order. The scaling form developed by Nagel and co-workers [5] accurately describes the relaxational behavior of cyclo-octanol over all experi-

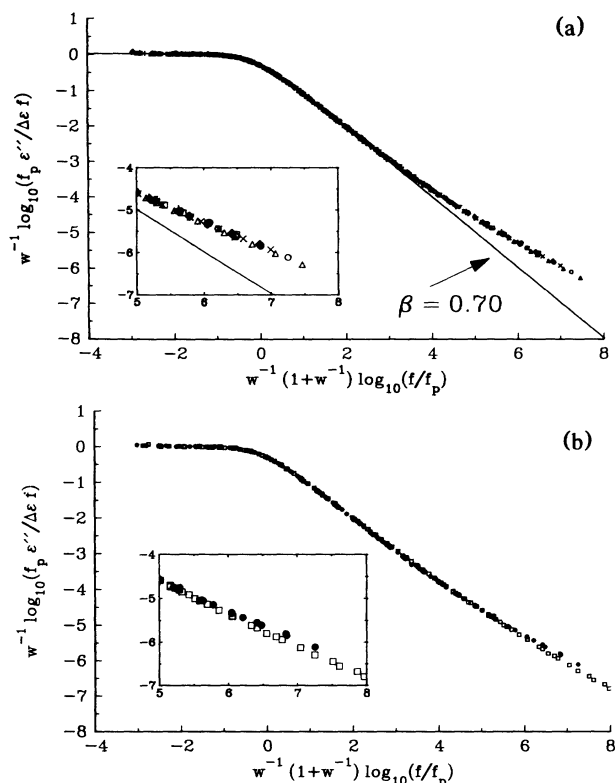


FIG. 4. Scaling plot of  $w^{-1} \log_{10}(\epsilon'' f_p / \Delta \epsilon f)$  vs  $w^{-1}(1 + w^{-1}) \log_{10}(t/f_p)$  after Dixon *et al.* [5]. (a) Data from cyclo-octanol. The solid line represents a fit to the KWW function with  $\beta = 0.70$ . The inset expands the scale at large values of the abscissa. The symbols correspond to 166 K ( $\Delta$ ), 168 K ( $\circ$ ), 169 K ( $\times$ ), 170 K ( $\blacklozenge$ ), 173.5 K ( $\square$ ), 175 K ( $\bullet$ ), 177.5 K ( $+$ ), and 180 K ( $\diamond$ ). (b) Comparison of the scaled data from cyclo-octanol ( $\bullet$ ) and glycerol ( $\square$ , from Ref. [5]), showing the similarity of the detailed shape of the scaling form for the two materials. The inset shows a slight, but systematic discrepancy between the two materials at large values of the abscissa.

mentally accessible temperatures and frequencies. Even more importantly, the similarity of the details of the scaling plots for cyclo-octanol and glycerol indicate that this scaling form is more universal than previously suggested and may apply to relaxations in other types of materials. We conclude that cyclo-octanol is an ideal candidate for further experimental and theoretical attention as a model glass and that the scaling form described by Dixon *et al.* [5] should be investigated for applicability to even more disparate materials.

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