

# Dynamic light scattering study of nonexponential relaxation in supercooled $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$

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(Received 15 June 1989; accepted 24 August 1989)

We have performed depolarized dynamic light scattering (photon correlation) measurements on the ionic glass forming mixture  $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$  above its glass transition in the temperature range 68–86 °C. We find the relaxation function is a stretched exponential. The average relaxation time follows an Arrhenius temperature dependence and can be related to motions on a molecular scale. The width parameter  $\beta$  does not vary with temperature and is  $\beta = 0.40 \pm 0.05$ . Combination of our  $\beta$  data with other literature values shows that  $\beta$  evolves with temperature over a larger range. At high temperature,  $\beta$  crosses over from  $\beta = 1$  to  $\beta < 1$  at a temperature which matches well with where the viscosity first deviates from a power law behavior.  $\beta$  then evolves downward with lowering temperature and then settles at 0.4 roughly 30 °C above the glass transition  $T_g$ . This behavior corresponds well with recent theory relating the glass transition to the ramification of phase space but it implies that the percolation of phase space occurs well above  $T_g$ .

## I. INTRODUCTION

In a supercooled liquid molecular motions slow appreciably near the glass transition temperature  $T_g$ . This slowing down is evidenced by both the large increase in the viscosity and the rapid decrease in the rate at which the liquid relaxes following any departure from equilibrium. The manner in which glasses relax has been studied extensively using a variety of techniques including neutron spin echo,<sup>1</sup> ultrasonic,<sup>2</sup> Brillouin spectroscopy,<sup>3,4</sup> and photon correlation spectroscopy.<sup>3,5,6</sup> Combined, these techniques probe motions in the liquid and glassy states occurring on time scales ranging from about 1 ps up to tens of seconds.

One common feature of these relaxation studies is the parallel behavior of relaxation times characteristic of a variety of molecular motions and the increase of the viscosity. This result is not particularly surprising. In simple viscoelastic models<sup>7</sup> for ideal Newtonian fluids, for example, the shear relaxation time is related to the viscosity by

$$\tau_s = \eta/G_\infty, \quad (1)$$

where  $\eta$  is the shear viscosity and  $G_\infty$  is the high frequency shear modulus. For rotational motions, the Stokes–Einstein–Debye model predicts that the rotational diffusion time varies as

$$\tau_r = \frac{3V\eta}{kT}, \quad (2)$$

where  $V$  is the molecular volume. This equation has been used previously by Higashigaki and Wang<sup>8</sup> to describe the relaxation time measured by Brillouin scattering from orthoterphenyl. Similarly, Mezei *et al.*<sup>1</sup> have suggested that the relaxation times which they observed in their neutron spin echo studies on the ionic glass  $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$  could be described by the Stokes–Einstein particle diffusion time

$$\tau_p = \frac{6\pi\eta R}{kTq^2}, \quad (3)$$

where  $R$  is the radius of the diffusing object and  $q$  is the scattering wave vector. Equations (1)–(3) all imply that there is a strong connection between the relaxation process and the viscosity.

The viscosities of several fragile glasses have recently been shown to follow a power-law divergence with temperature relative to a singular temperature for viscosities in the range  $\eta \lesssim 10$ –1000 cp.<sup>9</sup> This behavior is characteristic of the liquid phase and predicted by recent mode coupling theories.<sup>10</sup> It is ascribed to the coupling of the relaxation of long-lived, short-length scale density fluctuations to the viscosity. This power-law, however, breaks down at a temperature  $T^*$  where, we have shown,<sup>11</sup> nonhydrodynamic density fluctuations begin to develop. Given the close relationship between the viscosity and the relaxation processes, one may ask what affect this change in the viscosity produces in the nature of the relaxation function.

Another common feature observed in these relaxation studies is the highly nonexponential, long time decay of the relaxation function,  $\phi(t)$ .<sup>12</sup> One interpretation of this behavior is that in the viscous liquid, complex motions produce a distribution of relaxation times instead of one single relaxation as is observed in the high-temperature liquid. This implies a parallel process of independent relaxations. This distribution of relaxation times can be written as  $g(\tau)$ , then

$$\phi(t) = \int_0^\infty g(\tau)e^{-t/\tau} d\tau. \quad (4)$$

Experimentally, only  $\phi(t)$  is measured, but  $g(\tau)$  could be obtained through a Laplace transform. Such a transform has been characterized as “ill conditioned” and can be unreliable.

ble, although with accurate data an inversion can be achieved.<sup>13</sup> Usually the inversion is not necessary, the relaxation function  $\phi(t)$  itself being descriptive of the process. A widely accepted functional form used to describe the relaxation is the Kohlrausch–Williams–Watts or stretched exponential form,

$$\phi(t) = \exp[-(t/\tau)^\beta]; \quad 0 < \beta \leq 1. \quad (5)$$

In this instance the average relaxation time of the distribution is

$$\langle \tau \rangle = \tau \beta^{-1} \Gamma(\beta^{-1}), \quad (6)$$

where  $\Gamma(x)$  is the gamma function.

The width of the distribution is characterized by the smallness of  $\beta$ . For  $\beta = 1$ ,  $g(\tau)$  is a delta function associated with a single relaxation process. But the distribution of relaxations spreads as  $\beta$  tends toward zero. A single relaxation ( $\beta = 1$ ) is usually observed at the short time scales probed by Brillouin scattering ( $10^{-12}$  to  $10^{-9}$  s) and crosses over to the stretched form at the longer time scales probed by photon correlation spectroscopy ( $10^{-6}$  to  $10^2$  s),<sup>3</sup> although this is not always the case.<sup>14</sup> At long time scales, typical values of  $\beta$  range from 0.3 to 0.7 for polymers<sup>12</sup> and about 0.4 to 0.6 for several molecular liquids.<sup>15</sup> The error in these measurements is usually  $\sim 0.1$ .

Many models have been proposed to explain the stretched exponential which also has been observed in a variety of related systems including spin glasses.<sup>16</sup> Some of these models interpret the stretched exponential as resulting from the parallel process described above.<sup>17</sup> More recent models envision a series process.<sup>3,18</sup> In this instance the long time relaxations are spawned from the coupling together of a hierarchy of faster modes. None of these models predict how  $\beta$  evolves as the temperature is lowered toward  $T_g$ , but most conclude that if  $\beta$  evolves it will decrease as the temperature decreases. For parallel relaxation,  $\beta$  characterizes the width of the distribution, but for the series process,  $\beta$  monitors the “complexity”<sup>3</sup> of the coupling by which the shorter relaxations contribute to those at longer times.

Recently, Campbell *et al.*<sup>19–22</sup> have proposed a model to explain the stretched exponential which appears in both molecular glasses and spin glasses and to predict how  $\beta$  should evolve near  $T_g$ . This model, unlike those discussed above, stresses the changes which occur in the morphology of either phase of configuration space as  $T_g$  is approached. In the phase space picture regions of phase space visited by the system become increasingly ramified as the glassy state is approached. This ramification process continues with decreasing temperature and results in a  $\beta$  that approaches 1/3 at the percolation threshold. Below this percolation threshold the phase space is envisioned as having disconnected regions and hence is nonergodic. It was also suggested<sup>21</sup> and then subsequently shown<sup>22</sup> that the crossover from  $\beta = 1$  to  $\beta < 1$  is of significance. This crossover may occur when the glassy system phase space transforms from compact to non-compact and in spin glasses it may be associated with the Griffiths temperature. Whatever one may conclude from these inference, quantitative calculations<sup>22</sup> give credence to this transition and its physical significance in glasses should be explored.

The experimental knowledge of the behavior of  $\beta$  is not clear. In their communication, Campbell *et al.*<sup>21</sup> showed that for a few glassy systems  $\beta$  was unity at high  $T$ , then fell with declining  $T$  tending to 1/3 in the vicinity of  $T_g$ . However, values of  $\beta$  measured for many molecular glasses are somewhat higher than 1/3. The authors acknowledged this and suggested that both  $\beta$  and  $T_g$  might be lower if experiments could be extended to longer time scales.

In summary, we see that new ideas regarding glassy relaxations, the behavior of the viscosity which is intimately tied to relaxation, and the source of the glass transition in general have appeared. Stimulated by this, we have used dynamic light scattering to study the orientational relaxation in the mixture  $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$  in a temperature range slightly above the glass transition to observe the behavior of the average relaxation time and, more importantly, the behavior of  $\beta$ . This system is unique in that it is an ionic glass with cations that have the electronic structure of argon. It is also a fragile glass<sup>15</sup> and displays a power law dependent viscosity for large temperatures. We find that  $\langle \tau \rangle$  follows Eq. (2) well with  $V$  of molecular size. We do not find that  $\beta$  evolves in our temperature range but has a value near 1/3 as indicated by the percolation theories. Thus  $\beta \approx 1/3$  well ahead of the glass transition. By combining our  $\beta$  measurements with earlier work at different temperatures, we find  $\beta$  does follow the behavior implied by theory and suggest a relation of the transition of  $\beta = 1$  to  $\beta < 1$  to the beginning of the breakdown of hydrodynamics in the liquid.

## II. EXPERIMENTAL METHOD

A stock solution (50 ml) of  $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$  was obtained by melting appropriate weights of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Baker reagent grade) and  $\text{KNO}_3$  (Fisher reagent grade) in a beaker. This mixture was dried in an oven for one day at 250 °C. A gravimetric analysis revealed that the final stock contained less than 0.3% water by weight.

Considerable effort was taken to ensure particle free samples for our light scattering experiment. It was necessary to use a pressurized filtration bomb to force the viscous melt through a fitted glass filter at 250 °C. This filtrate passed into a 1 cm square cuvette that served as a light scattering cell. Often several rinses of the cell were necessary as particles seemed to dislodge from the cell's inner surface. This whole procedure was performed on a laminar flow clean bench. With care, samples that were very nearly particle free could be prepared. The cuvette filled with approximately 5 ml of sample was sealed with a ground glass cap and stored at 220 °C.

Temperature control of the sample was maintained by thermal contact with a regulated bath. The cuvette was enclosed by a brass block about which a coil of copper tubing had been soldered. A mixture of roughly 50% water and 50% ethylene glycol was heated by a commercial bath and pumped through the copper coil. Holes were placed in the brass block to allow light to enter and exit. The temperature of the cuvette was determined from a calibrated thermistor

placed in the brass block and was accurate to  $0.1^\circ\text{C}$ .

Dynamic light scattering or photon correlation spectroscopy was conducted in the homodyne mode using the 5145 Å line of an argon ion laser polarized in the vertical direction. The light scattered at  $90^\circ$  was passed through a Glan-Thompson polarizer to detect only the horizontal component of the scattered light. This VH scattering geometry has the advantages of eliminating unwanted stray light from the signal and being solely due to orientational fluctuations and not a combination of these and longitudinal fluctuations.<sup>6</sup> Both of these would tend to broaden the spectrum, hence artificially decrease  $\beta$ . A number of sources may contribute to the VH intensity but only the viscous orientational fluctuation will have relaxation times measurable by photon correlation spectroscopy. The light was then focused onto a pinhole placed roughly 50 cm in front of a photomultiplier tube (PMT). This arrangement produced good spatial coherence of the light which arrived at the cathode. Photopulses from the PMT were amplified and digitized and fed into a commercial correlator (Langley-Ford Model 1, a "full" correlator) which calculated the correlation function for 64 time intervals.

Due to the limited number of channels available on our correlator in comparison with the breadth of the light scattering spectrum, it was necessary to combine several individual data sets to obtain the complete relaxation function at each temperature. Each data set is described by a correlation spectrum

$$C_i(t) = B_i + A_i \phi^2(t) \text{ (homodyne)}. \quad (7)$$

The background  $B_i$  was calculated from the photon statistics available in the correlator. Starting with the spectrum obtained on the smallest time scale,  $\phi(t)$  was calculated,

$$\phi_1(t) = \left( \frac{C_1(t) - B_1}{A_1} \right)^{1/2}, \quad (8)$$

where  $A_1 \equiv \lim_{t \rightarrow 0} [C_1(t) - B_1]$ .  $\phi_2(t)$  was then calculated for the spectrum of next longer time scale and was adjusted to agree with  $\phi_1(t)$  at times for which the two overlap. In this manner longer time scale correlation spectra were combined with previous spectra to obtain the complete relaxation function.

This method should not be taken lightly. Preliminary analysis indicated that at some temperatures two distinct relaxations were occurring. This phenomenon disappeared, however, when additional spectra were taken at shorter times. This emphasizes the importance of accurately determining  $A_1$ . We also remark that our  $A_i$  were not determined in an absolute sense, that is, they all had effects of the spatial coherence on the detecting cathode convoluted in them. Since we normalized by  $A_1$ , this presents no problem because the optical collection geometry, and hence the coherence, did not change from run to run. At temperatures above  $80^\circ\text{C}$ , where it was not feasible (due to low count rates) to collect spectra at sufficiently short times, the true value of  $A_1$  was approximated. Using an expansion of  $\log_{10} [-\ln \phi(t)]$  in a Taylor series to first order in  $\log_{10} t$ ,  $C_1(0)$  was obtained from extrapolation of the data available at shortest times.

### III. RESULTS

Measurements of the relaxation function were obtained at five temperatures in the range from  $68$  to  $86^\circ\text{C}$ . The complete relaxation functions are reproduced in Fig. 1. Inspection of Eq. (5) reveals that a plot of  $\log_{10} (-\ln \phi)$  against  $\log_{10} t$  should yield a straight line whose slope is  $\beta$ . The average relaxation time is obtained from Eq. (6) where  $\tau$  is the time when  $-\ln \phi = 1$ . Such plots are shown in Fig. 2 and are seen to be linear and parallel. A linear least squares

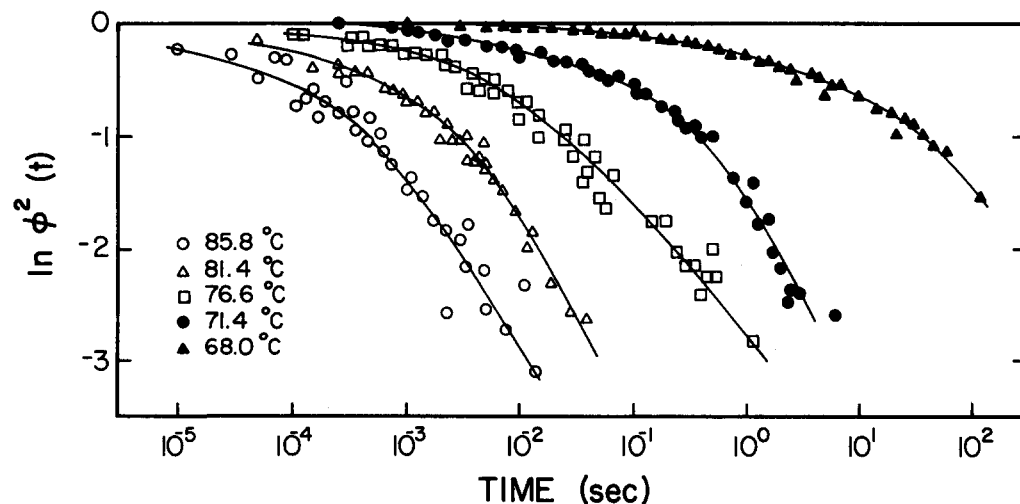


FIG. 1. Natural logarithm of the homodyne scattered light correlation function for five different temperatures.

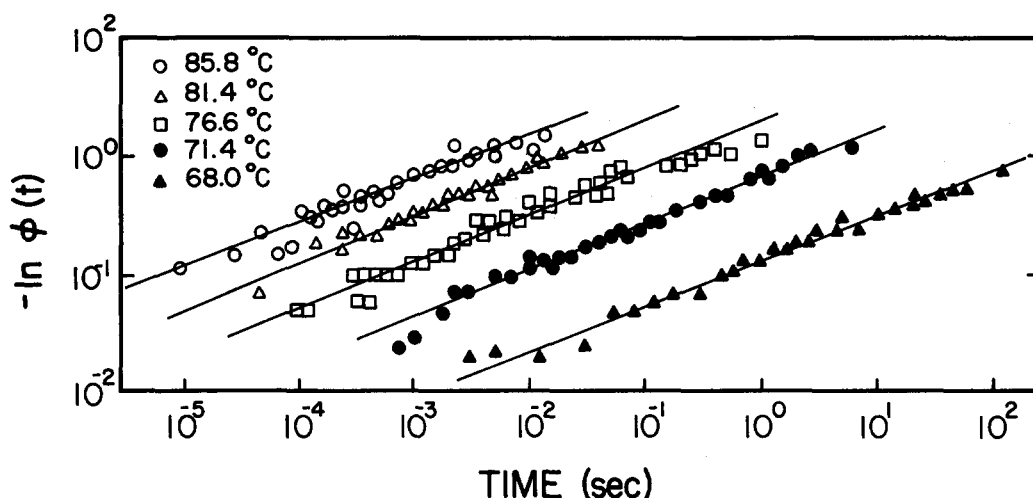


FIG. 2. Data of Fig. 1 plotted so that linear behavior implies a stretched exponential, Eq. (5), with slope  $\beta$ .

fit was applied to the data in the form shown in Fig. 2 to obtain  $\langle\tau\rangle$  and  $\beta$  which are tabulated in Table I. Our results for  $\langle\tau\rangle$  are plotted in Fig. 3 as a function of  $1/T$  with good comparison to the Brillouin scattering results of Angell and Torrel<sup>23</sup> and shear relaxation times calculated from earlier data<sup>24</sup> by them.

The large value of  $\langle\tau\rangle = 500$  s at  $68^\circ\text{C}$  and its rapid change with temperature as seen in Fig. 3 suggest we are in the glass transition region for experimental time scales. The glass transition temperature  $T_g$  is time scale dependent; thus, if we pick a reasonable time scale value of 1000 s, we find  $T_g \approx 67^\circ\text{C}$ . This is somewhat higher than previous estimates of  $60$  and  $65^\circ\text{C}$ ,<sup>15</sup> but given the time scale dependence, it does not represent a significant difference, especially with the  $65^\circ\text{C}$  value.

For our range of temperature, spanning roughly  $25^\circ\text{C}$  above the glass transition temperature, we observe a strong increase of  $\langle\tau\rangle$  with approach to  $T_g$ , but no evolution in the parameter  $\beta$ . Table I shows  $\beta$  to be  $0.40 \pm 0.05$ , which is near the value of  $1/3$  predicted by the percolation models.<sup>19-22</sup> The full evolution of  $\beta$  is shown in Fig. 4 where our results have been combined with those summarized by Angell<sup>15</sup> and data from Mezei *et al.*<sup>1</sup> At high temperatures a single relaxation is observed ( $\beta = 1$ ), but  $\beta$  quickly drops to  $0.4$  near  $100^\circ\text{C}$ .

TABLE I. Fit parameters of our light scattering data to the stretched exponential form, Eq. (5).

$T(^{\circ}\text{C})$	$\tau(\text{s})$	$\beta$	$\langle\tau\rangle(\text{s})$
85.8	$2.8 \times 10^{-3}$	$0.39 \pm 0.05$	$9 \times 10^{-3}$
81.4	$1.7 \times 10^{-2}$	$0.40 \pm 0.05$	$6 \times 10^{-2}$
76.6	$1.5 \times 10^{-1}$	$0.41 \pm 0.05$	$5 \times 10^{-1}$
71.4	$2.3 \times 10^0$	$0.39 \pm 0.05$	$8 \times 10^0$
68.0	$1.5 \times 10^2$	$0.40 \pm 0.05$	$5 \times 10^2$

$\beta$  is observed to drop to about  $1/3$  in agreement with the predictions of the percolation models. However, the value of  $1/3$  is reached well in advance of the glass transition  $T_g$ . It is well known that  $T_g$  is observation time dependent hence is not a fundamental quantity. The temperature where  $\beta$  stops decreasing, roughly  $100^\circ\text{C}$  in  $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$ , would be the significant temperatures for the percolation theories.

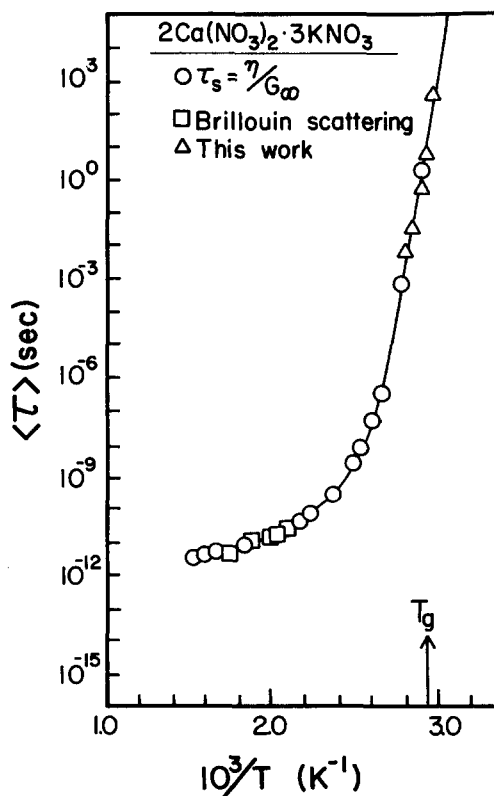


FIG. 3. The average relaxation time as a function of reciprocal temperature.

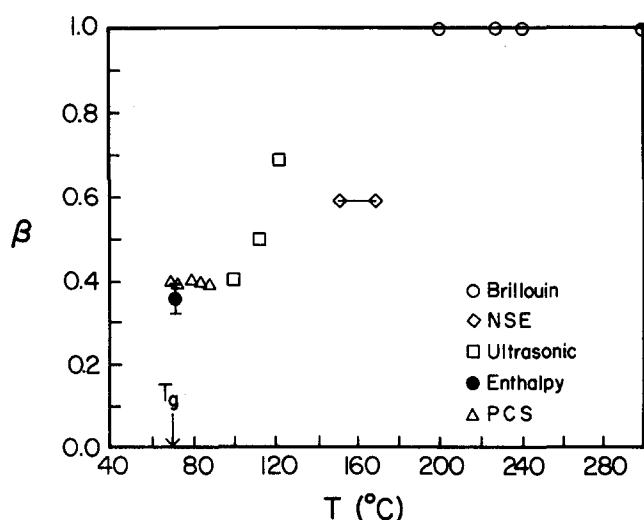


FIG. 4. Width parameter  $\beta$  as a function of temperature. The PCS data are the results of the measurements described here.

The theory would suggest that at this temperature the phase space depercolates and the system becomes nonergodic.

Also of potential significance is crossover from  $\beta = 1$  to  $\beta < 1$  behavior. We observe that a simple linear extrapolation of the three ultrasonic absorption measurements in Fig. 4 indicate that  $\beta = 1$  at about 148 °C. If we include the neutron spin echo data of Mezei *et al.* it appears this crossover is somewhere in the range 150 to 200 °C. From the plot of the viscosity<sup>25</sup> shown in Fig. 5, we find a match of this temperature range with that for which the viscosity first deviates from a power law, the temperature  $T^* \approx 150$  °C. The power law is a characteristic of the liquid phase<sup>9</sup> and has been predicted by mode coupling theories.<sup>10</sup>

In earlier work<sup>11</sup> on the molecular glass forming liquid salol we showed that at this temperature nonhydrodynamic structural relaxations first began eliminating the shortest length and time scale hydrodynamic fluctuations of the liquid. As the temperature fell, the structural relaxation time increased rapidly, eliminating more of the hydrodynamic modes until near  $T_g$  there were no such modes with time scales less than the observation time. The viscosity's deviation from power law behavior is a result of elimination of the hydrodynamic modes. Thus, the fact that  $T^*$  coincides with the  $\beta = 1$  to  $\beta < 1$  transition may be significant.

More data need to be examined to see if this correlation is true. Such data are not abundant but we present one other example. We have also investigated the limits of  $\beta$  for a mixture of 9% o-phenylphenol in o-terphenyl using data found in the literature.<sup>26</sup> A linear extrapolation of  $\beta$  approaches 1 at about 300 K. Unfortunately, the viscosity of this mixture is unknown. For pure o-terphenyl the viscosity fails the power law at  $T^* = 330$  K ( $\pm 10$  K) and would have diverged at 310 K. Dixon and Nagel<sup>26</sup> note that  $T_g$  of the mixture is depressed by as much as 10 K at higher concentrations (33% o-phenyl phenol). Thus one might expect that the viscosity of the mixture deviates from power law at a lower temperature than that of pure o-terphenyl, in favor of our correlation.

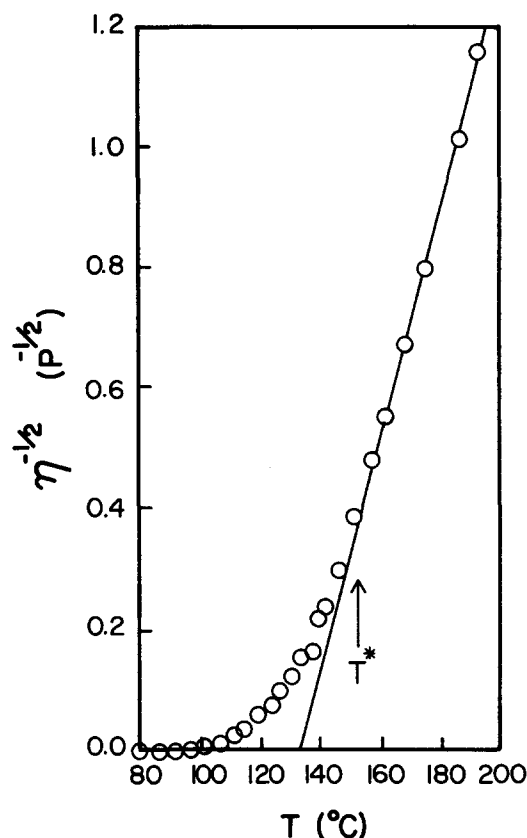


FIG. 5. Viscosity vs temperature. Straight line indicates power law behavior,  $\eta \sim (T - T_0)^{-2}$ .  $T^* \approx 150$  °C is where deviation from power law occurs.

The question whether the temperature  $T^*$  where the viscosity first deviates from power law behavior does in fact always match with the crossover from  $\beta = 1$  to  $\beta < 1$  requires more data for resolution. The physical significance of relating the mode structure of the liquid of the ramification of phase space would be useful in understanding the glass transition.

As seen in Fig. 3, the agreement of our measurements of  $\langle \tau \rangle$  with the shear relaxation time of Eq. (1) is good. We have found that our relaxation times can be deduced from Eq. (2), where  $(V)^{1/3}$  is of the order of 1 Å, a molecular length scale. We have also applied Eq. (2) to previous measurements obtained in this laboratory on the nonhydrodynamic mode in supercooled salol again to yield  $(V)^{1/3} \approx 1$  Å. Thus the non-hydrodynamic mode appears to be connected to motions on a molecular scale.

#### IV. CONCLUSION

We have used dynamic light scattering to study the relaxation of orientational fluctuations in the ionic glass forming mixture  $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$  near its glass transition temperature. The relaxation was a stretched exponential. We found the average relaxation time fit well with the relaxation time at other temperatures determined with other techniques and was due to motions of entities with molecular length scales. The width parameter  $\beta$  was found to be con-

stant for the range 68 to 86 °C ( $T_g \simeq 67^\circ\text{C}$ ) at  $\beta = 0.04 \pm 0.05$ .

Two key observations can be made about the behavior of  $\beta$  as a function of temperature as shown in Fig. 4. First,  $\beta$  transformed from a regime where  $\beta = 1$  to a regime where  $\beta < 1$  as predicted by recent theory involving diffusive relaxation in either ramified phase or configuration space. The transition temperature corresponded well with the temperature  $T^*$  where the liquid viscosity first deviated from power law. We have previously argued that also at this temperature nonhydrodynamic structural relaxations first begin to destroy the hydrodynamic modes of the system which are responsible for its "liquid-like" behavior. Thus we argue here that loss of these hydrodynamic modes not only destroys the power law singularity but also begins the process of the break up of phase space which ultimately leads to the glass transition.

Second, we observed that  $\beta = 0.4 \pm 0.05$  and remained constant for  $T \lesssim 100^\circ\text{C}$  well in advance of the glass transition near  $67^\circ\text{C}$ . This value is close to  $1/3$ , the value predicted by theory to occur at  $T_g$ . Thus it appears the percolation of phase space occurs significantly above the experimental-time-scale dependent  $T_g$ .

#### ACKNOWLEDGMENT

This work was supported by NSF Grant No. CHE 8618576.

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