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# TIME AND ENSEMBLE AVERAGED DYNAMIC LIGHT SCATTERING IN ORTHOTERPHENYL ABOVE AND BELOW THE GLASS TRANSITION

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## ABSTRACT

While traditional dynamic light scattering is useful for following structural relaxation in the liquid, in the glassy domain the technique is limited by the ultimate patience of the experimentalist; i.e., the structural relaxation can not be measured when the experimental time scale is less than the structural relaxation time. Nevertheless, we show how useful information regarding structural relaxation can be accessed from light scattering in the glass using a novel ensemble-averaged technique. Dynamic light scattering measurements performed on glass forming orthoterphenyl show an inequality between time and ensemble average correlation functions near and below the calorimetric glass transition temperature, $T_g$, and hence demonstrate ergodicity breaking. Our ensemble averaged measurements provide a measure of the so-called non-ergodicity parameter, $f_q$, below $T_g$. Results for orthoterphenyl indicate that $f_q$ is constant above $T_g$, but increases at lower temperatures in a manner that is consistent with Mode Coupling theory predictions.

## INTRODUCTION

Many liquids when cooled through their freezing temperatures can avoid the discontinuous, first-order liquid-to-crystal transition and supercool to an amorphous, glass phase [1-2]. This occurs because the rising viscosity of the liquid which accompanies the falling temperature can become large enough to kinetically inhibit molecular rearrangement into the thermodynamically more stable crystalline phase. This glass transition is imprecise, although calorimetric measurements of the heat capacity $C_p$ show, in most cases, a definite steplike change over a narrow temperature range the center of which is the glass transition temperature, $T_g$, which is cooling rate dependent. Hence the nature of this transition appears to be kinetically arrested thermodynamics, but there has long been suspicion that some more fundamental, phase transition explanation of the glass transition might be viable. This proposed transition is hidden or masked by the kinetics but is the underlying reason for vitrification.

The past decade has seen a new tact taken to describe the glass transition. A Mode Coupling Theory (MCT) describing the behavior of the density correlation function has been developed which has stimulated considerable activity in this field[3-8]. MCT predicts the viscosity to diverge in a power law fashion, $\eta \sim (T-T_c)^{-\gamma}$ where $\gamma > 0$, a behavior that has been seen experimentally at temperatures well above $T_c$[9]. A key aspect of MCT is that the glass transition is caused by a fundamental ergodicity breaking transition. Hence it awakens the suspicion of a transition underlying the kinetics as mentioned above. This ergodicity breaking is predicted to occur at the "ideal glass transition" temperature, $T_c$, tens of degrees above the calorimetric $T_g$ and is marked by a partial "freezing in" of density fluctuations at a level $f_q$, the

Debye-Waller or nonergodicity factor. Above $T_c$, the system is ergodic, that is the system can sample all of its allowed phase space, and time and ensemble averages are equal. Below $T_c$, the system becomes nonergodic, molecular motion is constrained, allowed phase space is not completely accessed, and time and ensemble averages are not equal. In recent revisions to MCT[5-8], the inclusion of thermally activated hopping processes ultimately restores ergodicity, but the density correlation function continues to be "pinned" near a level $f_q$ that rises abruptly near $T_c$ in a cusplike fashion

$$f_q = \begin{cases} f_q^c + (1-f_q^c)\varepsilon^{1/2}; & T < T_c \\ f_q^c; & T > T_c \end{cases} \qquad (1)$$

where $\varepsilon = (T_c - T)/T_c$. Both neutron [10,11] and light [12-14] scattering experiments have provided evidence for ergodicity breaking of the form Eq.(1) at a $T_c > T_g$, but no work exists to explicitly demonstrate this through an inequality of ensemble and time averages of the density correlation function.

We have examined the molecular, and so-called fragile glass former, orthoterphenyl (OTP) for temperatures of $130K \leq T \leq 267K$ using dynamic light scattering (DLS). This temperature range is below the conventional, MCT $T_c \approx 290K$ for OTP [11,15] and includes the calorimetric glass transition temperature $T_g \approx 243K$ [16]. We measured both the time and the ensemble averaged scattered light intensity correlation function, $g^{(2)}(t)$, a direct measure of the dynamic structure factor f(q,t). We find i) an explicit demonstration of ergodicity breaking; the time and ensemble averages of $g^{(2)}(t)$ are equal above, but not equal below the calorimetric glass transition temperature $T_g \approx 243K$. This occurs significantly below the ideal glass transition temperature $T_c \approx 290K$ found for OTP from both neutron scattering [11] and viscosity [17] measurements. ii) Despite this discrepancy, the nonergodic (i.e., nondecaying) part of the correlation function, the nonergodicity function $f_q$, still obeys Eq.(1) with $T_c = T_g$.

## EXPERIMENT

Suitable samples of o-terphenyl (OTP) were produced from 99% grade (Aldrich) stock melted at about 70°C and passed through 0.22μm Teflon filters into the light scattering cell. After degassing, the cells where flame sealed. For work above $T_g = 243K$, $1cm^2$ pyrex cuvettes were used and temperature control provided by circulated Methanol from a temperature controlled bath. These cuvettes typically fractured at about 230K, so smaller samples, contained in thick walled capillary tubing (2.5mm ID, 9mm OD), were used below $T_g$. Temperature control below $T_g$ was provided by a $LN_2$, cold finger cryostat.

An $Ar^+$ laser operating at about 400mW in $TEM_{00}$ [18,19] with $\lambda = 5145$Å provided incident light which was focused by a lens to a beam waist of about 30μm inside the sample. The scattering wave vector was $q = 25\mu^{-1}$ ($\theta = 90°$). The scattered light was collected by another lens and focused onto a 100μm pinhole located 50cm in front of the cathode of a photomultiplier tube. Photopulses from the PMT were digitized and fed to an ALV5000 correlator which computed $g_T^{(2)}(t)$, the time averaged, normalized intensity correlation. This is related to the field correlation function, f(q,t), through the Siegart relation [20]

$$g^{(2)}(t) = 1 + A_c|f(q,t)|^2 , \tag{2}$$

where $A_c \leq 1$ is an instrumental coherence factor. This field correlation function is the dynamic structure factor, i.e., the spatial Fourier transform of the liquid's density correlation function, the central element in the MCT theory. An important aspect of our work was that the coherence factor was periodically calibrated from an aqueous suspension of latex spheres (r=38nm) for which $A_c=0.95\pm0.03$.

A theoretical development of light scattering from non-ergodic media was first proposed by Pusey and van Megen (PVM)[18] and developed by others[21-23] in conjunction with the sol/gel transition. The formation of a rigid gel network contributes a static (non-fluctuating) component to the scattered light and leads to both homodyne and heterodyne contributions in $g_T^{(2)}(t)$. The heterodyne component produces an effective reduction of the observed amplitude of $g_T^{(2)}(t)$ and provides a measure of non-ergodic behavior.

Key to success of these approaches is proper evaluation of $g_T^{(2)}(0)$. In the case of gels, $g_T^{(2)}(1\mu s)$ is a suitable choice for $g_T^{(2)}(0)$ since even the fastest dynamics contributing to $g_T^{(2)}(t)$, the so-called "gel mode", generally occurs at times greater than 1μs. However, if the relaxation process being observed involves substantial decay at times less than 1μs, the lower limit of modern correlators, $g_T^{(2)}(1\mu s)$ no longer provides a measure of the quantity $g_T^{(2)}(0)$. Thus in general, changes in $g_T^{(2)}(1\mu s)$ cannot *a priori* be interpreted as evidence of non-ergodic behavior, since they could instead reflect the partial decay of $g_T^{(2)}(t)$ occurring at shorter times.

Since MCT predicts an initial decay (β-relaxation) extending from vibrational timescales ($t \approx$ 1psec) to a plateau, $f_q^c$, followed by slower collective α-relaxation[6-8], we opted instead to employ an alternative approach which circumvents the difficulty with $g_T^{(2)}(0)$. Ensemble averaged measures of the intensity correlation function, $g_E^{(2)}(t)$, were achieved by moving the sample at a fixed rate (~8μm/sec.) vertically relative to the optical plane while the correlator was running [22-24]. In this way $g^{(2)}(t)$ becomes an average over many spatially independent scattering volumes, that is, an ensemble average. We do not mean to imply that only one "ensemble member", i.e., a region of the fluid with an extent of one spatial coherence length, a coherence region, of the system resides in our scattering volume at any given time. Instead, one may envision many such regions inside the scattering volume creating a scattered light speckle pattern at the detector which carries information regarding the numerous coherence regions in the scattering volume. With motion of the sample, new coherence regions pass into the scattering volume and an average is obtained.

## RESULTS

Figure 1 displays some of our results for $g_T^{(2)}(t)$ and $g_E^{(2)}(t)$. For T=255K and 264K the ensemble and time averages are identical indicating ergodicity. For T=217K, however, these averages are not equal; an explicit demonstration of nonergodicity at this temperature. We find the transition from ergodic to nonergodic as indicated by comparison of $g_T^{(2)}(t)$ and $g_E^{(2)}(t)$ occurs at T=243±5K. This temperature is in close agreement with the calorimetrically determined $T_g$=243K [11,25]. This result is in contrast to earlier versions of MCT which predicted ergodicity breaking at $T_c>T_g$, but in accord with more recent versions in which hopping processes restore ergodicity at and below $T_c$. Our results indicate that ergodicity is restored so long as these processes have time scales shorter than the upper range of our experimental dynamic window, ~$10^3$ sec.

The pronounced decay in $g^{(2)}(t)$ for $T>T_g$ is the alpha relaxation which we have fit through Eq.(2) to a stretched exponential,

$$f(q,t) = f_q^c e^{-(t/\tau_\alpha)^\beta}.$$

We find a temperature independent $\beta=0.57\pm0.03$. The alpha relaxation time, $\tau_a$, shows a strong temperature dependence and becomes unmeasurably long at $T_g$ and below. The level from which the dynamic structure factor decays is the nonergodicity factor of the MCT theory which we find to be *constant* at $f_q^c=0.56\pm0.01$ for $243\leq T\leq 267$K.

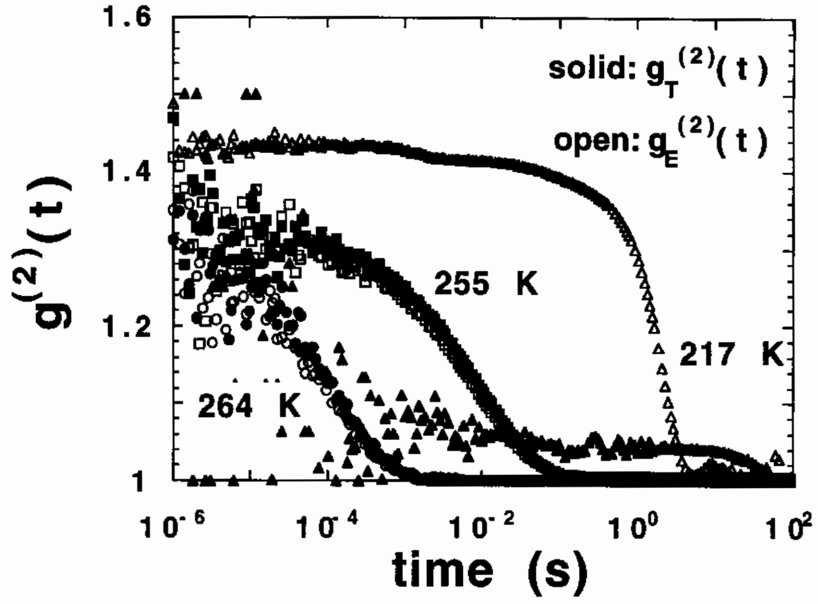

Fig. 1 Normalized intensity autocorrelation functions for light scattered at θ=90° from orthoterphenyl. Decays at T=255 and 264K are the alpha relaxation. Decay at T=217K in $g_E^{(2)}(t)$ is a beam transit term.

To understand the $T<T_g$ $g_E^{(2)}(t)$ spectrum consider again the speckle pattern due to scattering from a group of coherence regions in the liquid within the scattering volume described in the Experimental Section above. For a stationary sample if the relaxation time of these fluctuations is long compared to the experimental time scale, the detector sees a static speckle pattern. If instead the fluctuations have a two-step spectrum with one time scale faster the other slower than the experimental time scale, and if the shorter time scale is also too fast for the correlator, the speckle pattern will appear static but its visibility will be decreased below unity due to the faster time scale. If the system is translated in either case, the speckle pattern will fluctuate on the time scale of the motion. The latter, two time scale case, however, will retain information regarding the faster time scale because of it's decreased fringe visibility. This is what we observe. The decay near $10^{-1}$ sec. is the beam transit time [26] caused by the relative motion and is not fundamentally related to the glass. The height of $g_E^{(2)}(t)$ at times shorter than the beam transit is physically relevant and represents the decreased speckle visibility due to relaxation at time scales shorter than $10^{-6}$ sec., the lower limit of our correlator. These relaxations determine $f_q$ and hence our translating cell method allows us to measure $f_q$ even when the alpha relaxation time has exceeded the experimental time scale, i.e., when $T<T_g$.

Below 243K we monitored the plateau level while each spectrum was accumulating to insure a sufficient number of "ensemble members" are collected. This plateau approaches a limiting constant value as the number of ensemble members increases as shown in the inset to Fig. (2). Our complete set of results for $f_q$ for $130<T<267$K are shown in Fig. (2). The data for $T<T_g$ have considerably more error than those for $T>T_g$, but the trend of the former and the precise constancy of the latter demonstrate cusp-like behavior at $T_g \approx 243$K. As discussed above, Eq.(1)

has been verified in both OTP and other glass systems using other techniques but with $T_c$ values tens of Kelvin higher than $T_g$ [10-13]. For OTP the neutron data of Bartch et al. [11] indicate $T_c$=290±5K. This value of $T_c$ is corroborated by the power law behavior of the viscosity[17], where the MCT prediction of $\eta^{-1/\gamma} \sim (T-T_c)$ is fit best with $\gamma = 2.5$.

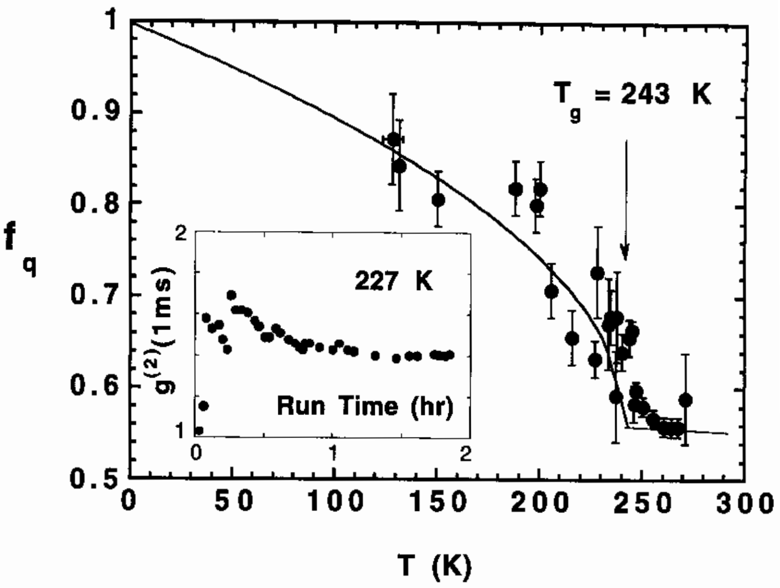

Fig. 2 Nonergodicity parameter $f_q$ versus temperature. Line is fit to Eq.(1) with $T_c$=243K. Inset shows plateau of $g_T^{(2)}(t)$ vs. run time.

## CONCLUSIONS

To summarize, our DLS results verify key aspects of MCT regarding ergodicity: we demonstrate explicitly that ergodicity is broken, and $f_q$ behaves Eq.(1) as illustrated in Fig. 2. A major discrepancy exists, however, in the temperature where the cusp in $f_q$ occurs. We see this to occur at $T_g$ whereas MCT predicts and earlier experiments find broken ergodicity at significantly higher temperatures, 47K higher for neutron scattering from OTP [11].

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