

Connecting structure and dynamics in glass forming materials by photon correlation spectroscopy

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We report photon correlation spectroscopy measurements of the α -relaxation in a series of glass forming liquids of widely varying fragility and demonstrate a correlation between the nonergodic level of the liquid and its fragility. This correlation, when combined with a previous correlation established between fragility and the stretching exponent that characterizes the nonexponentiality of the α -relaxation, implies that the α -relaxation should, in general, conform to scaling that is described by just two parameters: the nonergodic level and the glass transition temperature.

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The glass transition refers the continuous progression of an amorphous liquid into an amorphous solid upon cooling. During this process, little or no structural changes occur and the exact instant at which the system becomes nonergodic is intrinsically inexact. Consequently, the glass transition is a kinetic phenomenon in which liquidlike ergodicity persists only when the observational time scale exceeds that of the structural relaxation. By convention, a glass transition temperature, T_g , is defined as the temperature at which the relaxation time, τ , reaches approximately 100 s.

Over the years, the glass transitions of a variety of glass forming materials (polymers, simple liquids, and even metals) have been studied, and yet the underlying physics behind the transition remains unclear.^{1,2} One of the important insights gained about the nature of the glass transition is how the character of slowing down with decreasing temperature exhibits a pattern between two extremes. Liquids for which the relaxation time increases in an Arrhenius fashion with decreasing temperature are populated by covalently bonded, network-forming materials (e.g., SiO_2) and are described as “strong.”³ By comparison, “fragile” liquids display considerable deviation from the Arrhenius temperature dependence: a modest increase of τ with cooling far from T_g , but dramatic increases nearer T_g . In fact, when the $\log(\tau)$ is plotted against T_g/T , the slope near T_g is customarily used to define a fragility index, m .⁴

The salient features of the viscoelastic relaxation are best represented by the behavior of the dynamic structure factor $S(q,t)$ (also known as intermediate scattering function), which is the normalized density correlation function for density fluctuations of wave vector q . For the liquid above T_g , this function exhibits a characteristic two-step decay. The initial fast decay occurs on subnanosecond time scales and represents decay of $S(q,t)$ from $S(q,0)=1$ to a plateau level f_q known as the nonergodic level (NEL). At longer times corresponding to the viscoelastic relaxation, $S(q,t)$ decays to zero. This latter relaxation is commonly referred to as the α -relaxation and attains $\tau=100$ s near T_g . It is customarily described by a stretched exponential of the form

$$S(q,t) = f_q \exp\{-(t/\tau)^\beta\}. \quad (1)$$

The origin of the two-step decay lies in the cage effect,^{5,6} wherein the average displacement of a given particle is limited

at short times by the cage formed by neighboring particles. Here, the initial decay in $S(q,t)$ is a reflection of the decorrelation in density fluctuations, which results as particles explore the environs of their respective cage; a cage characterized by a highly anharmonic interaction potential.⁷ In the solid phase, the decay becomes arrested at the nonergodic level and the value of the level becomes synonymous with the Debye-Waller factor that characterizes the average mean-squared displacement of the particles. Indeed, the nonergodic level goes by many names including Debye-Waller factor (DWF), Edward-Anderson parameter, and glass form factor.⁸

Given the lack of a truly successful theory for the glass transition, it is natural for researchers to examine various correlations between glass structure (bond coordination, cohesive energy, short-range order) and the characteristics [f_q and β in Eq. (1)] of the dynamics near T_g . Some years ago, Boehmer *et al.*⁴ culled the literature to demonstrate a convincing correlation between the nonexponentiality (β) of the α -relaxation near T_g and the fragility of the material. Even more recently, correlations of the fragility to elastic properties of the solid glass have appeared. Buchenau and Wischnewski⁹ have shown a correlation of the fragility to the compressibility of the glass, and Novikov *et al.*^{10,11} have shown a correlation of the fragility to the Poisson ratio and to the NEL in the glass. The validity of the correlation to the Poisson ratio in this latter study has, however, been challenged by Yannopoulos and Johari.¹²

Recently, Scopigno *et al.*¹³ analyzed the inelastic x-ray scattering data of several glasses below T_g to determine the temperature variations of the NEL. In the study, the NEL was determined from a ratio of the elastic to inelastic integrated scattering intensity and Scopigno *et al.* observed that f_q^{-1} plotted against temperature (scaled to T_g) increases from unity at zero kelvin with a slope that correlates directly to the fragility of the corresponding liquid. The authors themselves characterize the result as “conceptually surprising,”¹³ as it appears to imply that the vibrational properties of the glassy phase (i.e., the temperature dependence of the DWF) somehow dictate the thermal and viscoelastic responses of the liquid.

Here we report the results of photon correlation spectroscopy (PCS) performed above T_g on a strong glass forming liquid, As_2O_3 . To within a calibration factor, we directly

measure the dynamic structure factor (in the hydrodynamic limit, $q \rightarrow 0$) and are able to directly determine the NEL, $f_{q \rightarrow 0} = f_o$, for temperatures above T_g in the liquid. We are also able to obtain $\tau(T)$ (and hence the fragility, m) and β by fitting individual spectra to Eq. (1). Results for As_2O_3 are combined with results for five additional glass forming liquids covering a wide range of fragilities. In agreement with Scopigno *et al.*¹³ and Novikov *et al.*,¹¹ we too observe a correlation between the NEL and the fragility. However, we find no conceptual surprise because the correlation *originates* in the liquid state and stems, we argue, from how the cage effect is influenced by changes in cohesive energy that generally accompany changing fragility. An important conclusion of our work is that the present correlation completes a triad connecting f_o , $\tau(T/T_g)$, and β , which suggests that the *dynamics* of the α -relaxation conforms to a scaling procedure which can, in principle, be described by the single *structural* parameter, f_o .

Samples of As_2O_3 were produced in a manner similar to Yannopoulos *et al.*¹⁴ by directly melting reagent grade As_2O_3 in a vacuum-sealed quartz ampoule at temperatures around 480 °C. The ampoule containing the sample was maintained at selected fixed temperatures in an optical furnace and vertically polarized light from a 0.8 W, 432 nm diode-pumped solid-state laser was focused into the cell. The light scattered at 90° was passed through a Glan–Thompson polarizer and imaged onto a 50 micron pinhole placed approximately 50 cm from the active area of a photomultiplier tube. Photopulses from the photomultiplier tube were then digitized and streamed to a commercial correlator which computed the intensity-intensity autocorrelation function, $C(q, t)$. This correlation function is related to the dynamic structure factor through the Siegert relation,¹⁵

$$C(q, t) = 1 + A_{coh} |S(q, t)|^2, \quad (2)$$

where A_{coh} is an instrumental constant¹⁶ determined independently from light scattering conducted on a suspension of polystyrene spheres to be $A_{coh} = 0.71 \pm 0.02$. Homodyne detection was maintained throughout, and further details of the photon correlation technique can be found elsewhere.^{15,16}

Examples of the depolarized (VH) spectra obtained from As_2O_3 are shown in Fig. 1. These spectra were individually fitted to Eq. (1) and displayed a reasonably temperature-independent stretching parameter (shown in inset) of $\beta = 0.81 \pm 0.03$ and nonergodic level $f_o = 0.91 \pm 0.03$.

To now assess the fragility of our As_2O_3 sample, we have plotted in Fig. 2 the logarithm of the relaxation time against inverse temperature (scaled to T_g). Our $T_g = 432 \pm 3$ K was determined by extrapolation of the relaxation time to 100 s. In Fig. 2 the scales have been chosen such that the fragility index, m , can be directly read with the aid of a ruler. For As_2O_3 , we find $m = 17 \pm 2$. This value is in excellent agreement with the value of 19 reported by Yannopoulos *et al.*¹⁴

Included in Fig. 2 are the relaxation times that we have previously measured for a variety of other glass forming liquids. These include four fragile glasses, orthoterphenyl (OTP),¹⁷ lithium metaphosphate (LiPO_3), sodium metaphosphate (NaPO_3), a mixed alkali metaphosphate ($0.5\text{Li}0.5\text{NaPO}_3$),¹⁸ and one intermediate liquid, boron triox-

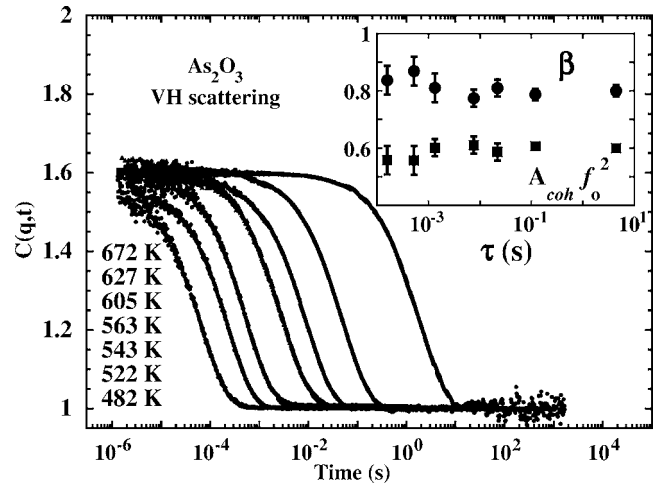


FIG. 1. Depolarized intensity-intensity autocorrelation functions for As_2O_3 at selected temperatures (each curve is sequential with the temperatures shown). The barely visible dashed lines are fits to Eq. (2) with Eq. (1). Inset shows temperature variation of both the stretching exponent (circles) and the amplitude of the correlation function, $A_{coh} f_o^2$, (squares) plotted against the relaxation time.

ide (B_2O_3).^{19,20} Relevant results for these glass forming systems are provided in Table I.

Also included as an inset in Fig. 2 are representative examples of the dynamic structure factor obtained by PCS for OTP, B_2O_3 , and As_2O_3 . These are shown together for comparison and two key features are evident. First, the nonexponentiality (smallness of β) increases with increasing fragility; a trend that is consistent with the correlation established by Boehmer *et al.*⁴ some years ago. Second, the amplitude of the relaxation (the nonergodic level, f_o) decreases with increasing fragility.

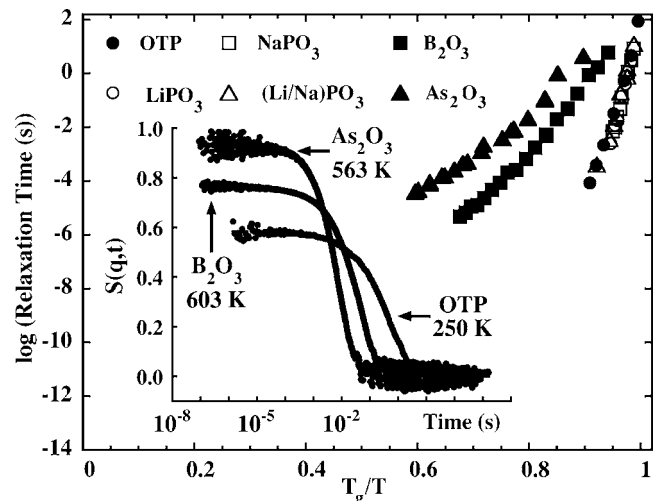


FIG. 2. Relaxation time plotted against inverse temperature following Angell (Ref. 3), showing the data for all six glass forming liquids considered in the present study. Inset shows the dynamic structure factor of three glass forming liquids at selected temperatures to illustrate the systematic decrease in the NEL with increased nonexponentiality of the relaxation. The barely visible dashed lines are the fits to Eq. (1).

TABLE I. Parameters describing the α -relaxation obtained by PCS.

System	f_0	m	β
OTP	0.56 ± 0.02	81 ± 3	0.57 ± 0.03
LiPO ₃	0.60 ± 0.03	92 ± 4	0.48 ± 0.03
NaPO ₃	0.60 ± 0.03	85 ± 4	0.48 ± 0.03
0.5Li0.5NaPO ₃	0.60 ± 0.03	74 ± 4	0.35 ± 0.03
B ₂ O ₃	0.75 ± 0.03	27 ± 3	0.65 ± 0.03
As ₂ O ₃	0.91 ± 0.03	17 ± 2	0.81 ± 0.03

To put this latter trend into better perspective, we have plotted in Fig. 3 our values of the nonergodic level versus the inverse of the fragility. Included with our own results are other values of the nonergodic level (at T_g) which have been culled from the literature. These all represent $q \approx 10^{-3} \text{ \AA}^{-1}$ and include PCS data for As₂O₃ by Yannopoulos *et al.*,¹⁴ Brillouin scattering on 0.4Ca(NO₃)₂-0.6KNO₃ (Ref. 21) and salol by Dreyfus *et al.*,²² and impulse stimulated Brillouin scattering on salol by Yang and Nelson.²³ For these literature sources, the nonergodic level at T_g was either read directly from the data or obtained by extrapolation of the published fitting function. The value of m was obtained from the extensive listing by Boehmer *et al.*⁴ A final datum in Fig. 3 is added for the glass form factor (in the hydrodynamic limit) reported for a hard-sphere model.^{8,24} A proper fragility cannot be determined for the hard-sphere model since its glass transition is athermal and the primary relaxation depends on the concentration of colloidal spheres.²⁵ For reasons that will become clear momentarily, we have placed the hard-sphere datum at $m = \infty$.

The correlation evident in Fig. 3 is illuminating and conveys a potent message. We see that the NEL spans a full range between that of the hard-sphere model, for which no cohesive energy is present, to values of near unity for the

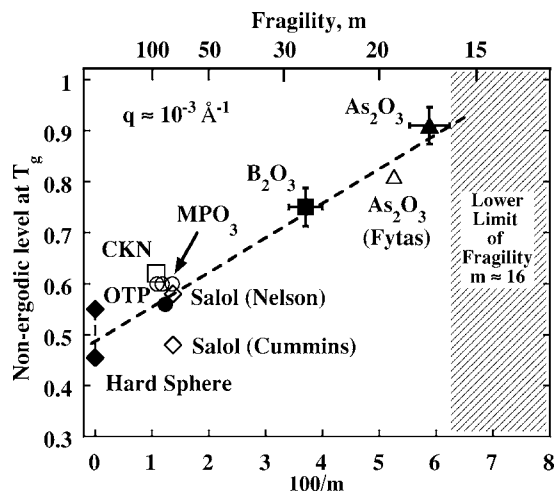


FIG. 3. Plot of the NEL at T_g versus the inverse fragility index. Included are other light scattering results taken from the literature (Refs. 14 and 21–23) as well as the NEL for the hard-sphere model (Refs. 8 and 24). The shaded region at the right marks a region of ill-defined fragility, and the dashed line is only a guide for the eyes.

strongly bonded oxide glass formers. It is further reassuring how the NEL approaches unity just as the fragility is nearing its formal lower limit of $m \approx 16$ (Ref. 4) and approaches the NEL of the hard-sphere model in the opposite limit. In some ways, this correlation seems inevitable. The NEL is the DWF and is a measure of the degree to which structure (when averaged over length scales comparable to wavelength of visible light) becomes partially decorrelated by virtue of localized rearrangements of the constituent atoms. In the network-forming As₂O₃, the atoms are covalently bonded and are constricted to maintain both a fixed separation and coordination. Here the microscopic mechanism of relaxation involves (activated) bond breakage and reformation, which yield very little decorrelation of the structure at short times. Indeed, the concept of a cage effect is difficult to envisage in such a covalently bonded network. At the other extreme are the fragile, molecular liquids in which the cohesive energy is smaller (or nonexistent in the case of the hard-sphere model) and the spacing and coordination restrictions are far more lax. By comparison, these structures possess a looseness that permits substantial decorrelation of the structure at short times.

This interpretation also resonates well with the recent molecular dynamics simulations by Bordat *et al.*,²⁶ who studied how the shape of the interaction potential in a binary Lennard-Jones system influences both the fragility and the NEL. They found that they could mimic the temperature dependence of the NEL as seen by Scopigno *et al.*¹³ and concluded that both the temperature dependence of the NEL and the increases in the fragility were the result of increases in the anharmonicity and capacity for intermolecular coupling of the interaction potential.²⁶

The correlation we demonstrate in Fig. 3 is not entirely new, but is being established by a different route through direct fitting of the dynamic structure factor in the time domain. Furthermore, our PCS experiment provides all the relevant quantities (f_0 , m , and β) in a single experiment. Scopigno *et al.*¹³ observed a similar correlation between fragility and temperature dependence of the NEL below T_g in the glass phase. Instead, our present correlation links the NEL in the liquid to viscoelastic relaxation in the liquid. We see the correlation of slopes of Scopigno *et al.* in the glass phase as merely a consequence of two limits to the NEL. One of these is in the liquid, where $f_0(T > T_g)$ assumes the reasonably temperature-independent value that is observed in our experiment. The other limit to the NEL is at zero kelvin where, by virtue of the third law of thermodynamics, f_0 must approach unity for all glass formers regardless of fragility. In contrast to Scopigno *et al.* who puzzled over how the vibrational features of the glass phase managed to connect with the properties of the viscoelastic relaxation of the liquid, we see no puzzle at all because the correlation between the NEL and the fragility originates in the liquid phase above T_g .

Instead, we emphasize how this present correlation between the NEL and the fragility, when combined with the well-known correlation between the fragility, the stretching exponent β , and the definition of m as a descriptor of the temperature dependence of $\tau(T/T_g)$, implies that the features of the viscoelastic α -relaxation [see Eq. (1)] in the widest diversity of glass forming liquids should conform to a sort of

universal scaling that can be completely described by just two parameters: T_g and f_o . Together these quantities convey the source of the glass transition itself, namely, the energetics ($k_B T_g$) that drive the decay of density fluctuations and the cage effect (f_o) which limits the initial structural decay. In this we see once more how the distinction between strong and fragile originates in the nature of the intermolecular interactions between particles of the liquid. The severity of

these interactions not only limit the initial structural decay, but also serve to modify [via $\tau(T/T_g)$ and β] the overall viscoelastic response.

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