# Self-Diffusion of *tris*-Naphthylbenzene near the Glass Transition Temperature

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We present a direct measurement of self-diffusion of a single-component glass-forming liquid at the glass transition temperature. Forward recoil spectrometry is used to measure the concentration profiles of deuterio and protio 1,3-bis-(1-naphthyl)-5-(2-naphthyl)benzene (TNB) following annealing-induced diffusion in a vapor-deposited bilayer. These experiments extend the range of measured diffusion coefficients in TNB by 6 orders of magnitude. The results indicate a decoupling of translational diffusion coefficients from viscosity or rotation. At $T_g$, $D_T$ is 400 times larger than expected from the Stokes-Einstein equation.

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The nature of the glass transition has recently been an area of intense experimental and theoretical interest. Measurements of dynamics in glass-forming liquids indicate a dramatic slowdown of both macroscopic (viscosity, $\eta$) and microscopic (rotational correlation time, $\tau_c$, and self-diffusion coefficient, $D_T$) observables as the temperature is lowered toward the glass transition temperature, $T_g$. In contrast to first order phase transitions, no significant structural changes accompany the slowing of dynamics near $T_g$, and thus an understanding of the glass transition has been sought through the study of dynamics. Despite a vigorous effort, a fundamental understanding of the molecular dynamics underlying the glass transition is not yet established. With an eye toward this goal, we present here the first direct measurement of self-diffusion at $T_g$ for a single-component glass former. These new measurements permit a critical comparison of the three relaxation observables, $\eta$, $\tau_c$, and $D_T$, and provide a test for conceptual and theoretical descriptions of molecular dynamics at the glass transition.

Previous experimental observations of dynamics in deeply supercooled liquids have provided results that are both interesting and, prior to measurement, quite unexpected. In an important work on low molecular weight organic glass formers, Fujara *et al.* [1] reported that the product $D_T\eta$ was not constant for *o*-terphenyl, but increased by a factor of 3 as the temperature was lowered into the supercooled regime. This was startling because both viscous flow and translational motion are similarly controlled by the rate at which individual molecules rearrange to find new neighbors. Why should two observables which depend upon the same fundamental dynamics show a difference in temperature dependence? Experimental results from high-temperature liquids, and the theories used to explain them, provide no insight into this behavior.

While these results are certainly remarkable, they are significantly limited by the dynamic range accessible in NMR experiments. Self-diffusion data was obtained at temperatures greater than $1.2T_g$; $D_T$ at this temperature is 6–9 orders of magnitude larger than the value expected at $T_g$. Optical experiments, measuring the translational and rotational diffusion of probes doped into supercooled liquids [2], have also been performed. Near $T_g$, these probe measurements observed that the rotational correlation time tracks the viscosity while translational diffusion does not. For several organic liquids, probe diffusion was 2–4 orders of magnitude larger at $T_g$ than expected [2,3]. There is no known way to obtain quantitative self-diffusion coefficients from the probe data.

We present here self-diffusion measurements for 1,3-bis-(1-naphthyl)-5-(2-naphthyl)benzene (TNB), one of the best characterized low molecular weight glass formers [4–6]. Our results show enhancement of translational diffusion relative to viscosity or rotation by a factor of 400 at $T_g$ and are thus qualitatively consistent with previous probe diffusion measurements. This enhanced translation cannot be explained by a homogeneous description of molecular dynamics in liquids, such as the Stokes-Einstein and Debye-Stokes-Einstein (SE-DSE) equations which are good models for high-temperature liquids. These results and the previous probe measurements support the view that dynamics in deeply supercooled liquids are spatially heterogeneous [7–9], as described below.

In order to measure self-diffusion in TNB, amorphous thin film bilayers of TNB and its partially deuterated analogue (TNB-$d_{14}$) were prepared by physical vapor deposition onto silicon wafers under high vacuum (see Fig. 1). Synthesis and purification of TNB and TNB-$d_{14}$ (with the two 1-naphthyl groups perdeuterated) were carried out as described previously [10]. Typically, 250 nm of TNB was vapor deposited followed by a 50 nm layer of TNB-$d_{14}$. Film thicknesses were determined *in situ* using a quartz crystal modulator and confirmed using ellipsometry and profilometry. Local surface roughness and total thickness variation across a 3 cm sample, as determined by atomic force microscopy (AFM) and profilometry, were typically smaller by an order of magnitude than the 35 nm depth resolution of the forward recoil

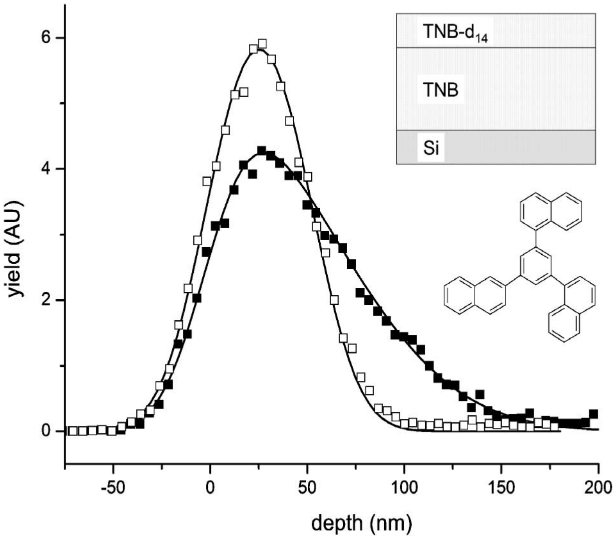

FIG. 1. Deuterium FReS data, converted to yield versus depth from the air/TNB-$d_{14}$ interface. Hollow symbols are an unannealed sample while the filled symbols are for a sample annealed for 1140 sec at 356 K. The solid lines are the best fits, giving a self-diffusion coefficient $D_T = 1.2 \times 10^{-14}$ cm$^2$/sec. The top inset is a representation of the deuterio/protio bilayer of TNB as initially deposited from the vapor phase. The bottom inset shows the molecular structure of TNB.

spectrometry (FReS) experiment. Annealing at temperatures ranging from $T_g$ ( = 342 K) to $T_g$ + 18 permitted diffusion across the initially sharp interface. Low energy FReS (1.6 MeV $\alpha$ particles, 6 $\mu$m Mylar stopper foil) was used to measure concentration profiles before and after annealing, as shown in Fig. 1. Diffusion on the time and distance scales of interest was assumed to be Fickian, and the self-diffusion coefficient, $D_T$, was determined from a single-parameter least-squares fit. Structural relaxation also occurs during annealing, but has a negligible influence on the measured $D_T$ values since $t_{\text{annealing}}/\tau_\alpha > 75$. Along with the assumption of Fickian diffusion, this was checked using multiple annealing times at a given temperature. The total error in the reported $D_T$ values is estimated to be 0.15 decades or less. Prior to vapor deposition, the silicon wafer with intact native oxide layer was spin coated with a 15 nm high molecular weight polystyrene film. This reduced the surface free energy and significantly reduced the rates of crystallization and dewetting of the TNB films. Samples used in the experiments exhibited no dewetting and were typically less than 5% crystalline, as determined by optical microscopy and AFM.

The values of the translational self-diffusion coefficient $D_T$ measured with the FReS technique are given in Fig. 2, along with higher temperature values measured by Chang and Sillescu [11] using static field-gradient NMR. The FReS data cover 2.5 decades and extend the range of measured $D_T$ values by 6 decades. A slight correction has been applied to the $D_T$ values shown in Fig. 2. The $T_g$ for TNB-$d_{14}$ is 2 K lower than protio TNB. Since the $D_T$ values were obtained from experiments where the interface width was comparable to the thickness of the original TNB-$d_{14}$ film, the effective $T_g$ of the mixture is 1 K lower than that of protio TNB. Thus, the measured $D_T$ values have been shifted up 1 K in order to provide the best estimate of $D_T$ for protio TNB in a protio TNB matrix.

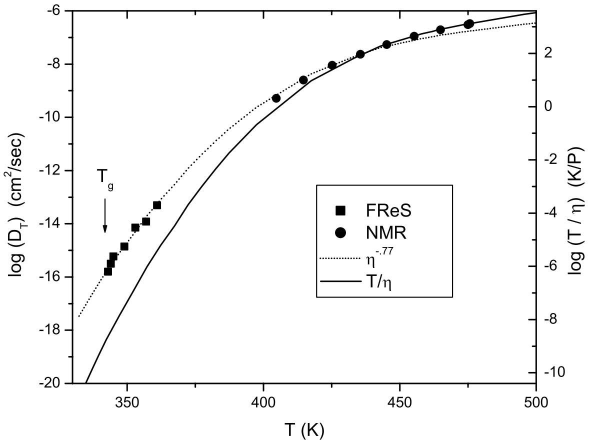

FIG. 2. Comparison of the temperature dependence of translational diffusion with the viscosity. $D_T$ for TNB determined from FReS and NMR [11] is given on the left axis. Temperature over viscosity [6] is given by the solid line, with scale on the right-hand axis, shifted in order to permit overlap of the high temperature values of the viscosity and $D_T$ values. The dashed line is $\eta^{-0.77}$, vertically shifted.

Figure 2 compares the temperature dependence of $D_T$ with that of the viscosity [6] $\eta$ (solid line). While the increase in viscosity is consistent with the slowing down of the $\alpha$ relaxation [12] as the temperature is lowered, a weaker temperature dependence is observed for $D_T$. The combined FReS and NMR measurements of $D_T$ can be reasonably fit from 435 K down to $T_g$ with $D_T \propto \eta^{-0.77}$. At $T_g$, the "enhancement" of translation relative to viscosity is 2.6 orders of magnitude.

The relationship between $D_T$ and $\eta$ is further examined in Fig. 3, along with previous measurements of translational diffusion in TNB using probes. The Stokes-Einstein relation, which is consistently found to be a reasonable description of high-temperature liquids, gives a value for translational diffusion that is proportional to $T/\eta$ and thus predicts a temperature independent value for the function plotted in Fig. 3. Clearly, both the probe and self-diffusion values are much larger than predicted at low temperature and thus are not consistent with a homogeneous description of dynamics in TNB. If one assumes that dynamics are spatially homogeneous, the data shown in Fig. 3 lead to the unappealing conclusion that mechanical relaxation of glass-forming materials is not controlled by molecular motion. These self-diffusion results were not wholly unexpected, as can be seen by the

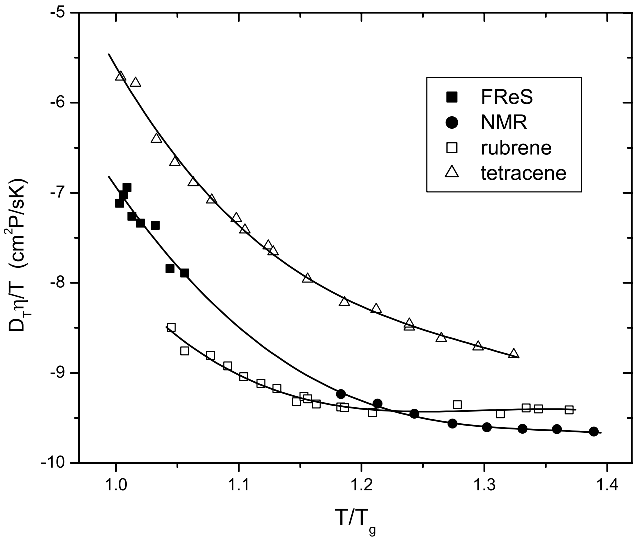

FIG. 3. $D_T$ from FReS and NMR [11] multiplied by $\eta/T$. Translational diffusion measurements of the probes rubrene and tetracene in TNB [3] are also shown. The significant temperature dependence of $D_T\eta/T$ is inconsistent with the Stokes-Einstein equation and provides evidence for the spatially heterogeneous description of dynamics in the supercooled regime. Solid lines are guides to the eye.

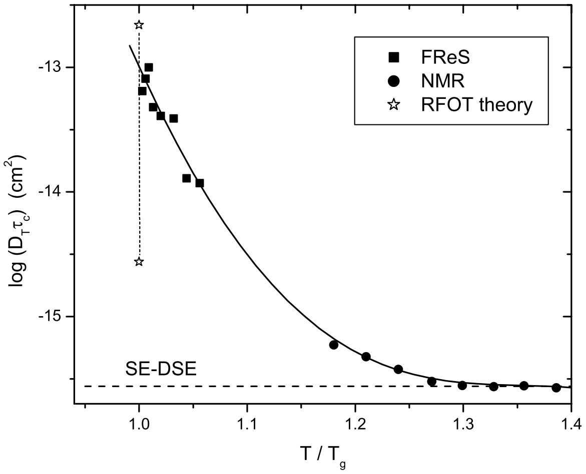

FIG. 4. Product of $D_T$ (FReS and NMR [11]) and the rotational correlation time $\tau_c$ (NMR [13]). The dashed line is the temperature independent value calculated from the Stokes-Einstein/Debye-Stokes-Einstein equations: $D_T\tau_c = (2/9)R^2$. The high temperature NMR data gives a hydrodynamic radius $R = 3.5$ Å. The vertical bar at $T/T_g = 1.0$ is the prediction made by the random first order transition model of Wolynes and co-workers [14,15] based on the fragility of TNB obtained from Refs. [6,12]; upper and lower points correspond to fragilities ($D$) of 10 and 47, respectively.

comparison with probe diffusion data in Fig. 3. Our FReS measurements of $D_T$ are important in order to quantitatively describe dynamics at the glass transition and simultaneously serve to validate the general conclusions of the more indirect probe measurements.

In addition to the comparison of $D_T$ with $\eta$, which is a macroscopic observable, it is insightful to examine the relationship between translation and rotation, two observables which both are described by single particle correlation functions. A plot of $\log(D_T\tau_c)$ versus scaled temperature is given in Fig. 4. The values of the rotational correlation times have been obtained directly from NMR measurements [13] of $\tau_c$ at low temperatures and by shifting the viscosity data appropriately to give an extrapolation to high temperatures. This assumption that $\tau_c$ is proportional to $\eta$ has been experimentally confirmed in two similar low molecular weight glass-forming systems [1,16]. $D_T\tau_c$ data can be compared to the value calculated from the SE-DSE equations, given as a dashed line. The deviation from the high-temperature value, where the hydrodynamic continuum limit is typically found to apply well, illustrates the remarkable decoupling of the two observables calculated from single particle correlation functions. From this data, we can calculate that the average distance translated by TNB molecules in one rotational correlation time ($\sqrt{6D_T\tau_c}$) at $T_g$ is 20 times further than the average distance translated during the same angular displacement at high temperatures. If one insists on a homogeneous description of dynamics in supercooled liquids, these results imply that every molecule in the system is behaving identically in this rather unphysical manner.

The view that dynamics in supercooled liquids are spatially heterogeneous provides a natural explanation for the data in Fig. 4. Experiments [17–20] and simulations [21–24] agree that regions of varying dynamics exist in supercooled liquids. Experiments near $T_g$ indicate that the distribution of local relaxation times can be several decades in width and that a typical slow region is a few nanometers in diameter. These regions of differing dynamics naturally give rise to nonexponential relaxation in ensemble average measurements. The decoupling between self-diffusion and rotation shown in Fig. 4 is thought to occur because $D_T$ and $\tau_c$, to a first approximation, average over different moments of the distribution, with $D_T$ more strongly emphasizing fast dynamics, while $\tau_c$ is determined primarily by the slowest molecules [25]. In contrast to the homogeneous explanation, this heterogeneous view does not require any individual molecule to translate long distances without rotating. Richert and Duvvuri [12] have very recently reported that the dielectric spectrum of TNB can be characterized by a temperature independent width from 345–417 K. While this width is consistent with substantial enhancement of translational diffusion, its temperature independence is surprising given the strong temperature dependence of the observed translational enhancement.

While the above explanation is qualitative, the self-diffusion data presented here are well suited for quantitative tests of theoretical models of the glass transition and thus will aid in the development of more accurate descriptions of dynamics in supercooled liquids and glasses. In that light, Fig. 4 shows a comparison between our data and the prediction of the random first order transition model of Wolynes and co-workers [14,15]. The enhancement of translational diffusion for this model, which incorporates a heterogeneous description of dynamics, depends upon the fragility. The fragility of TNB was determined from Vogel-Tammann-Fulcher (VTF) fits to two sets of data: Plazek and Magill's [6] viscosity data and recent dielectric spectroscopy data from Richert [12]. The fragility depends both on the data set and the temperature range of the fit; the corresponding predictions of translational enhancement range from 1.0 to 2.9 decades. This comparison is somewhat ambiguous as the theory assumes that the VTF equation is applicable over a wide temperature range; this is not the case for TNB.

The spatially heterogeneous dynamics which are responsible for the enhancement of translational diffusion near $T_g$ also have an important impact on other material properties such as crystallization rates. For more than 30 years, it has been known that the crystal growth rate of TNB changes less rapidly with temperature than does the viscosity [6]. Recently, this data (which extends down to $T_g + 26$ K) has been used together with a model of crystal growth to make a quantitative prediction of the temperature dependence of $D_T$ [26]. Reference [26] predicts that $D_T \propto \eta^{-1}$ above 413 K and that $D_T \propto \eta^{-0.74}$ from 373–413 K. As shown in Fig. 2, the combined FReS and NMR measurements of $D_T$ can be reasonably fit from 435 K down to $T_g$ with $D_T \propto \eta^{-0.77}$. The diffusion prediction from crystal growth rates is in good agreement with experimental measurements of $D_T$. The nontrivial implication of this agreement is that even in a spatially heterogeneous system crystal growth depends on the long time diffusion coefficient, as opposed to some other average of the local diffusivities.

We have reported quantitative measurements of self-diffusion in a single-component glass-forming material at $T_g$. Using ion beam analysis techniques, we have measured values of $D_T$ as low as $1.6 \times 10^{-16}$ cm$^2$/sec, which increases the range of measurements for TNB by 6 orders of magnitude. These results confirm the existence of an enhancement of translational diffusion relative to molecular rotation or viscosity in the deeply supercooled liquids.

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