

Dynamics of small-molecule glass formers confined in nanopores

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We report a comparative neutron scattering study of the molecular mobility and nonexponential relaxation of three structurally similar glass-forming liquids, isopropanol, propylene glycol, and glycerol, both in bulk and confined in porous Vycor glass. Confinement reduces molecular mobility in all three liquids, and suppresses crystallization in isopropanol. High-resolution quasielastic neutron scattering spectra were fit to Fourier transformed Kohlrausch functions $\exp[-(t/\tau)^\beta]$, describing the α -relaxation processes in these liquids. The stretching parameter β is roughly constant with wavevector Q and over the temperature range explored in bulk glycerol and propylene glycol, but varies both with Q and temperature in confinement. Average relaxation times $\langle\tau(Q)\rangle$ are longer at lower temperatures and in confinement. They obey a power law $\langle\tau(Q)\rangle \propto Q^{-\gamma}$, where the exponent γ is modified by confinement. Comparison of the bulk and confined liquids lends support to the idea that structural and/or dynamical heterogeneity underlies the nonexponential relaxation of glass formers, as widely hypothesized in the literature. © 2011 American Institute of Physics. [doi:10.1063/1.3560039]

I. INTRODUCTION

The effects of nanoscale confinement on glass forming liquids is presently an area of active interest to scientists because of the nontrivial structural and thermodynamic changes imposed on glass formers by confinement, including shifts in the glass transition temperature.¹ According to theoretical work articulating the relationship between structure and molecular mobility in bulk glass-forming liquids, relaxation is explained in terms of cooperatively rearranging regions, in which higher local free volume implies greater molecular mobility.² This intuitively plausible hypothesis has been experimentally confirmed by neutron scattering studies of small-molecule and polymeric glass formers in bulk.³ Our recent measurements of the mean-squared displacement $\langle u^2 \rangle$ of glycerol confined in nanoporous Vycor reverse this relationship between local free volume and molecular mobility.⁴ Values of $\langle u^2 \rangle$ were calculated on the basis of the Gaussian approximation, which presumes that the distribution of particle displacements at long times is Gaussian, as it would be in a system made up of harmonic oscillators in thermal equilibrium.

In a harmonic crystal made up of oscillators with characteristic angular frequency ω , $\langle u^2 \rangle$ is given by $3 k_B T / m \omega^2$. Molecular mobility drops as interparticle interactions grow stronger. The decrease in $\langle u^2 \rangle$ hints that there is a fraction of the liquid tightly bound to the matrix walls, increasing the effective spring constant for the diffusing glycerol molecules. Based on their broadband dielectric spectroscopy study of glass formers confined in so-gel glasses, Arndt *et al.* developed their “two-state exchange model” of the relaxation of

confined low-weight glass formers.⁵ On this picture, there is a surface or interfacial layer of molecules tightly bound to the walls while the remaining space is filled with bulklike liquid, although the dielectric relaxation in these regions is modified by the exchange of molecules between them. Comparing liquids with one (salol), two (pentylene glycol), and three hydroxyl groups (glycerol), they demonstrated that the thickness of the interfacial layer grows with increasing surface wetting and thickens as the temperature is reduced. Another dielectric study of hydrogen bonded glass formers by the same authors led to a more complex three-layered picture, where a solid layer is bound to the pore walls.⁶ The intermediate layer has a range of relaxation times, increasing from the slow dynamics of the solid layer up to the faster rates of the bulklike liquid. A recent molecular dynamics simulation of glycerol confined in cylindrical silanol nanopores also predicts the formation of three concentric layers.⁷ The hydrogen bond lifetime between glycerol molecules is unaltered, but longer living bonds are formed with the silanol matrix. Taken together, these studies provide a consistent microscopic picture of confined glass formers and demonstrate that confined glass formers are structurally and dynamically heterogeneous in ways differing from the bulk.

Structural and dynamical heterogeneity in the bulk glass formers is often cited in the literature as the underlying reason for their nonexponential relaxation $\phi(t)$, which is frequently modeled empirically by the Kohlrausch–Williams–Watts (KWW) function, or the stretched exponential:^{8,9} $\phi(t) \sim \exp[-(t/\tau)^\beta]$. The underlying microscopic basis for this particular functional form remains obscure at present, although it approximately solves the equations of the mode-coupling theory on the time scales of α -relaxation.¹⁰ As discussed further below, the stretching exponent β is taken to be a measure of dynamical heterogeneity, determining how varied

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the relaxation times are for the processes active in the liquid. The structural and dynamical heterogeneities induced by nanoconfinement makes confined glass formers useful systems for understanding the physical meaning of the phenomenological parameters τ and β in the KWW function. A direct comparison can be made of the Kohlrausch parameters of bulk and confined liquids.

We have continued these lines of investigation by studying three structurally similar glass formers confined in Vycor, varying the liquid-matrix wetting. For this study, we selected 2-propanol, propylene glycol, and glycerol as liquids, which have one, two, and three hydroxyl groups, respectively. Fewer hydroxyl groups lead to fewer hydrogen bonds per molecule and therefore weaker wetting of the silica substrate. With liquid-matrix interaction strength as a varying control parameter, we measured the effects of nanoconfinement on both molecular mobility and relaxation by means of quasielastic neutron scattering (QENS).

II. EXPERIMENTAL APPROACH

We selected three small-molecule alcohols for study. Isopropanol, or 2-propanol, ($\text{CH}_3\text{CHOHCH}_3$) is an aliphatic alcohol that undergoes a transition from supercooled liquid to glass at $T_g = 115$ K. Over several hours, isopropanol spontaneously crystallizes at $T_c = 135$ K. Propylene glycol, or 1,2-propanediol, ($\text{CH}_3\text{CHOHCH}_2\text{OH}$), has two hydroxyl groups attached to separate carbon atoms, which has a glass transition temperature of $T_g = 163$ K. Last, glycerol ($\text{CH}_2\text{OHCHOHCH}_2\text{OH}$) is a trihydroxypropane which enters a glassy state at $T_g = 189$ K.

The porous Vycor glass purchased from Corning Inc has a density of 1.5 g/cc and a porosity of 28%. Vycor is manufactured by cooling a liquid mixture of boron oxide and silica until it phase separates by spinodal decomposition. The boron-rich regions penetrating the silica-rich regions are removed by acid leaching, leaving behind a highly disordered network of pores with a 70 Å mean pore diameter. Samples were prepared in the following manner. The Vycor matrix was cut into 1 mm rectangular slabs using a diamond saw cutter, boiled in 30% aqueous hydrogen peroxide solution, and then dried by gentle heating (<5 °C/min to 200 °C) in a vacuum oven. To load, the Vycor slabs were submerged in a heated sample liquid. The detailed surface chemistry of the Vycor is not known, although given the cleaning procedure, we believe that it does not significantly differ from ordinary borosilicate glass. After removal, any remaining bulk material was wiped from its surface. If powdered Vycor were used, the presence of bulk globules of liquid between the grains would lead to a considerable bulk contribution to the scattered intensity. This contribution would have to be subtracted from the raw data.

QENS is used to qualitatively characterize and quantitatively identify dynamical parameters of single molecule motion.^{11,12} Neutrons which incoherently scatter (almost) elastically are Doppler shifted by the moving sample atoms, broadening the elastic line with a lineshape determined by the diffusion of the sample atoms. We used this technique at the high-flux backscattering spectrometer (HFBS) at the NIST Center for Neutron Research in order to compare the molec-

ular dynamics of three glass-forming liquids in bulk and in confinement.¹³ The 0.8 μeV resolution of HFBS resolves motions occurring on a time scale faster than 10 ns, and the Q -values of HFBS (0.25–1.8 Å⁻¹) probe lengths between 4–35 Å. All measurements were performed using the energy range of ± 17 μeV , which sets the lower end of the experimental time window above 100 ps. The background signal from the aluminum containing the samples (and the Vycor matrix) was subtracted from the raw data. Instrumental resolution was empirically determined by measuring a vanadium standard.

Model fits were obtained using the DAVE software package developed by NIST.¹⁴ The measured data are a convolution of the “true” scattering with a resolution, where the resolution was determined by scattering from a standard sample with no detectable dynamics, namely vanadium. Because of the limited energy window in backscattering, quasielastic data Fourier transformed into the time domain are limited by numerical errors. For this reason, our analysis was performed in the frequency domain, with the exception of the propanol data discussed below. Due to the large incoherent scattering cross section of hydrogen, we assume that this incoherent signal dominates in our wholly protonated samples, and that the quasielastic lineshape represents the autocorrelation function of the hydrogen atoms within the experimental time window of HFBS. The model fits therefore describe the diffusive motion of hydrogen atoms within the α -relaxation region.

III. RESULTS

Elastic scattering was measured as a function of temperature to identify when microscopic motion occurs on time scales resolvable by the instrument. In the elastic mode, only neutrons which scatter with no change in energy, to within the resolution of the instrument, are recorded. The elastic intensity is, therefore, proportional to the number of scattering units with motion slower than the resolution of the instrument. Given the measured instrumental resolution and selected energy transfer window, observed motion occurs within an experimental time region stretching from 100 ps to 10 ns. One observes a decrease in the elastic intensity at temperatures where motions are beginning to occur that are accessible to the time scales for the instrument. In this sense, the total elastic intensity is a measure of the nondiffusive or “immobile” fraction of hydrogen atoms in the sample.

Fixed window scans were performed while heating from the base temperature (50 K for propylene glycol and 4 K for the other samples). Figure 1 plots, in arbitrary units, the total elastic intensity obtained by summing over all 16 detector banks. The data has been scaled to permit a direct comparison of the bulk and confined data. In all three sample liquids, the total elastic intensity drops off more rapidly with increasing temperature in confinement than in bulk. It follows that the overall dynamics of the liquid at a given temperature is slower in confinement than in bulk. The scaled elastic intensity from the bulk glycerol drops off from the confined glycerol sample at lower temperatures before a change of slope sets in around 260 K. This suggests that local, secondary relaxations are influenced by confinement. There is a sharp drop in elastic intensity from bulk isopropanol at 184 K, indicating

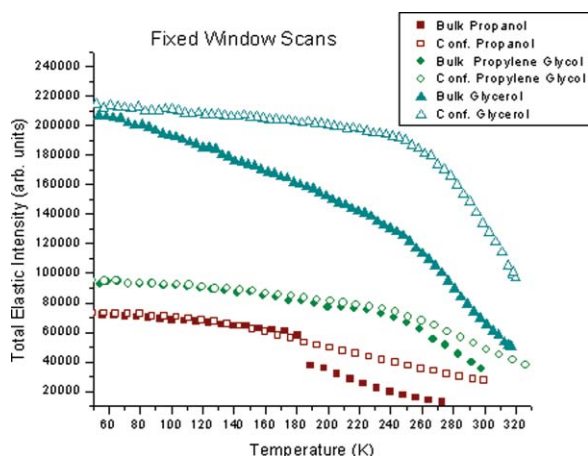


FIG. 1. Total elastic intensity from the bulk and confined liquids as a function of temperature heating at 1 K/min (selected data). In the confined liquids, the intensity drops off more slowly than in the bulk liquids. In bulk propanol, there is a sharp drop in elastic scattering around 184 K.

a sudden onset of motion resolvable by the instrument, a sign of a solid-to-liquid phase transition. This sharp drop is not observed in the confined liquid.

QENS measurements were performed on glycerol at $T = 290, 300, 310, 320, 330,$ and 350 K; and on propylene glycol at 240 (230 in confinement), $265, 290, 307,$ and 320 K. Figure 2 illustrates selected quasielastic data from bulk and

confined glycerol, comparing the temperature and wavevector dependence of the scattering. The overall trend of the glycerol data is followed by both propylene glycol and 2-propanol. The peaks have all been scaled to match the height of the resolution function at $Q = 1.11 \text{ \AA}^{-1}$, which has a full-width at half maximum of $0.8 \mu\text{eV}$. In bulk glycerol, quasielastic broadening, much wider than the instrumental resolution, increases at higher temperatures T and higher values of Q . Although the same overall trend occurs in confinement, the temperature and Q -dependence of the quasielastic broadening is clearly weaker. For the confined liquids, statistical noise, especially in the higher energy tails, makes the Q -dependence difficult to discern for $Q \geq 1.11 \text{ \AA}^{-1}$. The energy range measured here ($\pm 17 \mu\text{eV}$) dictates that we measure relatively long time relaxations. Even before the application of model fits, the QENS spectra for both the bulk and confined liquids behave broadly as one would expect for the diffusive motion of protons over the experimental time region of HFBS; higher energy transfers would correspond to faster, vibrational-type relaxations. The weaker temperature dependence of the broadening in confinement indicates that the diffusive dynamics of the liquid are frustrated by confinement. The QENS spectra of the confined liquids are noticeably narrower than their bulk counterparts and approach the instrumental resolution at low energy transfers, indicating that there is some fraction of the liquid with slow dynamics outside the experimental time window.

QENS Spectra: Glycerol

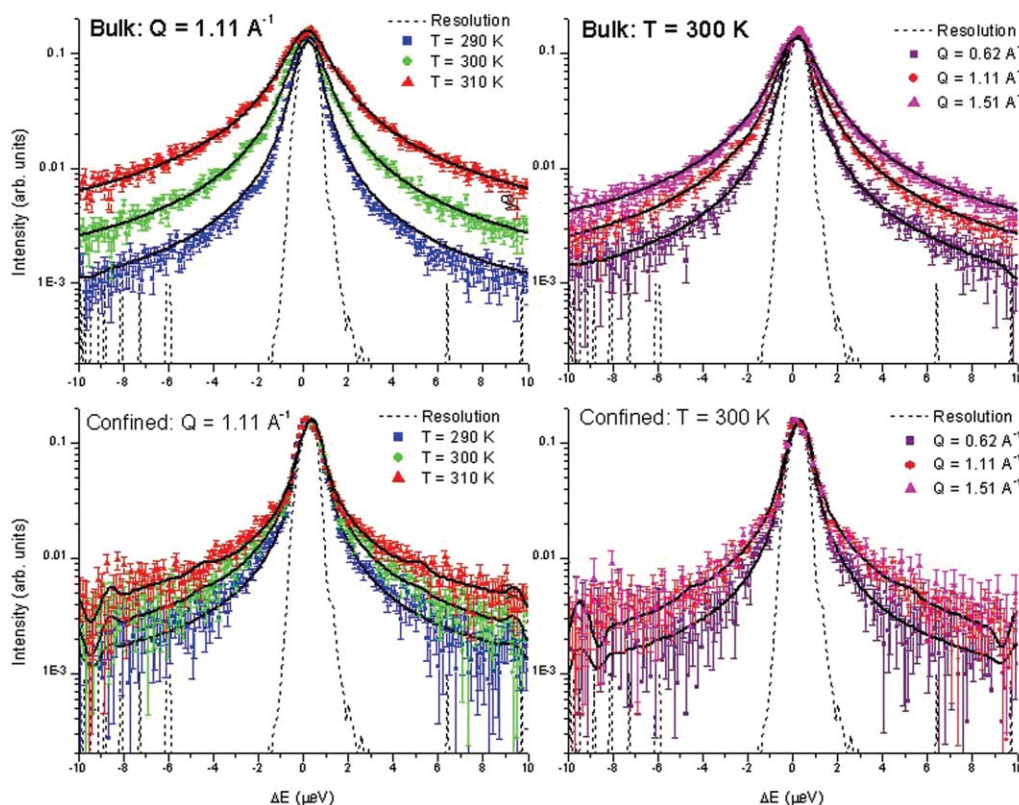


FIG. 2. Representative quasielastic data from bulk and confined glycerol. Model fits shown as solid black curves. No model fit is shown for confined glycerol at $Q = 1.51 \text{ \AA}^{-1}$ because the spectra beyond 1.11 \AA^{-1} cannot be readily distinguished due to statistical noise. Error bars throughout the text represent one standard deviation.

IV. DISCUSSION

By applying an appropriate model, the elastic scattering as a function of wavevector Q and temperature T can be used to quantify molecular mobility in liquid and solid samples. The elastic intensity $I_{el}(Q, T)$ decays from its value $I^{(0)}(Q)$ at the base temperature according to some elastic incoherent structure factor (EISF) $A(Q, T)$:¹⁵

$$I_{el}(Q, T) = A(Q, T) I^{(0)}(Q). \quad (1)$$

The effective Debye–Waller factor, or EISF, is the Fourier transform of the long-time limit ($t = \infty$) of the self-correlation function discussed further below. Harmonic oscillators are exactly described by the Gaussian approximation, according to which the spatial distribution of the particles at long times is Gaussian, implying that $A(Q, T)$ assumes the following form:

$$A(Q, T) = \exp\left[-\frac{Q^2 \langle u^2 \rangle}{3}\right]. \quad (2)$$

In principle, the elastic incoherent structure factor of bound scatterers is connected to their mean-squared displacement $\langle u^2 \rangle$ at long times $t = \infty$. The Gaussian approximation is the first term in a cumulant expansion valid for such scatterers, and that expansion can be truncated at Q^2 for perfectly harmonic crystals. Anharmonic contributions of the binding potential to the EISF are characterized by the non-Gaussianity parameter α_2 .

$$A(Q, T) = \exp\left[-\frac{Q^2 \langle u^2 \rangle}{3} + \frac{\alpha_2}{2!} \left(\frac{Q^2 \langle u^2 \rangle}{3}\right)^2 + \dots\right]. \quad (3)$$

For each temperature T , the elastic intensity $I_{el}(Q, T)$ versus Q can be fit according to Eqs. (2) or (3), where values for $\langle u^2 \rangle$, the mean-squared displacement, as a function of temperature come out as a fit parameter. We applied the Gaussian approximation of Eq. (2) to the fixed window scans, fitting only to $Q \leq 1 \text{ \AA}^{-1}$. We also fit the entire Q -range going to second-order in the cumulant expansion, as shown below in Fig. 3. Nearly identical values for $\langle u^2 \rangle$ are obtained according to both fit procedures. This is true even at the highest measured temperatures, where higher-order terms in the cumulant expansion are required to obtain a reasonable fit to the high- Q data. This is because values for $\langle u^2 \rangle$ are chiefly determined by the variation of $I_{el}(Q, T)$ at low Q .

Readers may find it gross or inappropriate to model freely diffusing particles as though they were undergoing small oscillations in a binding external potential. In a liquid system, the autocorrelation function is supposed to vanish everywhere at long times as information about the particle's initial position is lost. Nevertheless, because of the finite resolution of the spectrometer, the infinite time limit is never really reached. Correlations between the initial configuration of the system and the upper limit of the experimental time window need not completely vanish. While not trapped in an external potential well, the approximation employed here assumes that diffusing particles may be treated as bound. Vineyard showed

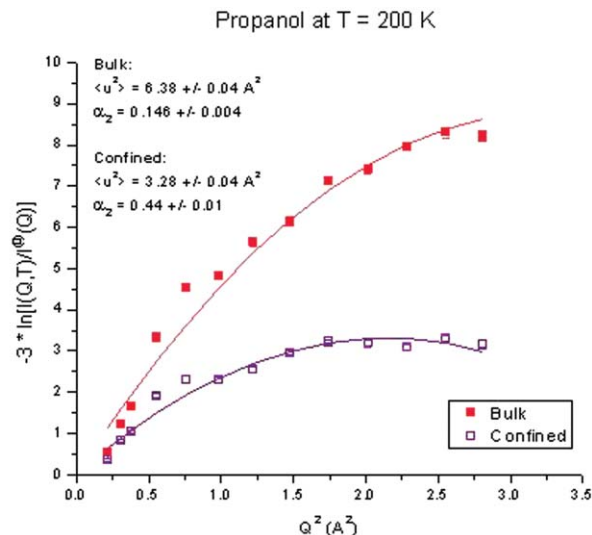


FIG. 3. Application of the cumulant expansion of the EISF, as in Eq. (3), to propanol. Values of $\langle u^2 \rangle$ extracted in this manner are nearly the same as values obtained by fitting Eq. (2) to the truncated data $Q \leq 1 \text{ \AA}^{-1}$.

that at intermediate times, the van Hove autocorrelation functions $G(\mathbf{r}, t)$ of ideal gases, harmonic oscillators, and continuously diffusing atoms are all Gaussian functions of position \mathbf{r} .¹⁶ He proposed to model autocorrelation functions $G(\mathbf{r}, t)$ of simple, classical liquids in the same way. The physical content of applying Eqs. (2) and (3) to our fixed window scan data is that the moving protons are distributed in a (roughly) Gaussian fashion at times longer than the slower limit of the HFBS experimental time window. This justifies treating the EISF $A(Q, T)$ as though it were an effective Debye–Waller factor. Therefore, despite the fact that Eq. (2) exactly applies only to harmonic motion in crystals in the infinite time limit, $\langle u^2 \rangle$ may be taken to be a robust, effective measure of mobility in liquid systems such as the ones studied here. The values of $\langle u^2 \rangle$ versus temperature T are plotted below in Fig. 4.

When heating bulk propanol, there is a sharp change in the total elastic intensity at 184 K, as shown above in Fig. 1.

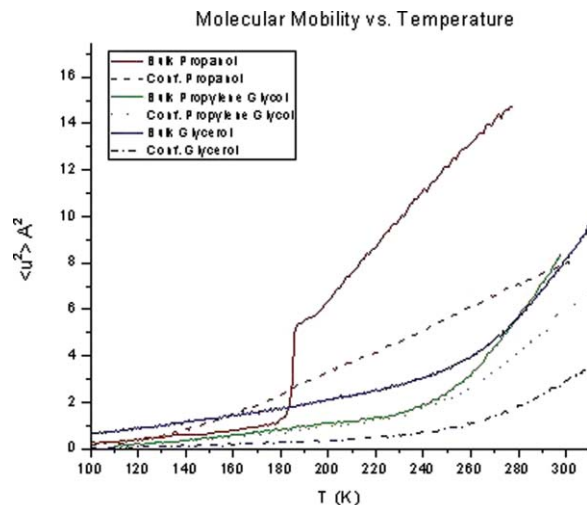


FIG. 4. Mean-squared displacement calculated according to the Gaussian approximation for the bulk and confined liquids.

This sharp change manifests itself as a large, abrupt gain in molecular mobility $\langle u^2 \rangle$. This appears to be due to the melting of microscopic crystallites which form, but are unable to grow to macroscopic size, due to the relatively quick cooling of the fixed window scan (1 K/min). Isothermal crystallization occurs at 135 K only after a period of several hours.¹⁷ When these crystallites finally melt, there is a sudden onset of motion resolvable by HFBS and the total elastic intensity drops. The crystallization of isopropanol is suppressed by confinement, as this sharp feature is not observed in confinement. The suppression of ordered phases is ubiquitous in confined systems, including such outstanding examples as the formation of water ice,¹⁸ the low-temperature antiferromagnetic phase of solid oxygen,¹⁹ and superfluidity in liquid helium.²⁰

As shown, $\langle u^2 \rangle$ is reduced by confinement in all three samples, reflecting a decrease in overall molecular mobility. In both the bulk and confined liquids, there is a change in slope in glycerol at $T \sim 270$ K and in propylene glycol at $T \sim 250$ K. Above $T = 184$ K, the $\langle u^2 \rangle$ -values of the confined propanol curve scale to $\langle u^2 \rangle$ -values of bulk propanol when multiplied by a factor $f = 2.1$. Above $T \sim 250$ K, the confined propylene glycol curves scales on top of the bulk curve when multiplied by a factor $f = 1.4$. However, the confined glycerol curve does not superimpose on top of the bulk glycerol curve when multiplied by any factor.

A naïve interpretation of this scaling result is that molecular mobility is less hindered when the liquid-matrix surface wetting is stronger, opposing the intuitively plausible idea that weaker surface wetting would increase molecular mobility. An alternative interpretation is that the interfacial layer is too slow to be directly observed by the spectrometer at these temperatures, and the values for $\langle u^2 \rangle$ plotted in Fig. 4 represent only modified mobility of the bulklike material occupying the center of the pore. How variation in molecular mobility with surface wetting and the $\langle u^2 \rangle$ -values reported here are to be understood might be resolved by a molecular dynamics simulation directly calculating $\langle u^2 \rangle$ for the different liquid layers or by a comparison to elastic scan measurements of the sample liquids confined in a hydrophobic substrate.

The reduction of molecular mobility in confinement does not bear any obvious relationship to shifts in the glass transition temperature T_g . When glycerol is confined in porous silica, both upward and downward shifts in the glass transition temperature are observed.^{4,21} One might be tempted to argue that a reduction in T_g should imply greater molecular mobility than the bulk liquid when compared at a common temperature T . The magnitude of T_g is determined by the strength of molecular interactions, with stronger interactions increasing the value of T_g . If T_g is, for example, decreased by placing glycerol in a confining silica host, then the interactions which drive the transition are weaker. The effective spring constant between the molecules drops, implying that $\langle u^2 \rangle$ increases.

Arguments of this kind—relating the value of a transition temperature T_c to the strength of interparticle interactions—are commonly used to “explain” why noble gases liquefy at low temperatures. But, we contend that this line of argumentation should not be glibly applied in the case of confined liquids, where the presence of the confining host significantly complicates any microscopic picture of liquid–solid

transitions. Even if it were true that confinement reduces the strength of guest–guest interactions, attractive guest–host forces may be sufficient to compensate any increase in $\langle u^2 \rangle$ resulting from reduced guest–guest interactions.

A decrease in overall molecular mobility, as measured by $\langle u^2 \rangle$, should be strongly expected on the basis of investigations of the macroscopic transport properties and molecular diffusion of liquids confined in porous silica.²² Measurements of molecular reorientation time can be used to measure the viscosity of confined liquids, and for rhodamine 6G in derivatized Vycor it was found that the local viscosity is larger than bulk and increases with decreasing pore volume. At the same time, Rayleigh light scattering experiments on azobenzene confined in porous Vycor have shown that the diffusion occurs about 50 times slower than in bulk. This is consistent with our present report of a decrease in overall molecular mobility in confinement. Other investigators have reported a similar decrease in $\langle u^2 \rangle$ for thin-films of polymeric glass-formers.²³

In a monatomic liquid, atoms are in a process of continuous diffusion over times longer than the typical time between interatomic collisions. The intermediate scattering function $I(Q, t)$ decays exponentially with time for these liquids, since the Green’s function for the diffusion equation decays exponentially with time:

$$I(Q, t) = \int_{-\infty}^{+\infty} S_{\text{inc}}(Q, \omega) e^{i\omega t} d\omega = \exp\left[-\frac{t}{\tau}\right]. \quad (4)$$

The relaxation time is given by $\tau(Q) = D^{-1}Q^{-2}$, where D is the diffusion constant. In molecular liquids, individual molecules have both translational and orientational degrees of freedom. Such molecules randomly move as a whole through the liquid while their parts orient and reorient themselves about their moving center of mass. On a standard model, the translation and rotational motions are statistically uncorrelated and obey diffusion equations in three and two dimensions, respectively. It can be shown in this case that the intermediate scattering function is given by the sum of two exponentials.¹² When this is Fourier-transformed into the ω -domain, the dynamic structure factor $S(Q, \omega)$ is given by the sum of two Lorentzians, one strongly dependent on Q encoding translational information, and one independent of Q encoding rotational information. When the scattering data for our samples is fit to this model, an unphysical Q -dependence for $\tau(Q)$ is obtained; e.g., for bulk glycerol at 310 K, the translational $\tau_{\text{trans}}(Q)$ does not go as Q^2 and the rotational $\tau_{\text{rot}}(Q)$ goes as $Q^{0.6}$. Similar departures were found by Sobolev *et al.* for ethylene glycol.²⁴ When Swenson *et al.* investigated bulk propylene glycol using QENS, they found their data was described well by the double Lorentzian model.²⁵ However, in that experiment, the elastic energy resolution was 15 μeV with an energy window of ± 0.5 meV, both wider than being considered here. For the dynamics within the experimental time window of HFBS, the translational and rotational components of the motion are probably strongly coupled, making the double Lorentzian model inappropriate for the time scales being considered here.

While the microscopic origin of the nonexponential relaxation of glass-forming liquids remains an open question, the intermediate scattering function $I(Q, t)$ associated with the diffusive motion in glass-forming liquids is frequently described by the KWW function or the stretched exponential:

$$I(Q, t) = f(Q, T) \exp \left[- \left(\frac{t}{\tau(Q, T)} \right)^{\beta(Q, T)} \right]. \quad (5)$$

Both the decay constant τ and the stretching parameter $0 < \beta < 1$ are, in general, functions of both the wavenumber Q and the sample temperature T . The factor $f(Q, T)$ represents the long-time limit of the relaxation. To obtain these parameters using the DAVE software, the Fourier transformed KWW function is convoluted with the instrumental resolution and is least-squares fit to the measured data. The model, shown as heavy black curves in Fig. 2, fits the glycerol bulk data well, with typical χ^2 values of 1–2. Quasielastic broadening from the confined samples is noticeably less than their bulk counterparts. Given statistical noise, values for τ and β could not be obtained for values of Q beyond 1.11 \AA^{-1} . For example, Fig. 2 shows that $Q = 1.11 \text{ \AA}^{-1}$ is not readily distinguished from $Q = 1.51 \text{ \AA}^{-1}$ in confined glycerol at $T = 300 \text{ K}$.

In fitting the quasielastic spectra to Fourier-transformed KWW functions, we are assuming that all measured broadening is due to primary, α -type relaxations. Isopropanol and propylene glycol both contain methyl groups whose rotational motion might be thought to contribute to the scattering. Swenson *et al.* did not extract diffusion constants from their bulk propylene glycol QENS data set at temperatures below $T = 340 \text{ K}$ due to the influence of methyl group rotations on the observed spectra. They estimated the rotational correlation time to be approximately 44 ps at $T = 300 \text{ K}$. This time scale is too short to be observed here. If fast methyl group rotations were visible to the spectrometer, they would contribute a broad, background-like signal. Neither a flat nor a broad background signal from methyl group rotations was necessary to obtain reasonable fits to the data.

More important than the fact that the data can be fit to this empirical model is the physical interpretation of the KWW function in terms of structural or dynamical heterogeneity in the liquid. The relaxation function ϕ , in this case a KWW function, is given by a superposition of exponentials with some distribution ρ of relaxation times determined by the form of ϕ .²⁶

$$\phi(t) = \int_0^\infty \rho(\tau) e^{-t/\tau} d\tau. \quad (6)$$

Thus, the distribution ρ of relaxation times is related to the inverse Laplace transform of the relaxation function: $\rho(\tau) = L^{-1}[\phi(t)]/\tau^2$. As $\beta \rightarrow 0$, the distribution ρ is broadened, indicating greater dynamical heterogeneities within the material.²⁷ In this sense, β is a measure of dynamical heterogeneity, where the limiting case $\beta = 1$ restores ordinary continuous diffusion and $\rho(\tau)$ becomes a Dirac delta function.

Figure 5 plots the stretching parameter β for glycerol; Fig. 6 plots the stretching parameter β for propylene glycol. In the bulk liquids, β is either constant or weakly dependent

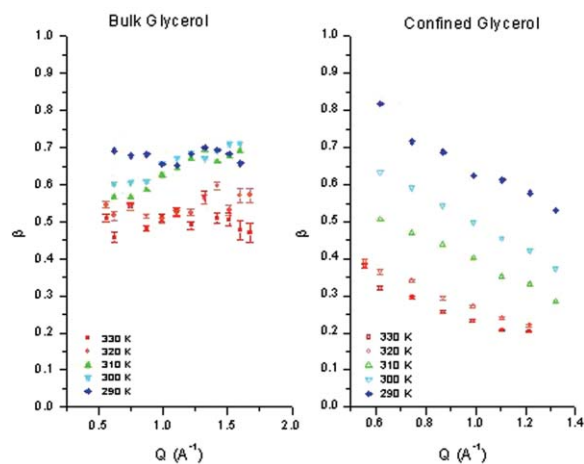


FIG. 5. Stretching parameter β of glycerol plotted as function of wavevector Q . In the confined liquids, β depends strongly on Q and temperature.

on Q . For bulk glycerol, Wuttke *et al.* used an iterative fitting procedure to determine a temperature-independent stretching parameter with a value of $\beta = 0.62$.²⁸ For the lower temperatures investigated, our data shows a temperature-independent value for β in close agreement with what these authors report, but at higher temperatures we obtain $\beta \approx 0.5$. However, as pointed out in that paper, fit values of the decay constant τ and stretching parameter β are strongly correlated, requiring caution when comparing different fit values. The β values for propylene glycol obtained from fitting the QENS data agree well with dielectric spectroscopy, which probes wavevectors $Q \sim 1 \text{ \AA}^{-1}$, performed at the glass transition temperature.^{29,30} In their neutron spin-echo measurements, Swenson *et al.* obtain a stretching parameter $\beta = 0.68$ for propylene glycol.²⁵

Qualitatively different behavior is observed in the confined liquids. While the stretching parameter β is either constant or weakly dependent on Q in the bulk liquids, it decreases monotonically in the confined liquids. Taking β to be a measure of dynamical heterogeneity, this implies that, in confinement, these liquids exhibit increasingly broader

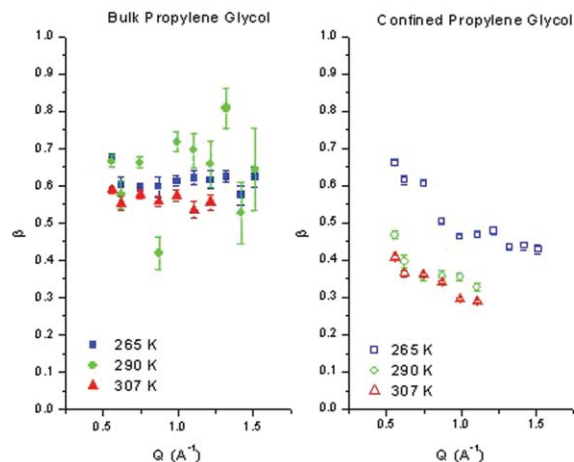


FIG. 6. Stretching parameter β of propylene glycol plotted as function of wavevector Q . In the confined liquids, β depends strongly on Q and temperature.

distributions of relaxation times on smaller length scales. Swenson *et al.* performed a neutron spin-echo study of liquid water confined in vermiculite clay.³¹ They found that β decreases with increasing Q , and reasoned that very different relaxation times on smaller, more *local* length scales “average out” when the system is probed at larger, more *global* length scales. From the temperature dependence of β , it can be inferred that as the liquid cools, the more mobile and faster liquid in the pore center slows, becoming more like the solid and interfacial layers wetting the pore walls. Swenson *et al.* saw this behavior for confined water. They argued that at lower temperatures water molecules interacting only with each other become more like water bound to the clay host.

Time–temperature superposition is sometimes invoked to combined data from different temperature ranges in order to fix relaxation functions of glass-formers over extended times. The intermediate scattering function $I(Q, t)$ is plotted against a reduced time $\tilde{t} = t[\eta(T_0)/T_0]/[\eta(T)/T]$, where $\eta(T)$ is the viscosity at a temperature T and T_0 is some reference temperature, in an attempt to collapse the data onto a single, master curve. This procedure embodies the idea that at higher temperatures over shorter times the system will behave as it would at lower temperatures and longer times. Time–temperature superposition, widely reported in bulk glass-forming liquids, is a well-known consequence of the mode-coupling theory.

It is uncertain whether time–temperature superposition is valid for our bulk data. The stretching parameter β of bulk propylene glycol is roughly temperature-independent, but this parameter β varies with temperature in bulk glycerol, at least at the higher temperatures. The decay shape in the bulk liquids, then, is not clearly amenable to being treated with time–temperature superposition. More interestingly, the stretching parameter β of the confined liquids varies strongly with temperature, making the decay shape a function of temperature. Consequently, time–temperature superposition is not valid for the confined liquids over the temperature range explored here. Additionally, it is not known how to define a reduced time \tilde{t} for the confined liquids, where the (effective) viscosity η of the confined liquid can vary locally throughout the pore volume. On the two-state exchange model, the thickness of the interfacial layer and the exchange rates between that layer and the core liquid vary with temperature. The temperature variation of β in the confined liquids is connected to this fact: liquid-matrix wetting makes the confined liquid structurally and dynamically different as the system temperature is varied, making it unlikely that high-temperature and short-time behavior will be the same as low-temperature and long-time behavior.

Using Eq. (5), one can calculate the average relaxation time even without any knowledge of the detailed form of the distribution function $\rho(\tau)$:

$$\langle \tau \rangle = \int_0^\infty \tau \rho(\tau) d\tau = \int_0^\infty \phi(t) dt. \quad (7)$$

For glass formers or other materials which relax according to a KWW function, the average relaxation time is calculated by integrating the relaxation function over all positive

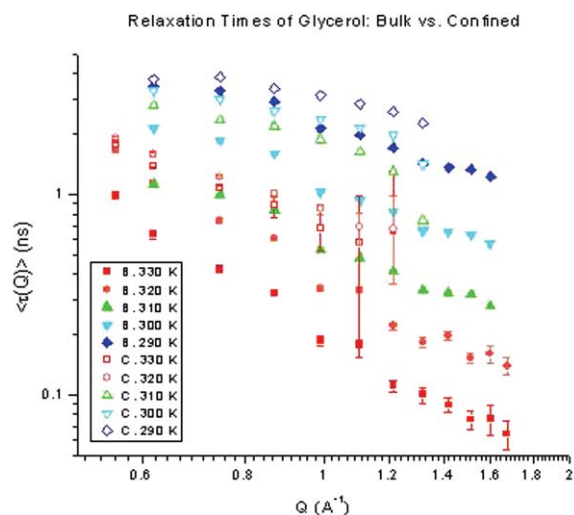


FIG. 7. Comparison of average relaxation times of bulk and confined glycerol. Average relaxation times of the liquids calculated according to Eq. (8).

times:

$$\langle \tau \rangle = \int_0^\infty \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] dt = \tau \frac{1}{\beta} \Gamma \left(\frac{1}{\beta} \right). \quad (8)$$

Thus, each decay constant $\tau(Q)$ can be scaled to an average relaxation time $\langle \tau(Q) \rangle$ based on $\beta(Q)$. Figure 7 plots the average relaxation time $\langle \tau \rangle$ versus Q for glycerol; Fig. 8 plots the average relaxation time $\langle \tau \rangle$ versus Q for propylene glycol.

The relaxation times are longer at lower temperatures for both the bulk and confined liquids. For bulk glycerol, the Q -dependence at high- Q is similar to those reported by Wuttke *et al.*:²⁸ at 300 K they report values of 1 ns and shorter for $Q \geq 1 \text{ \AA}^{-1}$. The Q -dependence of τ follows a power law behavior: $\langle \tau(Q) \rangle \propto Q^{-\gamma}$, where $\gamma = 2$ for continuous diffusion. For bulk glycerol at $T = 330, 320, 310, 300,$ and 290 K , the exponent γ takes the values $\gamma = 2.44, 2.24, 1.59, 1.51,$ and 1.23 , respectively. For bulk propylene glycol at $T = 307, 290,$

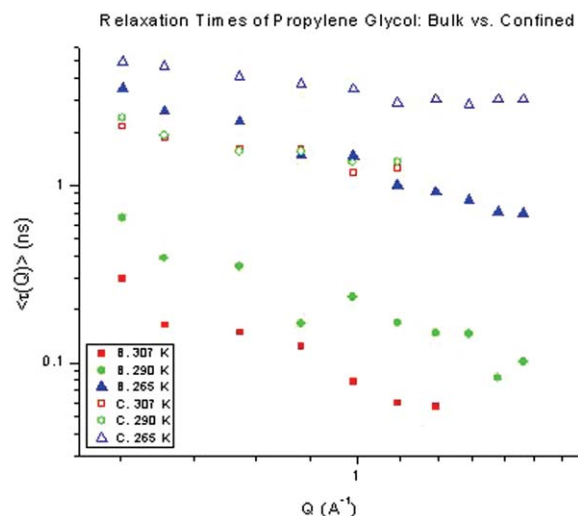


FIG. 8. Comparison of average relaxation times of bulk and confined propylene glycol. Average relaxation times of the liquids calculated according to Eq. (8).

and 265 K, the exponent γ takes the values $\gamma = 1.99, 1.65,$ and 1.68 , respectively. This increased departure from continuous diffusion as the temperature is lowered has been seen in bulk ethylene glycol, another H-bonding glass-former.³²

The confined liquids show different behavior: The relaxation times are longer in confinement than in bulk, and the power law behavior is modified. For confined glycerol at $T = 330, 320, 310, 300,$ and 290 K, the exponent γ takes the values $\gamma = 1.40, 1.37, 1.03, 0.77,$ and 0.68 , respectively. For confined propylene glycol at $T = 307, 290,$ and 265 K, the exponent γ takes the values $\gamma = 0.82, 0.79,$ and 0.55 , respectively. As in the bulk samples, there is an increasing departure from continuous diffusion at lower temperatures. This temperature dependence of the exponent γ was also observed in confined ethylene glycol.³²

The relationship between the strength of surface wetting and the modifications to the relaxation times is unclear. In terms of absolute values, the measured shifts in relaxation times at a given temperature of propylene glycol are larger than for glycerol. As in the case of $\langle u^2 \rangle$, two alternative interpretations suggest themselves. A naïve interpretation of these shifts is that relaxation is less effected when the liquid-matrix interaction is stronger, opposing the initially plausible idea that stronger surface wetting leads to slower dynamics. An alternative interpretation is that motions occurring within the interfacial layer are not (completely) observable by the spectrometer. In this case, the measured relaxation times are associated chiefly with the molecules occupying the center of the pore. As the coupling to the matrix wall grows in strength, interfacial molecules have slower dynamics and lower exchange rates with those occupying the center of the pore, leaving their behavior less altered than they would be for weaker surface wetting.

When fit only to a Fourier-transformed Kohlrausch function, the bulk 2-propanol data yielded implausibly low values for the stretching parameter $\beta = 0.2$ – 0.3 . If a flat background and an elastic δ -function contribution are included in the model, more plausible values of the stretching parameter are obtained $\beta = 0.5$ – 0.6 . The physical origin of this elastic contribution is unclear, although a dilute solid contamination (moisture) or residual crystallization might account for it. For this reason, we chose to analyze the propanol data in the time domain, deconvoluting it from the resolution function, and then truncating after 1100 ps. Figure 9 plots the resulting fit parameters. Propylene glycol and glycerol were reanalyzed this way as a consistency check. As in bulk glycerol and propylene glycol, the stretching parameter β is independent of Q , and increases with increasing temperature. For bulk propanol at $T = 221, 210,$ and 190 K, the exponent γ takes the values $\gamma = 1.68, 1.58,$ and 1.94 , respectively. Despite the fact that these values of γ are similar to bulk propylene glycol and glycerol, the Q -dependence of the average relaxation time most closely resembles continuous diffusion for the lowest temperature studied.

While quasielastic broadening over the resolution for the confined propanol samples was observed at the chosen temperatures, this broadening was not great enough to permit a confident analysis. Confinement appears to slow the dynamics of the confined liquid outside the dynamic range of

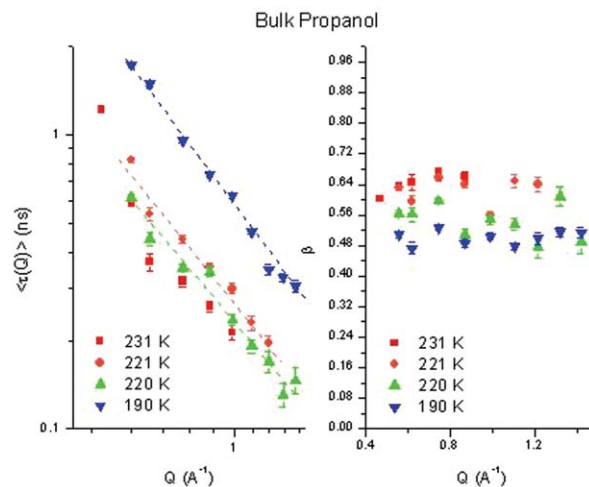


FIG. 9. Stretching parameter and average relaxation times for bulk 2-propanol. Dotted lines are guides to the eye.

the instrument. This is puzzling given that propanol should have weaker surface wetting than either glycerol or propylene glycol.

The two-state exchange model developed by Arndt *et al.* suggests a family of more sophisticated model functions than the single KWW function used to analyze the scattering data discussed in this report. If x is the fraction of molecules contained in the interfacial layer, then the double-differential cross section can be written as a weighted sum of the dynamic structure factors of the interfacial and bulklike layers:

$$\frac{\partial^2 \sigma}{\partial \Omega \partial E_f} = \frac{\sigma_i}{4\pi \hbar} [x S_w(Q, \omega) + (1-x) S_b(Q, \omega)]. \quad (9)$$

On this approach, the scattering data is decomposed into two fitting functions, describing the interfacial layer and core material as giving separate contributions to the total scattering. One possibility would be to postulate a δ -function for the interfacial layer, supposing that the molecules are immobile within the experimental time window of the spectrometer. Alternatively, a second KWW function could be used in place of the Dirac δ -function, and the acquired fit parameters would describe the dynamics of the layers separately.

While tempting, there are two difficulties in implementing such models. In the case of the present spectrometer, the confined liquids are much closer to the instrumental resolution of their bulk counterparts. Related to this difficulty is the proliferation of fit parameters. Without the addition of constraints, say on the fraction x of molecules forming the interfacial layer, the reliability of the fit remains open to doubt. It is unclear whether one can justifiably use the thickness of the interfacial layer determined by Arndt *et al.* by dielectric spectroscopy, as previous authors have argued that dielectric spectroscopy does not probe the same dynamics as neutron scattering.³³

V. CONCLUSION

We reported a comparative QENS study of three small-molecule glass formers, both in bulk and confined in Vycor. By applying the Gaussian approximation to our measurements of the EISF for these liquids, it was found that molecular mobility is suppressed by confinement. The Fourier transform of the KWW function fits the QENS spectra well, and qualitative differences in the general trends of the stretching exponent β and average relaxation time $\langle\tau(Q)\rangle$ appear. The stretching parameter β , a measure of dynamical heterogeneity, is roughly constant with Q in the bulk liquids, but varies with Q in confinement. Average relaxation times $\langle\tau\rangle$ are longer at lower temperatures and in confinement. They obey a power law in Q , where the exponent is modified by both temperature and nanoconfinement. The data lends itself to two mutually conflicting interpretations, depending on whether the instrument probes the behavior of all of the sample or only the core liquid within the center of the pores. Further theoretical and experimental investigations are necessary in order to resolve this ambiguity.

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