Nature of Molecular Rotation in Supercooled Glycerol under Nanoconfinement

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The dynamics of glass-forming liquids under nanoconfinement is key to understanding a variety of phenomena in nature and modern technology. We report a ^{13}C NMR spectroscopic study that directly demonstrates that α-relaxation in bulk glycerol involves an isotropic rotational jump of the constituent molecules. The activation energy of this motion is ∼78 kJ mol^{-1} in the bulk, which abruptly changes to a low value of ∼27.5 kJ mol^{-1}, characteristic of β-processes, upon confinement of glycerol into ∼2 nm pores in mesoporous silica. This observation implies that the molecular dynamics associated with structural relaxation near glass transition are inherently different in supercooled glycerol in the bulk and under extreme nanoconfinement.

1. Introduction

The current surge in interest in the behavior of liquids under confinement is motivated by a plethora of phenomena in which such situations are encountered in nature and in modern technology.[1–3] Some examples include transport of water and oil in soils and rocks, transport and other dynamical phenomena in liquids in cells and near membranes, and behavior of polymer thin films used as photoresists in the semiconductor industry. However, despite the application of a wide variety of molecular modeling and experimental techniques, including Monte Carlo, molecular dynamics, calorimetry, nulcear magnetic resonance (NMR), and dielectric relaxation, fluorescence spectroscopy, and solvation techniques, unambiguous mechanistic connections have rarely been established at the atomic level to explain the dynamical differences between liquids in the bulk and under confinement.[2] Moreover, the process of glass transition in glass-forming liquids has recently been found to be strongly affected by confinement of the liquid to nanometer length scales, and the corresponding response is observed to be nonuniversal.[4]

The glass transition temperature, T_g, can either increase or decrease with the dimensionality and extent of confinement. Confining in spherical or cylindrical pores of nanometer size may have two important effects on the dynamics of glass-forming liquids.[5] First, when the length scale of confinement becomes comparable to or smaller than that of the cooperatively rearranging regions responsible for structural or α-relaxation, then the effect of cooperative molecular dynamics is greatly diminished, thus speeding up the liquid dynamics, resulting in a drop in T_g. Second, as the length scale of confinement decreases, an increased fraction of molecules may begin to interact more and more strongly with the walls of the confining medium. This interaction, if present, may drastically change the dynamics of the molecules near the surface as compared to those in the interior. This latter effect usually results in a change in the effective T_g or in two separate T_g values corresponding to the molecules in the interior and those near the surface.

In addition to these spatial effects of nanoscale confinement, the structure and density of the liquid may also change under confinement. The extent of such effects and their importance in controlling the dynamics are only poorly understood.[2,5] A number of experimental studies of the effects of spatial confinement on the properties of glass-forming liquids have used complex polymeric systems under one- and two- dimensional confinement, for which understanding the effects of confinement on individual dynamic modes remains an extremely challenging task.[2] Low-molecular-weight (LMW) glass-forming liquids, such as glycerol and *ortho*-terphenyl, are ideal to study in this regard because the possible intra- and intermolecular dynamic modes in bulk liquids are relatively limited in number, are well-understood, and can be studied with a wide range of experimental and simulation techniques.[6–14]

The effect of spatial confinement on molecular dynamics and glass transition in simple molecular liquids have been studied quite extensively using NMR spin−lattice relaxation and dielectric relaxation techniques in the past.[5,15–19] However, it should be noted that although these studies may provide detailed information regarding the relaxation time and its temperature dependence, no direct information can be gleaned from such studies concerning the exact nature of the primary mode of molecular dynamics.

Another important but less appreciated problem with experimental studies of confinement effects has been the use of commercially available nanoporous materials, such as Vycor and Gelsil glasses as confining media.[2,3,5,15,20,21] These glasses are characterized by poorly constrained pore geometry with a wide range of pore sizes, shapes, and connectivities. In contrast to these materials, mesoporous silica, such as MCM-41, offers a good model matrix to study confinement effects because it contains uniform cylindrical pores of controlled size.[4]

Here, we report the results of a ^{13}C static NMR line shape study of molecular dynamics in glycerol in the bulk (i.e., unconfined) state and under nanoconfinement in mesoporous silica over the entire temperature range of supercooling: T_g (185 K) $\leq T \leq$ 295 K. The purpose of this study is to compare and contrast the atomic-scale dynamics of bulk and nanoconfined LMW glass-forming liquid, such as glycerol, and to develop new mechanistic understanding of the dynamical phenomena

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associated with glass transition in the bulk and under confinement. NMR line shape analysis of dynamical averaging of chemical shift anisotropy is a particularly useful tool to directly probe the molecular structure and dynamics over a wide range of temperatures and time scales, the latter typically ranging between 10^{-3} and 10^{-8} s.[22–24]

2. Experimental Methods

[13]C-Enriched glycerol (propane-1,2,3-triol) with selective enrichment at the carbon 2 (CHOH) position (99.999% purity with 99.5 atom % [13]C) was purchased from Isotec, Sigma-Aldrich. Since glycerol is hygroscopic, all samples were stored and loaded inside an Ar-filled glovebox.

For measurements on the unconfined (denoted as "bulk" hereafter) sample, the as-received glycerol was loaded into 4 mm ZrO_2 rotors and sealed with ZrO_2 caps and immediately transferred into the NMR probe that was kept in a dry nitrogen environment. The mesoporous silica matrix, MCM-41, with 2.2 nm pores was synthesized and calcined at 773 K in subsequent N_2 and O_2 flow, as reported elsewhere, for nanoconfinement of glycerol.[4] N_2 adsorption and X-ray diffraction techniques were employed to characterize the structure, BET surface area, pore size, and pore size distribution of the mesoporous silica matrix. Pores of MCM-41 were degassed at 473 K in vacuum and were filled with glycerol at room temperature at the 95−100% level in an Ar-filled glovebox. The confined samples were heated to 320 K to make sure that pores were fully filled and no bulk liquid was present.

The confined samples were sealed in a 4 mm ZrO_2 rotor with ZrO_2 cap. All NMR experiments were carried out using a Bruker 500 wide-bore spectrometer, operating at a Larmor frequency of 125.26 MHz for ^{13}C and a Bruker 4 mm double resonance variable temperature (VT) probe. The dry nitrogen gas boil-off from a high-pressure liquid nitrogen dewar was used for temperature control of the sample. All single-pulse ^{13}C static NMR spectra were collected using direct polarization with proton decoupling and rf pulses with a tip angle of 90° (2.9 μs). At low temperatures (185 K ≤ T < 233 K), an average of 32 transients were collected with a recycle delay of 60 s and were averaged to obtain each ^{13}C spectrum. For higher temperatures (295 K ≥ T > 233 K), each spectrum was obtained from an average of eight transients with a recycle delay of 30 s. The spectra collected at 185 K were processed with a line broadening of 40 Hz, and all other spectra were processed with a line broadening of 1−4 Hz.

3. Results and Discussion

The ^{13}C static NMR spectra of bulk and nanoconfined glycerol at 185 K are shown in Figure 1. These spectra correspond to the carbon 2 (CHOH) site of the glycerol (propane-1,2,3-triol) molecule. These two ^{13}C static NMR spectra are practically identical and are dominated by the chemical shift anisotropy (CSA) interaction. Simulation of this line shape yields the following principal components of the chemical shift tensor for the carbon 2 site: $\delta_{11} \approx 88$ ppm, $\delta_{22} \approx \delta_{33} \approx 68$ ppm, resulting in an isotropic shift $\delta_{iso} = 74.7$ ppm (Figure 1). The temperature-dependent evolution of the ^{13}C static NMR spectra of supercooled bulk and nanoconfined glycerol at temperatures ranging between 213 and 295 K are shown in Figure 2. It is clear from Figure 2 that with increasing temperature, the experimental line shape shows isotropic orientational averaging of the CSA, indicating isotropic reorientational motion or tumbling of the glycerol molecules. Such motion of glycerol molecules was also
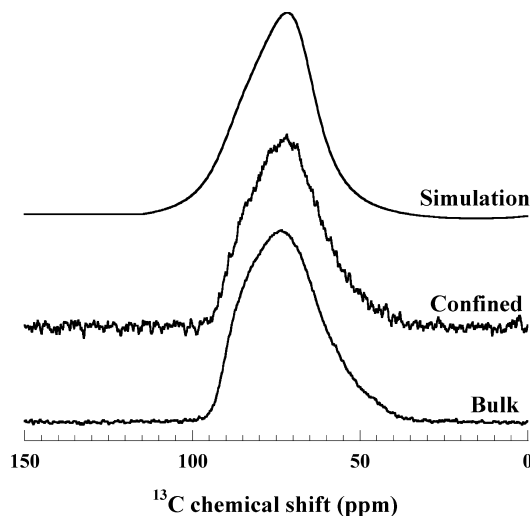

Figure 1. Experimental (bottom and middle) and simulated (top) ^{13}C static NMR spectra of bulk and nanoconfined glycerol (propane-1,2,3-triol), with selective ^{13}C isotopic enrichment at the carbon 2 (CHOH) site, at 185 K.

suggested in previous ^{13}C hole-burning NMR and ^{2}H stimulated-echo NMR studies on bulk glycerol at temperatures close to T_g.[25–27]

The ^{13}C static NMR spectral line shapes in Figure 2 can, indeed, be simulated well over the entire temperature range using a model of isotropic rotational jump or tumbling of the ^{13}C chemical shift tensor for the carbon 2 (CHOH) site, resulting in an "exchange" among N different orientations under the rigid molecule (T ≤ 193 K) powder pattern. The analytic expression for the resulting line shape is given by the real part of $g(\omega)$, where $g(\omega) = (1/N)(L/(1 -(L/\tau_{NMR}))$ and $L = \sum_{j=1,N}[i(\omega - \omega_j) + 1/T_{2j} + N/\tau_{NMR}]^{-1}$, ω_j is the frequency and T_{2j} is the reciprocal of the intrinsic line width corresponding to the orientation j, and $1/\tau_{NMR}$ is the frequency of the reorientational exchange or tumbling frequency of the ^{13}C chemical shift tensor.[22] In this analysis, the frequencies ω_j corresponding to 400 orientations (N) were generated by taking that many angular steps through the expression for the nonaxial powder pattern. The value of T_{2j} at each temperature was obtained from experimental measurements of ^{13}C NMR spin−spin relaxation times T_2 using a Car−Purcell pulse sequence.[28] A single average temperature-dependent tumbling frequency, τ_{NMR}^{-1}, is found to be sufficient for simulation of all spectra (Figure 2). This observation provides further confirmation that the glycerol molecule is reorienting as a whole, and intramolecular dynamical modes, if present, do not exert any influence on the ^{13}C NMR line shape.

The good agreement between simulated and experimental ^{13}C static NMR line shapes in Figure 2 indicates that the dominant mode of dynamics responsible for controlling these line shapes in both bulk and confined glycerol is the isotropic rotational jump of the constituent molecules over all possible angles with equal probability. The temperature dependence of the time scale τ_{NMR} of the isotropic tumbling motion of glycerol molecules, as obtained from the simulation of the ^{13}C static NMR line shapes of bulk glycerol, is compared with the previously reported α-relaxation time scale, τ_α, of bulk liquid in Figure 3.[7] The agreement between τ_{NMR} and τ_α over 6 orders of magnitude in time scale is remarkable, and it implies that dielectric or α-relaxation in supercooled bulk glycerol is controlled by isotropic tumbling of the constituent molecules in the temperature range: $T_g + 28$ K ≤ T ≤ $T_g + 110$ K. The activation energy of this motion is estimated to be ∼78 ± 6 kJ mol^{-1} in this temperature range.
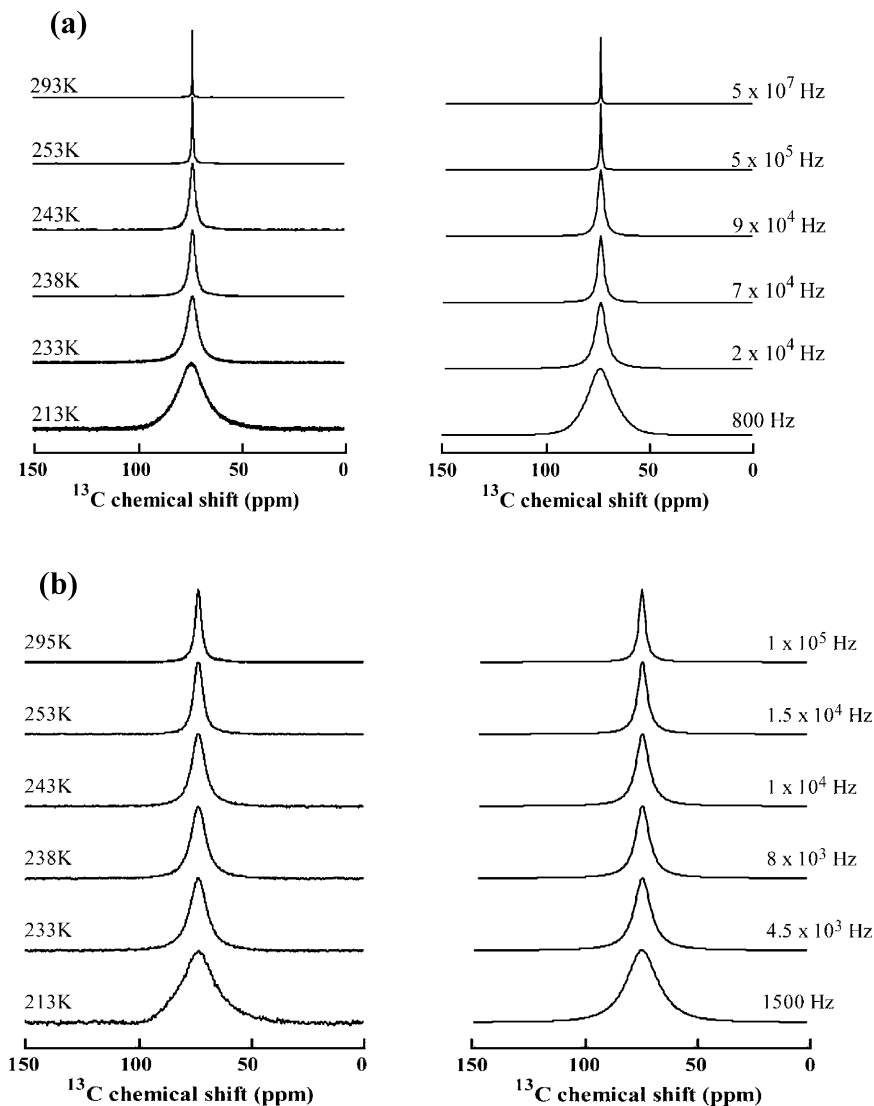
(a)

(b)

Figure 2. Temperature dependence of representative experimental (left) and simulated (right) ^{13}C static NMR spectra of (a) bulk and (b) nanoconfined supercooled glycerol. Corresponding temperatures and reorientational exchange frequencies (τ_{NMR}^{-1}) are given alongside the spectra. Spectra collected at 273 and 284 K have been omitted for clarity.
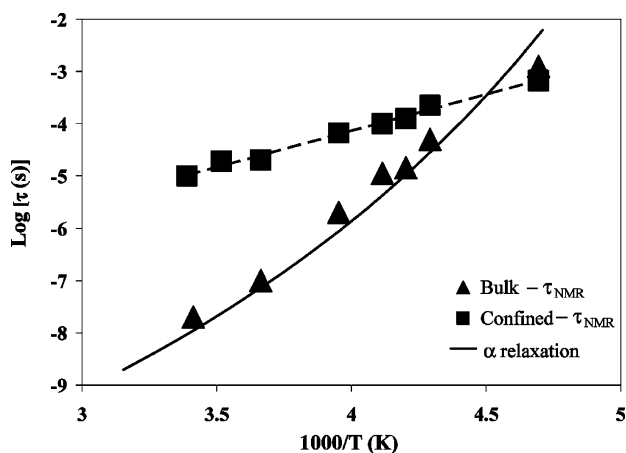

Figure 3. Temperature dependence of mean τ_{NMR} for bulk (triangles) and nanoconfined (squares) supercooled glycerol. Error bars are within the size of the symbols. The solid line denotes temperature dependence of τ_α (taken from ref 7) for bulk glycerol. Dashed line is an Arrhenius fit to the data for nanoconfined glycerol with an activation energy of ~27.5 kJ mol^{-1}.

The present ^{13}C NMR results provide a direct picture of the dynamical mode of glycerol molecules that involves isotropic reorientation of the constituent molecules. More importantly, these results demonstrate that the molecular reorientation process in glycerol remains unchanged in its character upon confinement and only its rate and temperature dependence are affected. In contrast to the bulk sample, the τ_{NMR} of the same isotropic tumbling motion of glycerol molecules in the confined sample displays a remarkably low activation energy of ~27.5 ± 2.5 kJ mol^{-1} (Figure 3). Such a dramatic change in the dynamical behavior upon nanoconfinement is reminiscent of similar behavior shown by dielectric relaxation times of some molecular and polymeric liquids under extreme confinement in small pores with diameters of ~2.5 nm or less.[5,15,19,29,30]

In the case of ethylene glycol (EG), a molecular liquid confined in 0.5−0.6 nm diameter pores in a zeolite (sodalite), this behavior was postulated to be due to single-molecule dynamics that is noncooperative.[19] This hypothesis is consistent with the fact that the dimensions of the EG molecules (~0.26 nm in diameter and ~0.52 nm in length) are comparable to the pore diameter of the zeolite. Confinement of ~0.5 nm diameter glycerol molecules in 2.2 nm pores of MCM-41 is, indeed,

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expected to result in a strong reduction in the length scale of cooperative dynamics of the molecular reorientation process compared to that in the bulk, although the scenario of single-molecule dynamics can be safely ruled out in the present case.

In the case of polymeric liquids, the situation is less straightforward, and a reduction in the length scale of cooperative dynamics along with the possibilities of highly hindered or altered molecular motions have been hypothesized to explain the low activation energy Arrhenius dynamics in the confined liquid.[5,15,29,30] However, in all these cases, the time scales of the Arrhenius dynamics were observed to be significantly faster than the α-relaxation time scale of the bulk liquid, especially near glass transition. In contrast, the results presented here in Figure 3 show that at temperatures above T_g, the τ_{NMR} in the confined glycerol sample is significantly longer than τ_α of the bulk liquid and converges with the latter only near T_g.

Similar dynamical behavior was observed by Arndt, Kremer and co-workers in their broadband dielectric relaxation studies of salol (phenyl salicylate) confined in nanoporous sol−gel glasses.[31–33] These studies indicated the presence of two dynamical populations of salol molecules under confinement. The dynamically fast population corresponds to the molecules in the interior of cylindrical nanopores that have relaxation times the same as the τ_α of the bulk liquid at high temperatures while their relaxation time scale decouples from τ_α as the temperature approaches T_g. On the other hand, the dynamically slow population corresponds to molecules close to and strongly interacting with the pore wall. The characteristic relaxation time scale of this population is significantly slower than the τ_α of the bulk liquid and approaches the latter at low temperatures close to T_g. Clearly, this dynamical behavior of the slow population in nanoconfined salol is similar to the temperature dependence of the τ_{NMR} of confined glycerol sample observed in this study (Figure 3). However, unlike the results of the dielectric relaxation studies of nanoconfined salol,[31–33] the ^{13}C NMR line shapes for the confined glycerol sample do not show any evidence of significant dynamical heterogeneity of bimodal nature that can be directly associated with the existence of two subsystems: one with bulklike behavior and the other that corresponds to regions of the liquid close to the surface of the pores.

This observation is not surprising, considering the fact that the dimensions the glycerol molecules ($\sim$0.47 nm in diameter, $\sim$0.52 nm in length, and with a hydrodynamic diameter of $\sim$0.6 nm) are only a factor of 4 smaller than the pore diameter (2.2 nm), and therefore, existence of separate dynamical populations across the pore diameter would probably be unphysical. This conjecture is corroborated by the fact that clear observation of bimodal dynamical heterogeneity was made in the dielectric relaxation of salol confined in pores with diameter ($\sim$7.5 nm) about a factor 15 larger than the molecular diameter ($\sim$0.5 nm).[34] Nevertheless, the possibility of the presence of significant dynamical heterogeneity in nanoconfined glycerol in the form of a wider spread of relaxation time scales compared to the bulk liquid cannot be completely ruled out. It may be noted in this regard that although a single value of τ_{NMR}^{-1}, representative of the mean jump frequency, is used to simulate the ^{13}C static NMR line shape at each temperature, the upper limit of dynamical heterogeneity represented in these line shapes can be estimated by simulating these line shapes with a Gaussian distribution of τ_{NMR}^{-1} values. Such simulations indicate that the upper limit of the full width at half maximum of this Gaussian distribution of τ_{NMR}^{-1} is $\sim$0.5 log units for the ^{13}C static NMR line shapes of the nanoconfined glycerol, and the agreement between

simulated and experimental line shapes becomes worse when the distribution is further broadened.

Our recent studies have shown that the calorimetric T_g of a similarly nanoconfined glycerol is higher (196 K) than that of the bulk liquid (189 K).[4] In contrast to this result, the temperature dependence of τ_{NMR} in the confined sample as shown in Figure 2 extrapolates to a value of $\sim$100 s, characteristic of T_g at a temperature that is significantly lower than the T_g of the bulk liquid. This apparent discrepancy between NMR and calorimetry can be explained only if τ_{NMR} actually represents a β-process in confined glycerol, while its τ_α decouples from τ_{NMR} and increases more rapidly at lower temperatures. In confined glycerol, the assignment of τ_{NMR} to a β-process is consistent with its remarkably low activation energy of $\sim$27.5 kJ mol^{-1}. This result implies that in the case of glycerol, the dynamics controlling the α-relaxation in the bulk and under nanoconfinement are inherently different in the temperature range near the glass transition. Such a transition in the rotational dynamics of the constituent molecules from an α-like to a β-like behavior may be indicative of a change in the thermodynamic state of glycerol upon nanoconfinement resulting from differences in the structure and density of the bulk and confined liquids.

4. Summary

^{13}C NMR line shape analysis demonstrates that α-relaxation in supercooled glycerol in the bulk involves isotropic reorientation or tumbling motion of the constituent molecules. The non-Arrhenius temperature dependence of the time scale τ_{NMR} of this tumbling motion implies increasingly cooperative molecular dynamics in the bulk liquid with decreasing temperature. In contrast with this dynamical behavior of the bulk liquid, the temperature dependence of τ_{NMR} displays an Arrhenius behavior with a low activation energy characteristic of a β-process upon confinement of glycerol into $\sim$2 nm pores in mesoporous silica. The τ_{NMR} in the confined liquid is significantly longer than the α-relaxation time scale τ_α of the bulk liquid at $T > T_g$ and converges with the latter only near T_g. The ^{13}C NMR line shapes of nanoconfined glycerol do not present any evidence of significant dynamical heterogeneity of bimodal nature corresponding to molecules in the pore interior and near pore surface. The observed changes in the time scale of the rotational dynamics of the constituent molecules and in its temperature dependence are hypothesized to result from confinement induced change in the structure and density of glycerol.

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