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Predicting the α -relaxation time of glycerol confined in 1.16 nm pores of zeolitic imidazolate frameworks

K. L. Ngai,  ^a P. Lunkenheimer  ^b and A. Loidl  ^b

Uhl et al. [*J. Chem. Phys.*, 2019, **150**, 024504] studied the molecular dynamics of glycerol confined in a microporous zeolitic imidazolate framework (ZIF-8) with well-defined pore diameters of 1.16 nm by broadband dielectric spectroscopy. Of interest is a fast process in the central part of the pores identified as the α -relaxation of the confined supercooled glycerol with relaxation times $\tau_{\alpha,\text{conf}}(T)$ reduced from $\tau_{\alpha,\text{bulk}}(T)$ of bulk glycerol and having a temperature dependence different from the super-Arrhenius temperature of the latter. The focus of Uhl et al. was relating the confined molecular dynamics to the cooperativity length scales $L_{\text{corr}}(T)$ of molecular motion above the glass transition, and deducing the limiting high-temperature value of the correlation length of about 1.22 nm. Not yet considered by anyone are the observed values of $\tau_{\alpha,\text{conf}}(T)$ and temperature dependence. Since the cooperativity length scales $L_{\text{corr}}(T)$ were found to be larger than the pore size of ZIF-8 over the temperature range studied and the density of the glycerol in the pore is possibly lower than the bulk, the cooperativity of the α -relaxation of glycerol confined in ZIF-8 is drastically reduced. Thus, within the framework of the Coupling Model (CM), $\tau_{\alpha,\text{conf}}(T)$ should be nearly the same as the primitive relaxation time $\tau_0(T)$ for glycerol when devoid of intermolecular coupling and cooperativity. Consistent with the absence of cooperativity of the glycerol confined in ZIF-8, we find the calculated $\tau_{\alpha,\text{conf}}(T)$ are either the same or slightly longer than the calculated values of $\tau_0(T)$. The quantitative prediction of the CM is verified. At this time we know of no other theory that can make such a quantitative prediction.

Introduction

The structural α -relaxation of molecular glass-forming liquids involves cooperative motion of molecules. The number of molecules participating in the cooperative motion and the cooperativity length-scale $L_{\text{corr}}(T)$ increase with decreasing temperature. Therefore a useful method to learn more about the molecular dynamics and the size of $L_{\text{corr}}(T)$ involved is by observing the changes when the liquid is confined in spaces of nanometer size.^{1–13} When molecular glass-formers are confined into spaces of nano-meter size, the structural α -relaxation usually changes its relaxation times and temperature dependence to deviate from the bulk behavior. Due to the diversity of the chemical structure of glass-formers, the confining host structure and its dimension, three common scenarios resulting from the effects of confinement have been observed and discussed in the review by Wübbenhorst and Napolitano.⁴ One scenario is a

complete change from the Vogel–Fulcher–Tammann (VFT) temperature dependence of the bulk relaxation time $\tau_{\alpha,\text{bulk}}(T)$ to Arrhenius dependence of $\tau_{\alpha,\text{conf}}(T)$ in confinement. The second scenario of $\tau_{\alpha,\text{conf}}(T)$ is that it follows the VFT-dependence of $\tau_{\alpha,\text{bulk}}(T)$ at high temperatures and down to a particular cross-over temperature and cross-over relaxation time before it changes to Arrhenius dependence. The third scenario is $\tau_{\alpha,\text{conf}}(T)$ having another VFT-dependence for all temperatures, irrespective of it being faster^{5–8} or slower¹² than $\tau_{\alpha,\text{bulk}}(T)$. All three scenarios were found in glycerol confined in metal–organic frameworks (MOFs) as host materials,^{13,14} and the third scenario was found in glycerol thin films vapor deposited on a substrate with thickness down to 1.6 nm.¹²

Since $L_{\text{corr}}(T)$ grows with decreasing temperature, it will exceed the dimension of the confined space or the pore diameter d if sufficiently small, and the molecular dynamics of the confined liquid will deviate from the bulk behavior because cooperative motion is not possible. When $L_{\text{corr}}(T)$ exceeds d , the α -relaxation time of the confined supercooled liquid $\tau_{\alpha,\text{conf}}(T)$ is reduced significantly from the bulk values $\tau_{\alpha,\text{bulk}}(T)$, exhibiting clear deviations from the typical super-Arrhenius temperature

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dependence of bulk liquids. Cooperativity can be totally suppressed at lower temperatures where $L_{\text{corr}}(T)$ far exceeds d .

Experimental studies of confinement have largely succeeded in observing the finite size effect on cooperative dynamics as expected. However, in many cases the pore dimensions of the confinement hosts are distributed, and there can be considerable interactions of molecules and the pore-wall, making it difficult to quantitatively interpret the data. Part of the difficulty was overcome by using metal organic frameworks (MOFs) as the confinement host, and in particular two special MOFs, namely the microporous zeolitic imidazolate frameworks (ZIFs) ZIF-8 and ZIF-11, with two different, well-defined pore sizes of 1.16 nm and 1.46 nm, respectively.¹⁴ Notwithstanding, some pores may not be filled by glycerol to the maximum number possible. The variation in the number of glycerol molecules per pore together with the interactions of the glycerol molecules with the pore walls was proposed before by Uhl *et al.*¹⁴ to explain the observed broader dielectric dispersion of glycerol confined in ZIF-8 and ZIF-11 than bulk glycerol.

As noted by Uhl *et al.*¹⁴ in the original paper, the pore aperture of ZIF-8 is 0.34 nm and the molecule size of glycerol is about 0.5–0.6 nm. The results of $L_{\text{corr}}(T)$ from Uhl *et al.*¹⁴ were compared to other studies of the cooperativity length scale from confinement measurements, and also with the relative temperature dependence of the amorphous-order length scale of glycerol recently deduced from nonlinear dielectric spectroscopy.^{15,16} The combined experimental data were consistently described by a critical divergence of cooperativity length-scale $L_{\text{corr}}(T)$. Notwithstanding the success, absent in the previous paper is the consideration of the relation of $\tau_{\alpha,\text{conf}}(T)$ to $\tau_{\alpha,\text{bulk}}(T)$, and the way to account for it quantitatively. This task is important for achieving a full understanding of the molecular dynamics of glycerol in nano-confinement made available by the data in ref. 14. The purpose of this paper is to give a quantitative prediction of $\tau_{\alpha,\text{conf}}(T)$ and its temperature dependence of glycerol in ZIF-8 based on $\tau_{\alpha,\text{bulk}}(T)$, and thus link $L_{\text{corr}}(T)$ to the dynamic properties. By this addition to that already considered before by Uhl *et al.*, the relevance of the experimental data in ref. 14 of glycerol confined in ZIF to the dynamics of glass-forming liquids is amplified.

Results and discussion

Two relaxation processes show up in the dielectric loss $\varepsilon''(f)$ of glycerol confined in ZIF-8 and ZIF-11 as a function of frequency at various temperatures of Uhl *et al.*¹⁴ The faster one was assigned to the α -relaxation of glycerol confined in ZIF-8 and ZIF-11. The origin of the slower process was given two plausible explanations.¹⁴ One is from a layer of glycerol molecules absorbed at the walls of the pores with slow dynamics due to interactions. The other is the Maxwell–Wagner (MW) relaxation^{17,18} that arises from the heterogeneous nature of the guest–host system. The ZIFs have exceptionally high chemical and thermal stability with strongly hydrophobic internal surfaces, and this had led Uhl *et al.*¹⁴ to suggest the formation of a surface layer

of glycerol at the wall unlikely. However, the ^2H solid-state NMR study by Khudozhitkov *et al.*¹⁹ of xylene isomers, benzene, toluene, and isobutane confined inside ZIF-8 did find bound guest molecules on the cage wall together with highly mobile guest molecules located in the central part of the pore, and also guest molecules squeezing through the window with subsequent release to the next cage. Whichever is the origin of the slow process, it is not important as far as the objective of the present paper is concerned. This is because the relaxation time of the slow process of glycerol confined in ZIF-8 is about 7 orders of magnitude longer than the fast relaxation,¹⁴ and hence it is fully decoupled from the fast process. The intercage diffusion process found by Khudozhitkov *et al.* is also unimportant because it is too slow¹⁹ to affect the relaxation of the highly mobile guest molecules, and this justifies the assumption made by Uhl *et al.* of no significant interactions between molecules in different pores and that jumps between pores or cages are unlikely.¹⁴ The fast process of confined glycerol observed by Uhl *et al.* is coming from the highly mobile guest molecules in the central part of the pore found in other molecules by Khudozhitkov *et al.*¹⁹ The objective of the paper is to predict quantitatively the relaxation time of the fast process originating from the highly mobile glycerol at the central part of the ZIF-8 pore.

In the paper by Uhl *et al.*,¹⁴ the confinement data at high temperatures above about 290 K indicate that L_{corr} becomes temperature-independent and levels off at about 1.22 nm, *i.e.*, the limiting high-temperature value of the correlation length $L_{\text{corr}}(T)$. The deduction is consistent with the temperature $T_A \approx 290$ K at which $\tau_{\alpha,\text{bulk}}(T)$ of glycerol changes its temperature dependence from Vogel–Fulcher–Tammann (VFT) to Arrhenius.^{20–25} Since $L_{\text{corr}}(T)$ increases with decreasing temperature, we can conclude that it is larger than 1.22 nm for all $T < T_A \approx 290$ K, and, *a fortiori*, $L_{\text{corr}}(T)$ is larger than the pore size of 1.16 nm of ZIF-8 over the temperature range of $\tau_{\alpha,\text{conf}}(T)$ obtained in ref. 14. From this, we can conclude that the cooperativity of the α -relaxation of glycerol confined in ZIF-8 is drastically reduced. Its relaxation time $\tau_{\alpha,\text{conf}}(T)$ should thus become close to the primitive relaxation time $\tau_0(T)$ of the Coupling Model (CM),^{8,9,26,27} which corresponds to the case of total removal of cooperativity or intermolecular coupling. The size of the glycerol molecule is roughly 0.5–0.6 nm,^{28,29} and about 5 to 6 molecules can fit into the 1.16 nm pores (see Table 1 in ref. 14). From this, one can deduce that the density of the confined glycerol ρ_{conf} is possibly lower than ρ_{bulk} of bulk glycerol. Such a reduction of density leads to an increase of the intermolecular distance and a large decrease of the intermolecular interaction and hence the cooperativity of the structural relaxation as well. Thus by considering either $L_{\text{corr}}(T)$ larger than the pore size or ρ_{conf} significantly lower than ρ_{bulk} , we arrive at the same conclusion of removal of cooperativity of glycerol confined in ZIF-8. As noted in the previous work, weak next-neighbor interaction remains and may effect minimal residual cooperativity of glycerol confined in ZIF-8, implying that at some temperatures $\tau_{\alpha,\text{conf}}(T)$ can still be slightly longer than $\tau_0(T)$.

Dielectric relaxation measurements of bulk glycerol were carried out over a broad frequency range $10^{-5} < f < 10^{13}$ Hz at

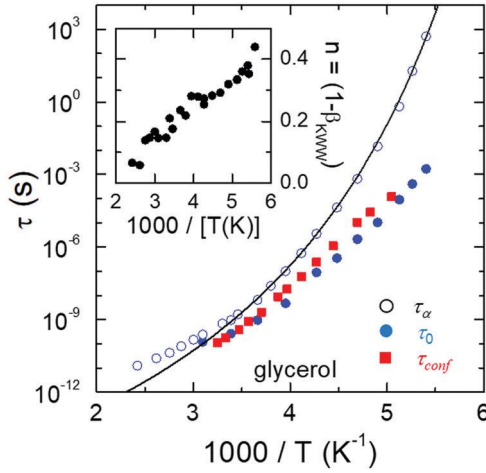


Fig. 1 Arrhenius plot of the average relaxation times of glycerol confined in ZIF-8 (red closed squares).¹⁴ For comparison, the $\tau_{\alpha,\text{bulk}}(T)$ data of bulk glycerol (open blue circles) and the VFT fit as reported in ref. 30 are shown. The closed blue circles indicate the primitive relaxation times $\tau_0(T)$ calculated from the CM eqn (2) as described in the text. The inset shows the temperature dependence of the coupling parameter, n , or equivalently $(1 - \beta_{\text{KWW}})$, in the KWW function, eqn (1), used to fit the dielectric dispersion of bulk glycerol spectra published in ref. 30–32.

various temperatures from 179 to 473 K.^{30,31} The data of the α -relaxation of bulk glycerol were analyzed in ref. 32 by fitting its frequency dispersion using the Fourier transforms of the Kohlrausch–Williams–Watts (KWW) function,

$$\varphi(t) = \exp \left[- \left(\frac{t}{\tau_{\alpha,\text{bulk}}(T)} \right)^{1-n(T)} \right]. \quad (1)$$

The fractional exponent, $[1 - n(T)]$, of the KWW function is temperature dependent and accounts for the narrowing of the width of the frequency dispersion with increase of temperature. The values of $n(T)$ and relaxation times $\tau_{\alpha,\text{bulk}}(T)$ obtained for bulk glycerol are shown in the inset and main frame of Fig. 1, respectively, together with the VFT fit to $\tau_{\alpha,\text{bulk}}(T)$. The primitive relaxation time $\tau_0(T)$ can be obtained from the experimental values of $\tau_{\alpha,\text{bulk}}(T)$ and $n(T)$ by using the time-honored CM equation,^{26,27}

$$\tau_{\alpha,\text{bulk}}(T) = \left[(t_c)^{-n(T)} \tau_0(T) \right]^{1/[1-n(T)]}, \quad (2)$$

where $t_c = 2$ ps was determined by neutron scattering and molecular dynamics simulations for typical glass formers^{26,27} and applied before to glycerol.^{26,32} Since the values of $n(T)$, $\tau_{\alpha,\text{bulk}}(T)$, and t_c are all known, $\tau_0(T)$ were calculated *via* eqn (2) without any adjustable parameter. The results of $\tau_0(T)$ are shown in Fig. 1 to compare with the experimental values of $\tau_{\alpha,\text{conf}}(T)$ of glycerol confined in ZIF-8 from ref. 14. The temperature dependence of $\tau_{\alpha,\text{conf}}(T)$ is nearly but not exactly Arrhenius and is also consistent with a VFT dependence in accord with the second or third scenario⁴ mentioned in the Introduction, and so is the temperature dependence of $\tau_0(T)$. It can be seen by inspection of Fig. 1 that $\tau_{\alpha,\text{conf}}(T)$ is slightly longer than $\tau_0(T)$ at lower temperatures, but the two are

practically the same at higher temperatures. The deviations at lower temperatures, mostly by less than a factor of 2, are consistent with the small residual cooperativity of the glycerol confined in 1.16 nm pores. The vanishing of the difference between $\tau_{\alpha,\text{conf}}(T)$ and $\tau_0(T)$ at higher temperatures may be due to the weakening effect of the small residual cooperativity at times shorter than 1 ns, just like that found in bulk glycerol at short $\tau_{\alpha,\text{bulk}}(T)$.

The cooperativity length scale $L_{\text{corr}}(T)$ of molecular motion of bulk glycerol at temperatures above the glass transition is important information. Its monotonic increase with decreasing temperature suggests correspondingly increasing cooperativity of the α -relaxation. The width of the frequency dispersion of the α -relaxation or the value of n in the fractional exponent of the KWW function is a direct link to cooperativity in the CM. It is also considered as a measure of the degree of dynamic heterogeneity.^{33,34} Assuming that heterogeneity and cooperativity are closely related, as both originate from intermolecular interaction/coupling, a correlation of $L_{\text{corr}}(T)$ with $n(T)$ can be expected. This is indeed brought out by the plot in Fig. 2.

Before closing, it is worthwhile to mention that a hydrogen-bonding network is formed in glycerol, and it may have a bearing on the cooperativity of the α -relaxation. Hence the reduction in the extent of hydrogen-bonding of glycerol can work together with the smaller number of interacting molecules confined in ZIF-8 pores to generate the observed $\tau_{\alpha,\text{conf}}(T)$. It is also interesting to compare the present results of 3D confinement of glycerol in ZIF-8 pores with those of 1D confinement of a glycerol thin film deposited on a substrate.¹² In the latter, the absorbed layer at the substrate and the free surface have opposite effects on the dynamics, but both contribute to the dielectric relaxation measurements to make theoretical treatment difficult. Nevertheless, the Coupling Model (CM) had been applied to similar cases to predict the enhanced surface mobility due to removal of cooperativity at the free surface.^{35–38} There are two cases of ultrathin films of polymers confined in galleries of nanocomposites but no interaction or absorption at the

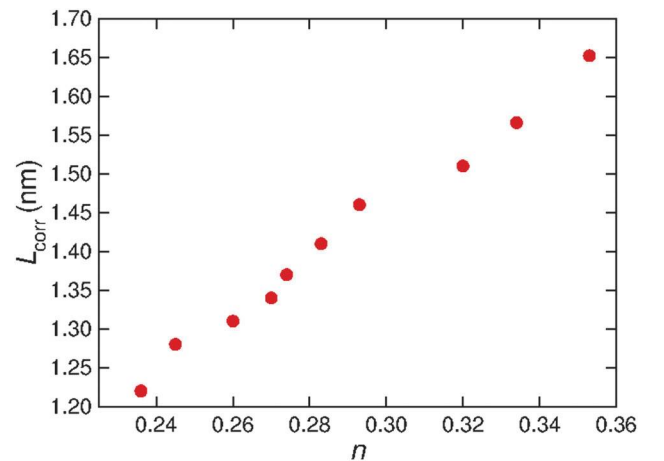


Fig. 2 Plot of $L_{\text{corr}}(T)$ vs. $n(T)$ of bulk glycerol. The $n(T)$ data are taken from ref. 31 and 32, and are also shown in the inset of Fig. 1. The fit curve shown in ref. 14 was used to determine $L_{\text{corr}}(T)$.

two surfaces. One is a 2 nm thin poly(methylphenyl siloxane) (PMPS) film intercalated into galleys of nanocomposites.⁶ The other is ~ 1 nm thin films of poly(ethylene oxide) (PEO) films confined within the galleries of hydrophilic silicates, sodium-montmorillonite (Na + MMT).³⁹ In both cases, confinement results in segmental α -relaxation $\tau_{\alpha,\text{conf}}(T)$ much shorter than $\tau_{\alpha,\text{bulk}}(T)$ of bulk PMPS and PEO by orders of magnitude, and the CM was successful to explain $\tau_{\alpha,\text{conf}}(T)$ quantitatively.^{7,35,40} Also $\tau_{\alpha,\text{conf}}(T)$ of a PEO thin film has Arrhenius temperature dependence with a low activation energy instead of the VFT temperature dependence of $\tau_{\alpha,\text{bulk}}(T)$, it fulfills either scenario 1 or 2 of Wübbenhorst and Napolitano,⁴ while $\tau_{\alpha,\text{conf}}(T)$ of a PMPS thin film seems to conform to scenario 3. Finally we mention quantitative successes of the CM in explaining $\tau_{\alpha,\text{conf}}(T)$ of *ortho*-terphenyl,⁸ poly(dimethyl siloxane),^{7,8} and poly(methylphenyl siloxane)²⁷ confined in 2 nm pores similar to glycerol confined in 1.16 nm pores, the focus of this paper.

Conclusion

The experiment by Uhl *et al.* provides accurate relaxation times $\tau_{\alpha,\text{conf}}(T)$ of the fast process coming from the highly mobile glycerol molecules in the central part of the pores of ZIF-8. The pore size is much smaller than the cooperative length-scale $L_{\text{corr}}(T)$ of the bulk, and the cooperativity of the confined glycerol is totally mitigated. They addressed only $L_{\text{corr}}(T)$, but left unexplained are the magnitude and temperature dependence of $\tau_{\alpha,\text{conf}}(T)$ of glycerol confined in ZIF-8, and the relation of $\tau_{\alpha,\text{conf}}(T)$ to $\tau_{\alpha,\text{bulk}}(T)$ of bulk glycerol. The cooperativity of glycerol is reduced by confinement to some minimal level because essentially only next-neighbor interaction survives. Thus $\tau_{\alpha,\text{conf}}(T)$ is practically the same as $\tau_0(T)$, the primitive relaxation time of the CM when cooperativity is totally suppressed. There is overall quantitative agreement between the experimental $\tau_{\alpha,\text{conf}}(T)$ and the calculated $\tau_0(T)$ over the entire experimental temperature range. These previously unexplained facts are of broad interest to the glass transition research community, and are challenging to explain quantitatively by any theory or model. At the present time, the coupling model is the only theoretical approach that can predict quantitatively the relaxation time $\tau_{\alpha,\text{conf}}(T)$ and its temperature dependence when cooperativity is totally removed. Since the results are in good agreement with the data, we submit that this is an advance of broad interest. The paper has potential for impact because it will stimulate others to do the same by other theories of the glass transition if possible.

Conflicts of interest

There are no conflicts to declare.

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