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Self-diffusion of glycerol in $\gamma$-alumina nanopores. The neglected role of pore saturation in the dynamics of confined polyalcohols

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Abstract

We report on Molecular Dynamics simulations of glycerol in $\gamma$-Al$_2$O$_3$ nanopores and shed light on the controversial observations of the behaviour of viscous fluids under confinement. While our results confirm the role played by the solid in determining the hydrogen-bond network at the interface with the liquid and hence its mobility, they additionally disclose an intriguing scenario where this mobility is remarkably influenced by a liquid-gas interface that is present in pores that are not fully saturated. This interface significantly reduces the number of inter-molecular hydrogen bonds in glycerol and sparks a faster dynamics than that measured in the bulk liquid. Consequently, the surprising enhancement of glycerol’s self-diffusion in $\gamma$-Al$_2$O$_3$ nanopores can be explained only if both degree of confinement and pore saturation are taken into consideration. Our simulations suggest that the discrepancies reported in the literature are most likely due to measurements performed in pores that are not completely filled with glycerol.

Keywords: Molecular Dynamics Simulations, Nanoporous Materials, Viscous Liquids, Diffusion

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1. Introduction

It is well known that spatial confinement in volumes of mesoscopic dimensions dramatically affects the thermodynamic and transport properties of molecular fluids [1]. Changes in the location of first-order transitions, structure and dynamics have been often reported for a wide variety of molecular systems in hard confining geometries [2, 3, 4, 5]. For the specific case of solid-fluid interfaces observed in confined systems, the space-dependent inter-molecular interactions provoke structural heterogeneities in the perpendicular direction to the interface [6]. Understanding the origin of the deviations from a typical liquid-bulk behaviour is crucial in many industrial applications, including heterogeneous catalysis, engine lubrication, surface coating and enhanced oil recovery. In this regard, statistical mechanical theories and computer simulation techniques, including Monte Carlo (MC) and Molecular Dynamics (MD) methods, have played a crucial role. Apart from density functional methods [7], most theoretical models of confined fluids do not describe spatial heterogeneities explicitly. The phenomenon is rather treated in terms of a phase-equilibrium problem between two macroscopically distinct phases, the bulk and confined fluid [8, 9, 10]. By contrast, in particle-based simulations the spatial distribution of the fluid within the confining media is described explicitly, allowing to study the link between molecular structure and mobility.

While many computer simulation studies have focused on associating liquids, such as water confined in slit-shaped nanopores and nanotubes [11, 12, 13], hydrocarbons [14] and solutions of polar substances [15], little attention has been given to organic viscous glass-forming liquids, despite the interest of the condensed matter community in understanding how their glass transition might be modified by nanoconfinement [16]. The sugar alcohol glycerol (C₃O₃H₈) has been one of the most extensively studied molecular glass-formers in experiments over the last few decades [17, 18, 19, 20]. Recent experiments on the mobility of liquid glycerol under hard confinement have led to especially intriguing, but apparently contradictory, conclusions [21]. On the one hand, a breaking of the
conventional free volume rules for molecular mobility was reported from spectroscopy measurements of glycerol in a mesoporous silica glass [22]. The authors observed that molecular motion was strongly suppressed upon confinement, but the local free volume between molecules was higher than in the bulk phase. On the other hand, D’Agostino et al. [23] reported an unexpected significant enhancement of glycerol’s self-diffusivity when confined in mesoporous γ-Al₂O₃. The ratio of the effective self-diffusivity within the porous media to the free bulk-liquid self-diffusivity was found to be as high as ∼1.33. Anomalously high self-diffusion coefficients had previously been observed for water and alkanes in partially filled porous materials [24, 25]. Such a phenomenon has generally been attributed to the fast interphase exchange between the vapour and condensed phases within the confining volume. Nevertheless, although it is well known that the critical point of the vapour-liquid coexistence in simple fluids is shifted to lower temperatures in confined environments [26, 27], these arguments do not explain the high mobility of glycerol due to its negligible vapour pressure at the studied temperatures. It was hypothesized that the perturbation in the translational molecular motion was generated by a disruption of the H-bond network of the liquid due to topological defects in the solid substrate [23]. Previous computer simulation studies of glycerol in fully saturated cylindrical channels of hydroxylated silica have demonstrated that confinement induces the classical effects observed for simple van der Waals glass-forming liquids, including structural heterogeneities and a dramatic slowing down of the relaxation dynamics [28].

Inspired by such an unsolved conundrum, we herein investigate the structure and dynamics of glycerol in nanopores of γ-Al₂O₃ by performing classical atomistic MD simulations and complement our results with our experimental Pulse-Field Gradient–Nuclear Magnetic Resonance (PFG-NMR) measurements.
2. Experimental and Computational Details

Experimentally, the time a porous solid (pellet) is left immersed in a liquid reservoir, referred to as soaking time, determines the amount of liquid diffusing into the solid’s pores as well as its concentration profile. In Table 1, we report the glycerol’s self-diffusion coefficients in a $\gamma$-Al$_2$O$_3$ pellet (see Fig. 1(a)), measured using PFG-NMR. The soaking time determines the degree of pellet’s saturation, $M(t)/M_\infty$, with $M(t)$ and $M_\infty$ the mass of liquid in the pellet at $t$ and at $t \to \infty$, respectively. Additional details on the experimental setup and the dependence of the degree of saturation on the soaking time are given in the Supporting Information, S.I.. Interestingly, the glycerol’s diffusivity in the bulk liquid ($D_{\text{bulk,exp}} = 1.44 \times 10^{-8}$ cm$^2$ s$^{-1}$) is found to be lower than that in confinement, especially at $M(t)/M_\infty << 1$. To the best of our knowledge, this is the first clear experimental evidence of this phenomenon. The ratio $M(t)/M_\infty$ measured at the different times has been fitted to the analytical solution provided by Crank [29] using $D_{\text{fill}} = 2.55 \times 10^{-6}$ cm$^2$ s$^{-1}$ as fitting parameter (see S.I. for details). The resulting curve is shown in Fig. 1(b). At each soaking time, the distribution of glycerol within the porous matrix can be assumed to vary solely with the radial coordinate $r$ and the resulting profiles $C(r,t)/C_a$, also given by Crank [29], are reported in Fig. 1(c), where $C_a$ is the liquid concentration at $r = a = 0.1$ cm, thus being roughly equivalent to the density of pure bulk glycerol $\rho_{\text{bulk}}$. At short times, we will find pores in the alumina pellet with different degrees of saturation depending on their distance from the interface, and the overall behaviour will be influenced by this distribution of glycerol. In the present letter, we aim to explain the role of saturation and degree of confinement on the glycerol diffusivity.

We restrict our study to slit-shaped pore geometries, modelled by placing two identical layers of the solid substrate of dimensions $10a \times 6b \times 2c$, with $a = 5.587$ Å, $b = 8.413$ Å, and $c = 8.068$ Å, exposing fully-hydroxylated $\{100\}$ crystallographic planes of area $A_c = 10a \times 6b$, in front of each other at a mutual distance $l_z$ along the $z$ direction of the simulation box. Larger systems with...
Figure 1: (a) The degree of saturation of the pores within the mesoporous γ-Al₂O₃ support is controlled by the soaking time $t$. The geometry of the porous support is here approximated with a cylinder of radius $a = 0.1$ cm. (b) The experimental $M(t)/M_\infty$ values at $t_1 = 0.083$, $t_2 = 0.166$, $t_3 = 0.500$, $t_4 = 1.000$ and $t_5 = 24.000$ h are fitted to the analytical solution of the uptake by a cylinder using $D_{\text{fill}} = 2.55 \times 10^{-6}$ cm$^2$ s$^{-1}$ as fitting parameter [29]. (c) Time-dependent distribution of glycerol within the porous support as a function of the radial position $r$ at different soaking times and representative simulation configurations corresponding to small slit-shaped nanopores with well defined concentrations $c_{\text{conf}}$ (A: 0.4, B: 0.6, C: 0.8, D: 1.0, E: 1.2 g cm$^{-3}$).
Table 1: PFG-NMR values of the global self-diffusion coefficient of glycerol in mesoporous pellets of \(\gamma\)-Al\(_2\)O\(_3\) at different soaking times and their corresponding overall saturation \((M(t)/M_\infty)^a\)

| Soaking Time (h) | \(M(t)/M_\infty\) | \(D_{\text{exp}}\) \(10^{-8}\) cm\(^2\) s\(^{-1}\) | \(D_{\text{exp}}/D_{\text{bulk,exp}}^b\) |
|------------------|-----------------|--------------------------|-----------------|
| 0.083            | 0.537           | 4.350                    | 3.020           |
| 0.166            | 0.707           | 3.370                    | 2.340           |
| 0.500            | 0.976           | 2.150                    | 1.493           |
| 1.000            | 0.976           | 2.000                    | 1.388           |
| 24.000           | 0.976           | 1.980                    | 1.375           |

\(a\) Measurements at \(T = 300\) K. \(b\) \(D_{\text{bulk,exp}} = 1.44 \times 10^{-8}\) cm\(^2\) s\(^{-1}\)

\(A_c = 20a \times 12b\) have also been simulated to check for finite size effects. Different confinement distances between the centres of outermost surface H atoms of specularly symmetric crystalline \(\gamma\)-alumina layers were considered: \(l_z = 20, 40\) and 60 Å (the difference in volume when considering the distance from outermost O atoms is 3.39%, 5.12% and 10.50% for pores of \(l_z = 60, 40\) and 20 Å, respectively). These inter-wall distances lie within the range of the typical pore dimensions of \(\gamma\)-Al\(_2\)O\(_3\) nanocrystals [23]. In order to study the effect of nanopore saturation at each \(l_z\), we performed simulations at different confinement concentrations \(c_{\text{conf}} = N M_w/A_c l_z N_A\), where \(N\), \(M_w\) and \(N_A\) are the number of glycerol molecules, glycerol molecular weight and Avogadro’s number, respectively. The product \(A_c l_z\) represents the pore volume available for the glycerol molecules. In particular, we studied systems with \(c_{\text{conf}} = [0.4, 0.6, 0.8, 1.0, 1.2]\) g cm\(^{-3}\). Such systems would be representative of the points A, B, C, D, and E of Fig. [1] respectively. Since \(c_{\text{conf}}\) is a ”coarse-grained” quantity that defines the amount of glycerol in a given pore volume, the case of \(c_{\text{conf}} = 1.2\) g cm\(^{-3}\) (corresponding to the fully saturated pore) equals the density of pure bulk glycerol \(\rho_{\text{bulk}}\) at \(T = 300\) K and \(P = 1\) bar. Interactions of glycerol were described via inter- and intra-molecular potentials of the OPLS/AA force-field family [30, 31]. Crystal atoms were treated as stationary (rigid) charged Lennard-Jones (LJ) sites with parameters taken from the CLAYFF force-field [32]. LJ parameters...
for unlike interactions between glycerol and $\gamma$-$\text{Al}_2\text{O}_3$ were determined via geometric mixing rules as proposed by Striolo and coworkers [33]. MD simulations of the confined systems under three-dimensional periodic boundary conditions were performed in the $NVT$ ensemble at $T = 300$ K. Structural and dynamical properties were calculated from 100 ns long equilibrium trajectories. Details of the simulations and algorithms used are reported in S.I.

3. Results

Our simulation results show that the interactions established at the solid-liquid interface and the degree of confinement play both a key role in determining the glycerol spatial distribution in $\gamma$-$\text{Al}_2\text{O}_3$ nanopores. Fig. 1(c) clarifies the effect of reducing $c_{\text{conf}}$ from 1.2 g cm$^{-3}$ (snapshot E) to 0.4 g cm$^{-3}$ (snapshot A) on the organization of glycerol in the pore for the specific case of $l_z = 60$ Å. Upon decreasing the confinement concentration, we detect the nucleation of a low-density cavity (or bubble), which eventually leads to two fully separated liquid films adsorbed at the crystal surfaces and entrapped between flat solid-liquid and liquid-gas interfaces. Given the low vapour pressure of glycerol, the probability of observing glycerol molecules within the volume occupied by the gas phase is virtually zero. Consequently, the gas phase will be referred to as vacuum throughout the remaining of this letter. The value of the confinement concentration at which bubbles and separated films are observed strictly depends on the pore size or, equivalently, on the confinement length $l_z$. In general, for $c_{\text{conf}} \leq 0.6$ g cm$^{-3}$ all pores exhibit two fully separated liquid films, regardless of their size.

In Fig. 2, we report the glycerol’s center of mass density profiles, $\rho(z)$, along $z$. Regardless the confinement length, changes in the liquid concentration barely affect the shape of the density profiles in the proximity of the surface. The decay of density oscillations indicates that the effect of the substrate on glycerol is limited to approximately 20 Å. This effect is especially evident within 5 Å of the crystal surface, where the glycerol molecules appear to be highly constrained.
Figure 2: Density profiles of glycerol’s center of mass along the $z$ coordinate in slit nanopores of confinement length $l_z$ at different concentrations. $\rho(z)$ is normalized by the bulk density of neat glycerol, $\rho_{\text{bulk}}$.

The formation of layers can have an effect on the diffusion of confined glycerol, as it not only introduces energy barriers hampering molecular diffusion between adjacent layers, but it can also disrupt the H-bond network in bulk glycerol. Our simulations show that the average number of H-bonds per OH group in bulk glycerol is $\langle n_{\text{HB/OH,bulk}} \rangle \approx 2$, in excellent agreement with Busselez et al. [28]. This value changes if glycerol is confined in $\gamma$-Al$_2$O$_3$ as shown in Fig. 3 where the reduced number of H bonds per OH group, $n_{\text{HB/OH}}^\gamma = \langle n_{\text{HB/OH,conf}} \rangle / \langle n_{\text{HB/OH,bulk}} \rangle$, is reported as a function of $c_{\text{conf}}$ for different confinement lengths. It is interesting to note that the bulk value for $\langle n_{\text{HB/OH,bulk}} \rangle$ is not reached even in pores of 60 Å at a bulk-like concentration of glycerol in the pore. The difference is due to the disruption of the glycerol-glycerol hydrogen bond network at the solid-liquid interface, where the three OH groups of the glycerol molecules preferentially form H-bonds with the $\gamma$-Al$_2$O$_3$ hydroxylated groups (details are presented in S.I.).

At lower concentrations, the disruption of the H-bond network becomes more
Figure 3: Average number of H-bonds per OH group in glycerol as a function of the confinement concentration, $c_{\text{conf}}$, in slit nanopores of confinement length $l_z$. Results are normalized by the value in the neat liquid phase $\langle n_{\text{HB/OH,bulk}} \rangle$. Note that H-bonds between glycerol and OH groups on the solid surface are not considered. Solid lines are a guide for the eye, while the vertical dashed line indicates the region where two separated liquid films are formed.

relevant, following the formation of the vacuum-liquid interface, where for example, a reduction of almost 40% of the H-bonds is observed for $l_z = 20$ Å when $c_{\text{conf}} = 0.4$ g cm$^{-3}$. In other words, if the pore is not fully saturated, the average number of H-bonds per OH group in liquid glycerol significantly decreases, due to the formation of a low-density cavity or two separated liquid films that create a vacuum-liquid interface, where the number of glycerol molecules available to accept or donate a H bond is smaller than in the bulk (see S.I.).

The correlation between the number of H-bonds and overall relaxation dynamics in associating liquids such as water is well known [34]. Thus a direct dependence of the global translational dynamics on the degree of pore saturation would be expected in the studied systems. To test this hypothesis, we calculate the self-diffusion coefficient of glycerol, $D_{\text{conf}}$, at different confinement concentrations and lengths. Due to the anisotropy and spatial inhomogeneity in the confined liquid, neither the standard three-dimensional Einstein relation nor the
Kubo relation over the whole confined volume would be suitable approaches \[35\]. Consequently, $D_{\text{conf}}$ is computed as the density-weighted average of the lateral diffusion coefficient in finite slabs centered at different $z$ positions across the simulation cell:

$$D_{\text{conf}} \equiv \langle D_{||}(z) \rangle = \frac{\int_{l_z} D_{||}(z) \rho(z) dz}{\int_{l_z} \rho(z) dz}.$$  \hspace{1cm} (1)

The two-dimensional parallel component of the diffusion coefficient in a given slab $\delta_z$, defined by the spatial interval $(z, z + dz)$, reads

$$D_{||}(\delta_z) = \lim_{\tau \to \infty} \frac{\langle |\vec{r}_{xy}(t + \tau) - \vec{r}_{xy}(t)|^2 \rangle_{\delta_z}}{4\tau P_{\delta_z}(\tau)},$$  \hspace{1cm} (2)

where $\vec{r}_{xy}(t)$ is the two-dimensional position vector of a glycerol molecule in $\delta_z$ at time $t$ and $P_{\delta_z}(\tau)$ is the survival probability for particles to remain in that slab (see Ref. \[35\]). The resulting dependence of $D_{\text{conf}}$ on the confinement concentration is reported in Fig. 4(a). The values are normalized with the diffusion coefficient of neat glycerol obtained from MD-NVT runs at $T = 300$ K and $\rho_{\text{bulk}} = 1.2$ \text{g cm}^{-3}, i.e., $D_{\text{bulk}} = 1.28 \times 10^{-8}$ \text{cm}^2 \text{s}^{-1}.

At $c_{\text{conf}} = 1.2$ \text{g cm}^{-3} (pore completely saturated), the self-diffusivity ratio, $D_{\text{conf}}/D_{\text{bulk}}$, is lower than 1 for any $l_z$, suggesting a slower diffusion in the pores than in the bulk. By contrast, in pores that are partially saturated ($c_{\text{conf}} \leq 1.0$ \text{g cm}^{-3}), the above ratio increases significantly, especially at $l_z \geq 40$ Å. At $c_{\text{conf}} = 1.0$ and 0.8 \text{g cm}^{-3}, the measured ratios are larger than those at $c_{\text{conf}} = 0.6$ and 0.4 \text{g cm}^{-3}. This effect cannot be exclusively due to the global disruption of H bonds in liquid glycerol, given that $n_{\text{HB/OH}}^*$ shows a monotonic decrease from $c_{\text{conf}} = 1.2$ \text{g cm}^{-3} to 0.4 \text{g cm}^{-3}$ (see Fig. 3). To gain a deeper insight, one should consider two interconnected factors: (i) the structural heterogeneity reported in Fig. 2 and (ii) the local number of glycerol-glycerol H-bonds (see S.I.). It is the simultaneous presence of both factors that determines the diffusion profiles along the $z$ direction shown in Fig. 4(b). These profiles suggest a highly suppressed dynamics at the solid-liquid interface, where $D_{||}(z)/D_{\text{bulk}} \ll 1$, and a gradually increasing mobility far from it. In fully-saturated pores with $l_z = 40$ and 60 Å, $D_{||}(z)/D_{\text{bulk}}$ asymptotically approximates to 1 close to the pore center (tending to bulk-like conditions). When such
Figure 4: (a) Average self-diffusion coefficient of glycerol in slit nanopores of size $l_z$ at different confinement concentrations $c_{\text{conf}}$ obtained from integration of the (b) local parallel component of the self-diffusion coefficient as a function of the $z$ position (see Eq. 1). Experimental measurements as a function of glycerol uptake are reported in the inset of (a). All the values are normalized with the diffusion coefficient in the isotropic bulk fluid $D_{\text{bulk}}$ for comparison. Lines are added as a guide for the eye.

In conclusion, our study demonstrates that the dynamics of glycerol in fully saturated pores is primarily affected by the reduction of mobility at the solid-liquid interface. This is a consequence of a higher density and structural order in the contact layer as compared to the bulk liquid, due in part to the presence of H-bonds with the $\gamma$-Al$_2$O$_3$ hydroxyl groups. Pores that are not fully saturated exhibit a cavity, approximately located in their centre, that does not contain glycerol and causes a disruption of the H-bond network within the liquid,
which in turns enhances the glycerol self-diffusion. The competition between the strong structural order at the solid-liquid interface and the disruption of H bonds far from it, leads to an overall self-diffusion that is faster than that in the pure bulk liquid under certain conditions of pore size and liquid concentration. In particular, we found a significant enhancement in the self-diffusion of nanoconfined glycerol for pore sizes $l_z \geq 40 \, \text{Å}$ and confinement concentrations $c_{\text{conf}} \leq 1.0 \, \text{g cm}^{-3}$. The present study provides a fundamental guideline to understand recent experimental observations on the dynamics of glycerol in confined media [23], which is consistent with the dynamics of glycerol observed in thin films [36] and highlights the importance of liquid-gas interfaces in the dynamics of confined viscous fluids.

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Appendix A. Supporting Information

Detailed information on experimental techniques, simulation algorithms and supplementary figures on the local distribution of mass and analysis of time-fluctuations in the H-bond network can be found in the online version, at http://

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