

Hybrid materials made up of ionic liquids confined in porous silica and chalcogenide

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ABSTRACT

In the present work, the structure and dynamics of IL confined in amorphous silica and chalcogenide pores with different pore sizes are investigated by means of molecular simulation. This work sheds light on the complex behavior of hybrid materials made up of ionic liquid confined in inorganic porous materials.

Keywords: hybrid materials, ionic liquid, silica, chalcogenide, molecular simulation

1 INTRODUCTION

Hybrid materials made up of an inorganic porous material filled with a room temperature ionic liquid (IL) represent a novel class of materials with promising applications [1]. Owing to the high specific surface area of the porous material and the peculiar properties of IL such as low volatility, low flammability, high ionic conductivity, and high thermal stability, these materials find applications such as energy-storage devices (electrochemical batteries, supercapacitors), lubricants, and drug delivery systems. Among this new class of material, silica- and chalcogenide-based gels, which are hybrid materials made up of ionic liquids confined in a porous network, exhibit properties that can be tailored. Describing the properties of such hybrid materials requires better understanding the effect of confinement and surface forces on the structure and dynamics of IL. From an experimental point of view, several groups have examined the effect of confinement of IL in porous silica (see for instance Ref.[2]). These works have shown that, in a similar fashion to molecular liquids, the behavior of confined IL departs from the bulk; both the thermodynamics (phase transition, structure) and the dynamics (self and collective dynamics and transport) can be modified upon confinement in porous materials or adsorption on surfaces. However, for the case of porous chalcogenides, only few studies have been focused on the interactions between ionic liquid and chalcogenide surfaces [3], [4]. Because of the soft nature of chalcogen elements (S, Se, and Te), the polarizability of the internal surface of chalcogenide gels is much higher than those of metal oxides and porous carbons and therefore provides an entirely new medium through which to

study the interaction with ionic liquids. From a theoretical point of view, the molecular organization and interactions of IL adsorbed on solid surfaces or confined in pores can be understood using molecular simulation tools. Most authors have investigated the behavior of confined or adsorbed IL using classical MD. All these molecular simulation studies considered systems in the canonical ensemble (NVT). In order to better understand the properties at ambient temperature and pressure ($T = 300$ K and $P = 1$ atm) of IL confined in porous silica and chalcogenide GeS_2 ($g\text{-GeS}_2$, g standing hereafter for glass), we report in the present work MD simulations in the isobaric-isothermal ensemble (NPT), in which the temperature T and the total pressure of the systems are kept constant. GeS_2 ($g\text{-GeS}_2$, g standing hereafter for glass) Thanks to the use of this ensemble, we are able to determine the density of the IL confined in gels in conditions relevant to real experiments and samples. We consider the structure and dynamics of a widely used imidazolium-based IL confined in amorphous silica and chalcogenide nanopores. We address the effect of pore size by considering pores of a several width.

2 METHOD AND COMPUTATIONAL DETAILS

Figure 1 shows the IL, silica and chalcogenide surfaces as well as the models of silica- and chalcogenide based gels (i.e., IL confined in silica and chalcogenide pores) considered in this work. The silica nanopores considered in the present work were obtained by carving a slit pore of a width H out of bulk amorphous silica. Details about the procedure used to obtain the slit pores can be found in Ref. [7] Silica slit pores of a width $H = 2.0, 2.4, 2.8, 3.2, 3.6,$ and 4.0 nm were prepared. Following the procedure in Ref. [8], the silica surfaces were partially hydroxylated by saturating oxygen dangling bonds with H atoms in order to obtain a silanol surface density of 5.3 OH/nm². This silanol surface density was chosen as it is close to that of porous silica glasses such as Vycor. For what concern chalcogenide pores a model of $g\text{-GeS}_2$ was obtained by means of first-principles molecular dynamics. Details of the procedure

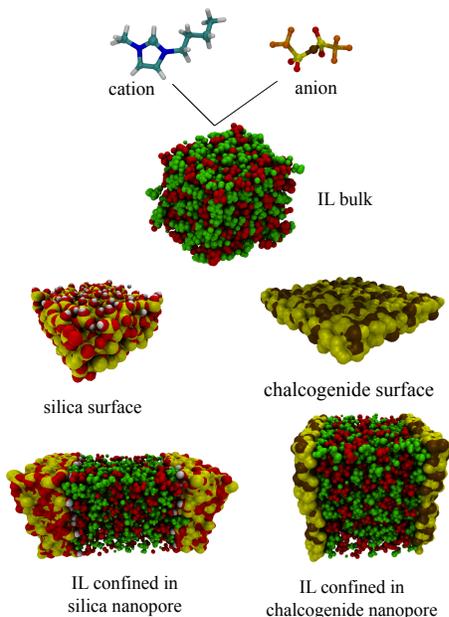


Figure 1: (Color online) Typical molecular configurations for IL, silica and chalcogenide surfaces. We also show typical molecular configuration for the IL confined in a silica pore of a width $H = 4.0$ nm and in a chalcogenide pore of a width $H = 3.6$ nm.

used can be found in Ref. [9] and [10]. This realistic model of GeS_2 surface contains 480 atoms and has a size of $2.358 \times 2.358 \times 2.358 \text{ nm}^3$ with 1.2 nm along the z direction of free volume on the top and the bottom. This system was replicated 2×2 times along the xy plane. The nanopores of size 3.6 and 4.8 nm were obtained by inserting $4.7 \times 4.7 \times 1.20 \text{ nm}^3$ and $4.7 \times 4.7 \times 2.40 \text{ nm}^3$ vacuum slabs in between the facing chalcogenide surfaces. For what concern the IL confined in silica nanopores, the potential details can be found in Ref.[5]. For IL confined in chalcogenide nanopores, we used the same potential for the IL and for the chalcogenide surfaces the potential parameters and atomic charges employed in Ref. [11] and [12]. For each pore the amount of IL inserted within the porosity was estimated so that the initial IL density inside the pore is close to the bulk density ($\sim 1.43 \text{ g/cm}^3$ at $T = 300 \text{ K}$). The cations and anions of the IL were placed randomly inside the pores and then relaxed using a MD simulation of 500 ps at 1200 K in the canonical ensemble (NVT). The systems were then equilibrated for another 500 ps at 300 K. To obtain a final physical density inside the pores, a MD simulation of 1 ns in the isostress-isothermal ensemble ($N\sigma T$ simulations at 300 K and 1 atm) was performed. The temperature and pressure were controlled using a Nosé-Hoover thermostat and barostat (relaxation time parameter: 0.01 and 0.1 ps, respectively). Then, 5 ns of NVT simulation were used to analyze the structure and

dynamics of the confined IL (sampling every 1 ps). In order to check the effect of the starting configuration, we considered different initial systems; (1) the ions were placed randomly within the pore or (2) a slab of bulk IL was inserted within the pore. Both initial configurations led to the same final equilibrium state. The simulations were integrated using the Verlet algorithm with a timestep of 1 fs. All the simulations were performed with the molecular dynamics code DLPOLY.

3 RESULTS AND DISCUSSION

Before discussing our results, we first describe the strategy used to estimate the physical density of the confined IL in equilibrium with an external environment imposing its temperature and pressure. We use isobaric-isothermal simulations in which all the diagonal elements P_{xx} , P_{yy} , and P_{zz} are constrained independently. This type of isobaric simulations, which strictly speaking should be referred to as isostress simulations ($N\sigma T$), are appropriate in the context of the present study as they allow both the shape and volume of the system to vary (so that, once equilibrated, the system is in equilibrium in all directions with the external pressure of 1 atm). As pointed out in the introduction, the motivation for using this ensemble was to be able to determine the density of the IL confined in ionogels in conditions relevant to real experiments and samples. For all systems, the volume of the simulation box decreases by a small amount ($\sim 4\%$) which indicates that the initial density of the confined ionic liquid is not far from the equilibrium density (for an external pressure of 1 atm). If no ionic liquid is inserted in the pores, the two walls attract each other due to the attractive interactions between the two surfaces separated by a distance h (dispersion interaction that scales as $1/h^2$).

3.1 Structure of the confined ionic liquid

For all pores, significant layering is observed as the density profiles for the IL anion and cation exhibit marked density oscillations. Such a significant layering, which is characteristic of confined liquids, has been already observed in MD simulations of IL confined in solid pores. The solid surface disorder introduces a dispersion in the position of the first adsorbed ions, which in turn leads to a broad density peak close to the surface. Such a peak is necessarily broader than what is usually observed in molecular simulations of ionic liquids adsorbed or confined in pores made up of structureless walls (i.e. without any surface corrugation) or crystalline walls (such as quartz). The structure of the confined IL was further investigated by measuring structural order parameters (details about the definition of the order param-

eters $S_{alkyl}(\theta_a)$ and $S_{ring}(\theta_r)$ can be found in Ref. [7]. For all pore sizes, more than 75% and 60% of the IL in the interfacial region (defined as 1 nm from the silica or chalcogenide surface) shows $S_{alkyl}(\theta_a) > 0.85$ for the silica and chalcogenide pores, respectively. This result indicates that the cation alkyl chain is preferentially adsorbed with a perpendicular orientation with respect to the solid surfaces. Furthermore, a small part of the IL cation is adsorbed with a parallel orientation with respect to the solid surfaces. In the bulk-like region, $S_{alkyl}(\theta_a)$ does not exhibit any clear orientational preference, which shows that the IL recovers its bulk-like properties in this region. The analysis of the $S_{ring}(\theta_r)$ shows that more than 75% and 40% of the confined IL cation in the interfacial region shows $S_{ring}(\theta_r) < -0.2$ for the silica and chalcogenide pores, respectively. No ordering preference is observed in the bulk-like region. These results show that the IL cation prefers an orientation in which the ring and the alkyl chain are nearly perpendicular to the pore surface. This effect is more pronounced for the silica surface in comparison to the chalcogenide surface. This effect can be ascribed to the more ionic character of the silica surface whereas the more polarizable surface of chalcogenide pores induces a smaller effect on the short-order induced-orientation of the IL at the liquid-solid interface. Overall, the IL cation beyond the adsorbed layer recovers its bulk-like properties, with an almost constant distribution $S_{ring}(\theta_r)$ for this region. This result suggests that the influence of the surface on the orientation of the adsorbed IL cation rapidly drops off beyond the contact layer. In order to gain information on the structural ordering of the IL anion, we calculated the C-S••S-C torsional (θ_{tors}) angle of the IL anion to quantify the percentage of *trans* and *cis* conformation. $\theta_{tors} < 85^\circ$ was used to define the *cis* conformer and $\theta_{tors} > 120^\circ$ to define the *trans* conformer. For the bulk IL, $\sim 90\%$ of the anions are in the *trans* conformation which corresponds to the most stable configuration in the liquid bulk phase as it minimizes steric repulsion between the symmetric sulfonyl and trifluoromethyl groups. For an IL similar to that considered in the present work, 1-ethyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide, a $\sim 75\%$ content of *trans* conformer was determined in the bulk IL using Raman spectroscopy and *ab initio* calculations [13]. In the present work, the *trans/cis* ratio decreases with decreasing the pore size for both the silica and chalcogenide pores. This confinement effect on the *trans*-to-*cis* conformational rearrangement can be ascribed to the fact that the *cis* conformation of the IL anion allows more efficient packing of the anions at the solid surface (note that such packing effects also affect the crystalline structure of this IL which also exhibits a *cis*-conformation [14]). In particular, the *cis* conformation allows the four sulfonyl oxygens of the anions to interact with the H

atoms of the solid surfaces. These results are in qualitative agreement with Raman spectroscopy experiments on ionic liquid confined in gel in which it was found that the percentage of anion *trans* conformer is lower than for the bulk IL [15],[16]. As mentioned above, the structure of the confined IL, including the conformation of the anion, can be described as the sum of two populations. For instance for the silica pores, let $Q_{surf} = 35 \pm 2.4\%$ be the percentage of *trans* conformation of the IL anions in the vicinity of the silica surface and $Q_{bulk} = 90 \pm 5.2\%$ the percentage of *trans* conformation of the IL anion in the pore center (bulk-like region). For a given pore size H , the overall percentage of *trans* conformation can be written as:

$$Q(H) = Q_{bulk}v_{bulk} + Q_{surf}v_{surf} \quad (1)$$

$$= Q_{bulk} \frac{H - 2\sigma}{H} + Q_{surf} \frac{2\sigma}{H} \quad (2)$$

$$= Q_{bulk} + \frac{2\sigma}{H}(Q_{surf} - Q_{bulk}) \quad (3)$$

where v_{bulk} and v_{surf} are the volume fractions of the IL in the pore center and of the IL in the vicinity of the silica surfaces, respectively. $\sigma \sim 1$ nm is the size of the adsorbed layer of IL on the silica surface; in the equation above, we assume that the vicinal region (i.e. the region in which the properties of the ILs are affected by the silica surface) is σ thick. Indeed, previous works have shown that, for most liquids, the confined liquid is affected up to two layers from the surface and then recovers its bulk properties. Good agreement is found between Eq. (3) and the data obtained from our molecular simulations. This result confirms that the structure of the confined IL can be described using a simple two population model in which average structural properties are simply related to surface to volume ratio of the porous material. Similar considerations can be found for the case of IL confined in chalcogenide pores.

3.2 Dynamics of the confined ionic liquid

To gain insights into the dynamics of the confined IL, the mean square displacements in the xz plane (2D-MSD, where y is the direction \perp to the pore surface) of the IL cation and anion were computed for all the pore sizes investigated. For all pore sizes, even after 4 ns at room temperature, the Fickian regime (i.e. in which the 2D-MSD scales linearly with time t) is not reached. At a given time t , 2D-MSD for the confined IL is lower than that of the bulk IL due to the effect of confinement and surface forces which tend to slow down the IL. This interpretation is confirmed by the fact that the 2D-MSD at a given time decreases with decreasing the pore size (i.e. increasing the surface to volume ratio of the pore). Since the Fickian regime is not reached

after 4 ns, we cannot estimate the self-diffusivity of the confined cations and anions. As an indication of the self-dynamics of the confined IL, we estimated for both the cation and anion its 2D-MSD at 4 ns. In agreement with our conclusion above, both the cation and anion become slower upon decreasing the pore size H . For instance, for the silica pores width $H = 3.6$ nm and $H = 4.0$ nm, the IL cation and anion show mobilities ~ 2.5 and ~ 5.5 times greater than those for the pore with $H = 2.0$ nm, respectively. Similar results are found for the IL confined in chalcogenide pores. As in the case of the bulk IL, the dynamics of the cation is faster than that of the anion, in agreement with experiments [17]. The faster dynamics of the cation arises from its homogeneous electrostatic field, which leads to a weaker interaction with its environment. In contrast, the anion, which creates a heterogeneous field with both positive and negative regions, interacts strongly with its environment so that its dynamics is slower. We note that the flexible alkyl chain and planar structure of the cation backbone of the imidazolium species also contribute to its faster dynamics. Interestingly, as in the case of structural properties, a simple two population model provides a simple quantitative description of the average value obtained from the MD simulations.

However, the ionic conductivity of the confined IL is very close to that of the bulk IL. This result is in agreement with our previous work in which the conductivity of an IL confined in a pore fully loaded with the IL was found to be similar to that of the bulk [5]. Although the self-dynamics of the IL becomes slower upon confinement, the ionic conductivity, which is related to the collective motion of the charges, is not affected drastically by confinement and surface interactions.

4 Conclusions

Classical MD simulations of an imidazolium-based IL confined in amorphous silica and chalcogenide pores are reported. Thanks to the use of the isobaric-isothermal ensemble, we are able to determine the density and structure of the confined ionic liquid at equilibrium conditions relevant to real hybrid materials consisting of inorganic porous materials filled with ionic liquids at ambient temperature and pressure. We find that the structure and dynamics of the confined ILs are affected by the confinement, surface interactions, and reduced dimension of the system. As far as the structure of the confined IL is concerned, despite the important screening of the electrostatic interactions (owing to the small Debye length in ionic liquids), the local structure of the confined IL is found to be mostly driven by electrostatic interactions. However, the IL confined in chalcogenide pores shows structureless properties (for example in terms of IL orientation with respect to silica pores at the interface). This difference is ascribed to the strong

ionic character of the silica surface in comparison to the more polarizable surface of chalcogenide pores. This work also sheds light on the behavior of ionic liquids in such hybrid materials by showing that both their structural and dynamical properties can be described as the sum of a surface contribution arising from the ions in contact with the surface and a bulk-like contribution arising from the ions located in the pore center (more generally as a function of the surface-to-volume ratio of the host confining system). In contrast, the ionic conductivity of the confined ionic liquid, which is a collective dynamical property, is close to the bulk ionic conductivity. While further work is needed to clarify the physical state of IL confined in hybrid organic-inorganic materials, the results above help better understanding their properties and the role of the surface to volume ratio of the host material.

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