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Effect of molecular shape on rotation under severe confinement

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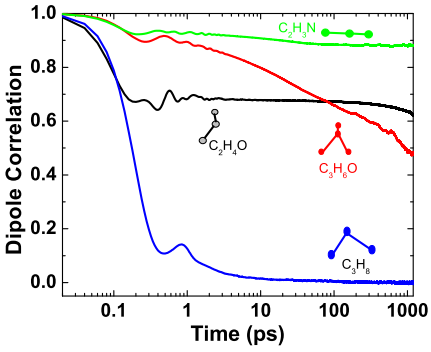
HIGHLIGHTS

- Orientational structure and dynamics of four molecules in ZSM5 is studied separately.
- The selected molecules have similar kinetic diameters and moments of inertia but different shapes.
- Rotation of all four molecules confined in ZSM5 occurs at two different time scales.
- Effect of molecular shape on the orientational structure and dynamics is studied.
- Asymmetry of charge distribution plays a determining role in the rotational behavior of confined molecules.

GRAPHICAL ABSTRACT



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ABSTRACT

Orientational structure and dynamics of molecules is known to be affected by confinement in space comparable in size to the molecule itself. ZSM-5 with porous channels of ≈0.55 nm is such a porous medium, which offers a strict spatial confinement on low molecular weight hydrocarbons. An important factor that determines these properties is the shape of the confined molecules. We employed molecular dynamics simulation to study the orientational structure and dynamics of four molecules that differ in shape but have similar kinetic diameters and moments of inertia, confined in ZSM-5. The effect of molecular shape on the orientational structure and dynamics of propane, acetonitrile, acetaldehyde and acetone in ZSM-5 is studied by means of probing the differences in the orientational distribution of molecules in the ZSM-5 channels, and extracting time scales of the decay of correlation functions related to rotational motion. Orientational correlation functions of all the four molecules exhibit two regimes of rotational motion. While the short time regime represents free rotation of the molecules before they collide with the pore walls, the long time orientational jumps driven by inter-channel migrations give rise to a very slow varying second regime. Of the molecules studied, orientational structure and dynamics of propane is found to be least affected by confinement under ZSM-5, whereas charge and shape asymmetry of other molecules makes their interchannel migration-driven rotation slow. The time scales involved in the rotational motion for the molecules studied are compared with similar studies reported in literature. This study reveals the important role that molecular shape plays in the behavior of confined molecules.

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1. Introduction

Understanding fluid behavior under confinement in porous materials is essential from both application and fundamental physics point of view (Cole et al., 2009; Ruthven, 2005; Karger and Valiullin, 2013; Buntkowsky et al., 2007). Confining a fluid has a strong influence on its structure and dynamical properties, and the behavior of confined fluids shows significant deviation in comparison to bulk fluids (Koga et al., 1998; Mansoori and Rice, 2015; Giovambattista et al., 2006; Hirunsit and Balbuena, 2007; Verdaguer et al., 2006; Mattia and Gogotsi, 2008; Bergman and Swenson, 2000; Ghorai et al., 2003; Demontis and Suffritti, 1997). Also, from an industrial viewpoint the study of confined fluids is important for various applications such as gas/oil recovery, catalysis, separations, and cellular dynamics, etc. (Liu et al., 1999; Zheng et al., 2003; Deamer and Akeson, 2000; Sun and Crooks, 2000; Ajayan and Iijima, 1993; Ajayan et al., 1995). As a consequence, study of structural and dynamical behavior of fluids confined in porous materials has received substantial attention (Wang et al., 2003; Cole et al., 2004; Gautam et al., 2017; Lash and Engelder, 2011; Snow, 2011; Cole et al., 2006).

In particular, several studies have been focused towards the investigation of hydrocarbons confined in zeolites (Bhide and Yashonath, 2002; Clark et al., 1999; Gergidis et al., 2000; Gautam et al., 2011, 2008a; Gorny et al., 2012, 2017). Zeolites are also technologically relevant in petrochemical industry, as molecular sieves, ion exchangers, and catalytic cracking, etc (Gautam et al., 2011; Tomlinson, 1998; Smit and Maesen, 2008). Diffusive properties of hydrocarbons in zeolites are dependent on several factors, including the molecular structure and size of the hydrocarbon, temperature and loading. To better understand the behavior of hydrocarbons under confinement it is important to study the translation and orientational (rotational) motion of these molecules. While the long range translational diffusion plays a crucial role in the catalytic and separation based applications, rotational motion is also important to study as it can affect other properties including the translational diffusion (Bhowmik et al., 2012, 2014). For example, Banerjee et al. have shown how rotational motion of nitrate and acetate ions in aqueous solutions can enhance their translational diffusivity (Banerjee et al., 2017). Also, it is well established that the translation motion and related dynamics are significantly influenced by milder confinement of molecules, wherein the confining space dimensions are considerably larger than the confined molecule. On the other hand, orientational motion is only affected when the confining space dimensions are comparable to the size of confined molecules. For instance, a study of water confinement by the layered saponite structure, having inter layer spacing of 0.8 and 1.4 nm, shows that rotational motion is not significantly influenced, while the translation motion is found to be affected (Chakraborty et al., 2006). In contrast, a molecular dynamics study of water confinement in TiO_2 pores with varying sizes (1.3, 2.8, 5.1 nm) shows two different regimes of rotational motion (Solveyra et al., 2013). If the confining space is small enough, confinement can also gives rise to qualitative changes in the rotational motion, as reported by Farimani et al. (2013). They showed that a single water molecule encapsulated in a buckyball (C_{60}) exhibits harmonic motion, in contrast to stochastic rotational motion of water in bulk.

Zeolites, by virtue of their smaller pores can provide an environment of severe confinement on hydrocarbons. For example, ZSM-5 zeolite contains porous channels of ≈0.55 nm in size. This porous medium provides a strict spatial confinement on low molecular weight hydrocarbons. Hydrocarbons such as, acetylene, propane, propylene, and 1,3-butadiene, with kinetic diameters between 0.33 and 0.52 nm, exhibit isotropic behavior in rotational motion when confined in Na-Y zeolite pores, which are nearly two to four times bigger in size (1.2 nm supercages) in comparison to the confined molecules (Gautam et al., 2006; Mukhopadhyay et al., 2002; Sharma et al., 2009, 2010; Gautam et al., 2008b). On the other hand, as the size of confining space is reduced with ZSM-5 zeolite pores and become comparable to the confined molecule, the rotational motion of propylene (Gautam et al., 2011) as well as ethane (Gautam et al., 2016) is observed to be hindered and displays librational motion. This behavior is also in agreement with the neutron scattering studies reported by Jobic et al. on rotational motion of ethane and propane in Na-ZSM-5 pores (Jobic et al., 1992). They found that ethane rotation in Na-ZSM-5 is uniaxial and not isotropic. This indicates reduction in degree of disorder and stronger restriction in rotational motion with increasing confinement. Further, under strict confinement imposed by the ZSM-5 channels, the rotational properties of confined ethane have been observed to exhibit an anomalous loading dependence in both experimental (Jobic et al., 1992) as well as computational (Gautam et al., 2016) studies. In both these studies, it was found that the rotational motion of ethane in ZSM-5 gets enhanced at higher loading. These studies show that ZSM-5 is a good candidate to study the confinement effect on the rotational motion of different hydrocarbons.

As noted earlier, an important aspect that affects the behavior of confined fluids is the molecular shape of the confined component. Several studies highlighting the importance of molecular shape have been reported in literature. For example, Schenk et al. have shown that the molecular sieves used in the catalytic conversion of alkanes favor the formation of reaction intermediaries that have molecular shapes commensurate with the pores of the sieves (Schenk et al., 2001). The influence of molecular shape on the solute transport processes has been discussed by Van der Bruggen et al. (1998, 1999) and Santos et al. (2006). Thalladi et al. reported the effect of molecular geometry on the melting point of n-alkanes (Thalladi and Boese, 2000). The effect of molecular shape for model asymmetrical molecules on the rotational motion has also been reported (Fragiadakis and Roland, 2015).

In the present study, our aim is to investigate the effect of molecular shape on the orientational structure and dynamics of molecules under strict geometrical confinement imposed by ZSM-5 zeolite. The effect of molecular shape is investigated by studying four molecules, having similar kinetic diameters but different shapes, confined in ZSM-5. For this, we needed molecules that could be modeled using a similar formalism for simulations. TraPPE-UA force field provides a formalism for simulating hydrocarbon molecules in a simpler united atom approach, which is computationally less expensive compared to an all atom simulation (Martin and Siepmann, 1998). We therefore selected four molecules, which have comparable kinetic diameters and for which TraPPE-UA parameters were explicitly available. The four molecules we have selected are propane, acetonitrile, acetaldehyde and acetone (refer Table 1). All these molecules have a kinetic diameter between 0.36 and 0.46 nm (Matteucci et al., 2006;