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Molecular dynamics of tris(2-ethylhexyl)phosphate in 2D confinement

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1. Introduction

Several natural and industrial processes involve confined fluids and so the quest to understand their intrinsic properties under confinement has intensified. Whereas Tris(2-ethylhexy)phosphate (TEHP) is extensively used as an flame retardants in lithium ion batteries, there is paucity of data on its properties under geometric confinement. Broadband dielectric spectroscopy (BDS) is employed to study TEHP confined in porous silica membranes having parallel cylindrical pores with diameters of 4, 8 and 10.4 nm. BDS probes glassy dynamics of molecules over a wide frequency and temperature ranges. It is suitable for studying dynamics of molecules in confined spaces down to mesoscopic and molecular levels. Glassy dynamics can either be rotational diffusion, translational diffusion or a combination of both.

2. Experimental results

Fig 1. shows relaxation rates of bulk and confined TEHP obtained from maximum frequencies of imaginary parts of dielectric spectra. Two processes are observed: the primary α-relaxation process due to rotational fluctuations of structural sub-states and the secondary *β*-process which results from libration motion of single P-O units. The temperature dependence of the *β* process follows Arrhenius' Law, but the *α* process follows a Vogel-Fulcher-Tamman law. Primary α-relaxation is associated with glassy dynamics and is therefore strongly affected by spatial constraints, at least near the glass transition temperature where the increase in relaxation rates with decreasing pore sizes is observed. At low temperatures, *α* relaxation rates in silanized 10.4nm pores is slightly enhanced. Dynamics of molecules under 2D confinement is always governed by the interplay between surface effects and confinement effects. The dynamics are faster if confinement effects dominate, otherwise it is retarded. In 4nm pores dynamics are slightly slower than in the bulk at high temperatures, but becomes faster at low temperatures, an evidence of competition between surface effects and confinement effects.

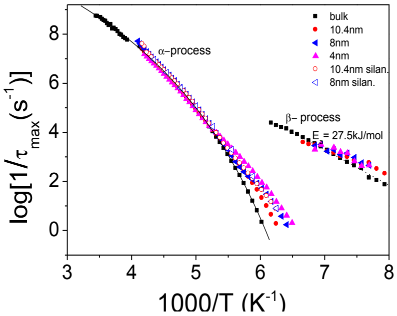

Fig. 1: Temperature dependence of structural (α) and β relaxation rates. The solid line is a fit by VFT equation while the dotted line is an Arrhenius fit. Open symbols represent dynamics in silanized silica membranes.

While slowing down of dynamics due to surface effects is a clear cause of interaction between guest molecules and walls of the host systems, increase in dynamics in confined geometries is still a subject of controversy [1]. It has often been explained in terms of hindered growth of cooperative regions [1,2,3] – a concept which unfortunately lacks a physically quantitative picture since it is difficult to access the inherent length scale of these cooperative regions experimentally. We attribute the faster dynamics of confined TEHP to changes in molecular packing leading to altered density and dipole-dipole interactions. The ratio of interacting dipoles moments to non-interacting dipole moments (Fig. 2) increases as temperature decreases from 240K, yet at around 200K it decreases for confined molecules but continues to increase albeit weakly for bulk TEHP.

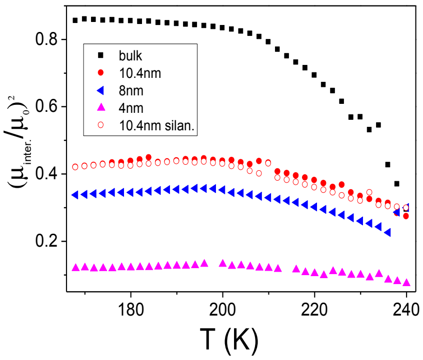

Fig.2: Temperature dependence of the ratio of interacting dipole ($\mu_{inter.}$) to non-interacting dipoles (μ_0)

3. Conclusion

Glassy dynamics of TEHP molecules constrained in finite 2D geometries are dominated by confinement effects, which lead to faster relaxation rates as pores sizes decrease. This phenomenon is best explained in terms of changes in density and the corresponding changes in dipole moments under confinement.

4. Reference

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