

Local Dynamics of Poly(ethylene oxide) Confined in 1nm Slits

V. Kuppa and E. Manias

Department of Materials Science and Engineering,

The Pennsylvania State University,

325-D Steidle Building, University Park, PA 16802, USA

ABSTRACT

Molecular Dynamics simulations are used to explore the short-time dynamics of nanoscopically confined poly(ethylene oxide). Both bulk and confined systems have been studied using an atomistically detailed force field so as to comparatively illustrate their differences and complement experimental results. Our aim is to elucidate the origins of the counter intuitive distribution of relaxation times for C-H bond re-orientation for PEO in severe confinements, as experimentally observed in solid state ^2H NMR studies. In contrast with the respective bulk PEO system, where a transition from distinct solid to liquid like dynamics is seen with increasing temperature, for the confined chains there is a coexistence of fast and slow segmental dynamics over a wide temperature range. Our studies have revealed that factors such as local density inhomogeneities, proximity of Li^+ , and translational motion, synergistically contribute to the generation of fast PEO segmental dynamics in 1nm confinements.

INTRODUCTION

The last few years have seen an increased interest in organic/inorganic “hybrid” materials as model systems to study confined polymers. One of the most actively explored classes of such materials is that of polymers intercalated between mica-type, inorganic layers[1] in which polymers are present in slit pores a few monomers wide. Such extreme confinements lead to radical alterations in materials behavior and the resultant exciting new physics is increasingly the focus of much research [1–4]. A variety of techniques have been employed to probe the structure and dynamics in these severe confinements, and a very striking picture is emerging for the local segmental dynamics of PEO in nm-thin slit pores [5–7] ; namely a coexistence of fast and slow dynamics for C-H bond reorientation across a broad temperature range is unveiled. We have performed molecular dynamics computer simulations to investigate these systems, especially tracing the origins of the counter-intuitive distribution of relaxation times for C-H bond re-orientation across temperatures. Our ultimate goal is to trace the physics behind the dynamics of polymers in severe confinements and to explain macroscopically observed experimental behavior.

MOLECULAR DYNAMICS SIMULATION DETAILS

Two different force fields developed in earlier simulations of bulk PEO by Muller-Plathe [8] and Smith *et al* [9, 10], were evaluated in our confined geometries, where the interactions with the montmorillonite sheets were modeled after Hackett *et al*[11]. Both sets of parameters reproduce well the structural PEO details of the confined

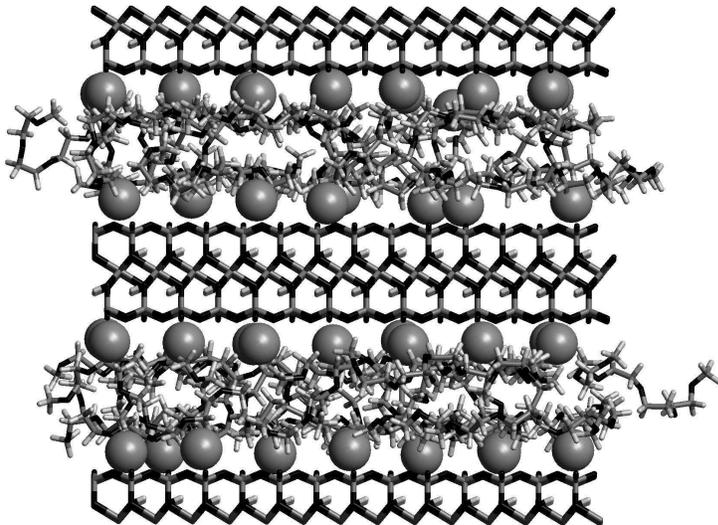


FIG. 1: Snapshot of the simulation box with double slit geometry. Li^+ ions are represented by their van der Waals spheres, so as to clearly show their positions with respect to the inorganic walls. All other molecules are represented by their bonds (“stick” model).

systems as observed experimentally. However, the force field from [9, 10] mimics better the polymer segmental dynamics and Li^+ motion as quantified by NMR experiments [7]. For bulk PEO, Constant NPT simulations were performed in a manner similar to those described in [9, 10], with a cutoff radius of 0.9nm and a distance dependent dielectric constant [12]. The bulk systems consist of 8 Li^+I^- pairs solvated by 69 PEO hexamers. The box size was varied, so as to match the PEO density to the experimental data [13] at each temperature. P and T were stabilized by a weak coupling to their reference values, via the Berendsen method[14].

The confined systems were simulated at constant NVT. Periodic boundary conditions were employed in all three directions, and a box size of $3.696 \times 3.656 \times 3.558\text{nm}$ was used, which corresponds to two PEO/ Li^+ films intercalated between two inorganic layers, as shown in fig. 1. This double slit geometry of PEO/ Li^+ MMT allows for more accurate evaluation of the long range electrostatic forces [15]. The confined films are 0.8nm thin, and each consists of 23 PEO hexamers and 21 Li^+ ; both the film thickness, as well as the PEO and Li^+ numbers, were chosen to agree with the experimental values [5]. Long range corrections in the electrostatics were included through the generalized reaction field method (GRF) [16], with an effective dielectric constant of 3.0 beyond 1.0nm . The time step in all simulations was 1fs , and for each temperature, after energy minimization and an equilibration MD run of 10ns , productive runs of $2\text{-}6\text{ns}$ were recorded, depending on T.

C-H BOND DYNAMICS

Focusing on the short term (ns) dynamics in our confined systems, our aim is to complement the experimental NMR studies and provide insights on the relevant molecular scale processes underlying the local segmental dynamics in nanoconfined PEO. In order to compare against the NMR experiments, we modeled both intercalated and bulk Li^+ /PEO systems over the experimental temperature range [5]. Since in MD simulations the dynamics of entities can be directly followed through the time-trajectory of the particles, we monitor the C-H bond reorientational relaxations as a measure

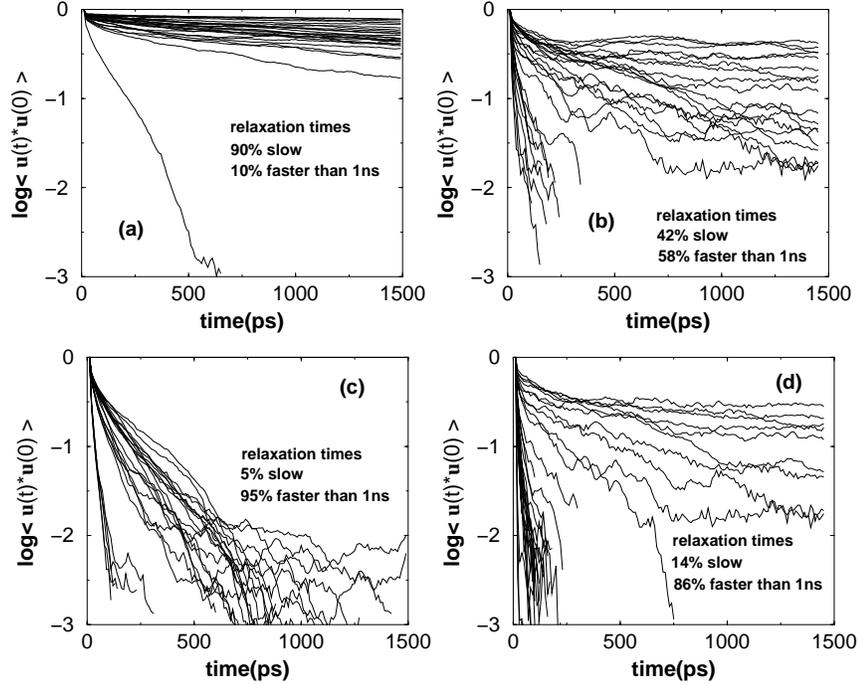


FIG. 2: Typical time autocorrelation functions of the PEO's C-H bond vectors. The inset text is the ensemble distribution for the corresponding system/temperature. (a) bulk, 273K ; (b) nanoscopically confined, 273K ; (c) bulk 423K ; (d) nanoscopically confined, 423K.

of the local segmental dynamics, paralleling the NMR experiments. In particular, we define and follow the time autocorrelation functions (ACF) of the C-H bond vector, which effectively measures the same temporal relaxation as the ^2H NMR studies. In figure 2 we show the log of the ACFs of a few typical C-H bond vectors for bulk (figs. 2a, 2c), and confined (figs. 2b, 2d) systems, for the lowest and highest temperatures simulated (273K and 423K respectively). We see that the bulk has a much more homogeneous dynamical behavior than the confined systems, with characteristic solid-like and liquid-like dynamics seen for the lowest and highest temperatures. The confined systems exhibit a more wide distribution of dynamic responses, even at these two extreme temperatures (in concert with the NMR results). Comparison of the highest and lowest temperature responses for the confined system shows that marked populations of the C-H bonds are characterized by fast reorientation for the lowest T, and also very slow (solid-like) motions for the highest T, in a significant departure from the behavior of the bulk PEO (figs. 2a-d). Our simulations capture the essential behavior of the bulk and confined system dynamics, as seen experimentally in the NMR, even though we focus on a much shorter time scale than what the experiment probes.

MOLECULAR ORIGINS OF SEGMENTAL DYNAMICS

In order to quantify the local segmental dynamics of confined PEO, we analyzed

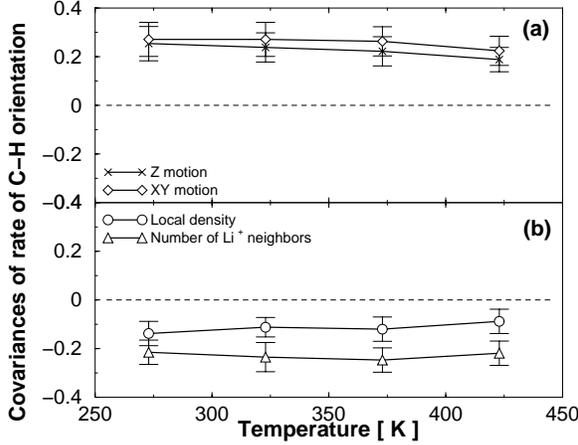


FIG. 3: (a) Covariances of the C-H bond reorientation rate with translational motion of the respective carbon, both in the z direction and in the xy plane. (b) Covariances of the C-H reorientation rate with local density around the C-H bond and with the number of proximal Li^+ ions.

closely the correlations between the rate of reorientation of the C-H bond vectors and the various factors that could possibly have an effect on it. This was possible through our definition of the covariance between two variables:

$$\text{cov}(\delta\phi, X) \equiv \frac{\langle (\delta\phi - \langle \delta\phi \rangle) \cdot (X - \langle X \rangle) \rangle}{\sqrt{\sigma^2(\delta\phi) \sigma^2(X)}} \quad (1)$$

where $\delta\phi$ is the rate of change of the C-H bond direction, $\langle \delta\phi \rangle$ is the ensemble average of the rate of change of the C-H bonds in the system, X is the factor whose effect on the reorientation we wish to measure, and $\langle X \rangle$ is the ensemble average of X . $\sigma^2(\delta\phi)$ and $\sigma^2(X)$ are the corresponding ensemble variances, of $\delta\phi$ and X respectively. Using this equation, we can quantify the influence of different physical mechanisms on the reorientation behavior of the C-H in the confined system (fig. 3). Earlier simulation studies of polystyrene in similar confined geometries[17] have shown that the local segmental relaxations are *strongly* connected to local density variations in the confined film [17]. Probing the same correlation here for the PEO systems, *i.e.* the covariance of the rotational relaxation of a C-H bond versus the local density around this C-H bond (fig. 3), we see a definite connection between the two. Specifically, this covariance is negative across all temperatures, denoting that the rate of bond vector reorientation is *faster* for C-H bonds located in regions of *lower* local density. This is exactly the same behavior reported for the nanoscopically confined PS[17]. However, the low absolute value of the covariance suggests that there must exist more factors which contribute to the dynamical behavior of PEO in confinement. In this regard, conceptually the simplest covariance is between the translational displacement of C-H bonds and their reorientation behavior. We explored two different correlations in this context, connecting C-H reorientations to translations parallel to the confining surfaces, *i.e.* in the xy plane, and perpendicular to them, *i.e.* in the z direction. As seen in figure 3(a), there is a positive correlation between translational motions of the C-H bonds and their rotations. This means that the *greater* the motion of the C-H bond, the *faster* the rate of reorientation of the corresponding bonds. This is not unexpected, since polymer segments that move in space are also more likely to undergo rotation around the carbons(fig. 4), as part of the polymer backbone flexing

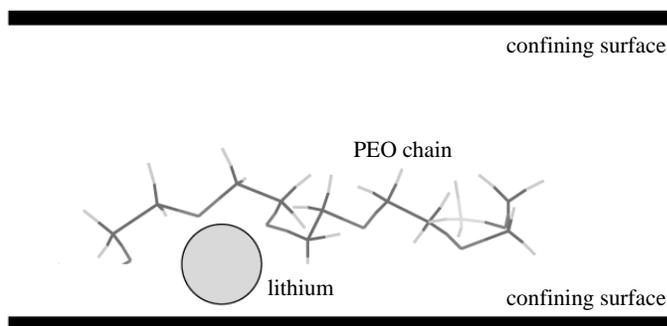


FIG. 4: Li^+ mediated anchoring of PEO chain to the wall. Electrostatic forces between polymer/ Li^+ and Li^+ /confining surface cause the chains to be immobile even at high T.

and trans-gauche isomerizations. For our simulation box geometry, motions in the z direction correspond to adsorption/desorption events of C-H moieties, which intuitively are expected to contribute the most to the C-H rotational relaxation. However, the covariances of the C-H reorientation with the z and xy motions are comparable, which means that motions in the plane parallel to the walls are as important as motions perpendicular to them for the reorientation of the respective C-H bonds.

The correlation between the reorientation rate of the C-H bond vectors and the number of Li^+ in the vicinity of that C-H bond is perhaps the most interesting covariance identified in our study. The negative value of this covariance implies that the *larger* the number of Li^+ located close to a bond, the *slower* its rate of reorientation is. The explanation for such an observation can be traced to the arrangement of the PEO chains and Li^+ cations in the slit pore. It is known, both from earlier simulations [11] and NMR spin lattice relaxations studies [7], that the lithium cations reside in the vicinity of the wall surfaces, attracted by the strong electrostatic potential of the negatively-charged silicate layers. The PEO chains are mostly arranged parallel to the walls, with multiple oxygens coordinated to the Li^+ cations [11](fig. 1). This materials arrangement effectively allows the Li^+ , which are strongly coupled to the wall surfaces [18], to mediate an indirect anchoring of the PEO chains to the solid surfaces as seen in fig. 4b. Consequently, the greater the number of lithiums close to a particular C-H bond, the greater is the anchoring of that chain fragment to the solid surface. In this manner, reduced mobility is imposed on the chain fragments which are highly coordinated to lithiums, leading to a lower rate of reorientation for the C-H bonds. This hindrance to motion –implicitly reflected in the negative value of our covariance– is also directly seen in the system trajectories, for all the simulated temperatures.

CONCLUSIONS

Molecular dynamics simulations were used to study the physics of poly(ethylene oxide) oligomers in severe confinement. Focusing on short time scales (few ns), we were able to draw parallels with and capture the response observed by solid state NMR

on similar systems. A coexistence of fast and slow relaxation times for C-H bond reorientation was observed for the nanoscopically confined PEO, over a wide temperature range. The molecular origins of these confinement induced segmental dynamics lie in the synergistic result of several concurrent mechanisms: Specifically local density variations, translational motion and proximity of coordinated Li^+ cations, were connected to the dynamical inhomogeneities observed in the confined systems. Fast relaxing C-H segments are primarily present in regions of low local density and no/few coordinated lithiums; whereas lithium coordination to the ethylene oxide groups resulted in the pinning of chains on the confining walls, inducing solid-like segmental dynamics even at high temperatures.

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