

## Segmental Dynamics of polymers in 1 and 2nm slit-pores

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 computer simulations are used to study the structure and dynamics of 1nm wide films of poly(ethylene oxide)(PEO) confined between mica type layered silicates of different cation exchange capacities(CEC). The simulation setup mimics the experimental systems formed by intercalation of PEO in silicate clays with differing numbers of inherent charges. Counterbalancing lithium cations are present in the interlayer gallery to offset the negative charge on the silicate platelets created by the isomorphic substitution of trivalent aluminum by divalent magnesium ions. It is seen that the presence of the lithium has a significance influence on the behavior of the system, with PEO segmental motion strongly dependent on the number of  $\text{Li}^+$  present in the slit pore. In particular, the coexistence of fast and slow modes for C-H bond dynamics is heavily affected due to the strong interaction between the  $\text{Li}^+$  ions and partially charged PEO oxygen. In conjunction with local density inhomogeneities, the coordination between lithium and oxygen is responsible for the anomalous segmental dynamics of nanoconfined PEO.

### INTRODUCTION

Polymer/layered-silicate nanocomposites have become an attractive set of organic/inorganic materials, not only for their obvious potential as technological composites, but also for providing convenient macroscopic systems to study the fundamentals of nanoscopically confined polymers[1]. One promising way to synthesize polymer nanocomposites is by intercalating polymers in layered inorganic hosts[2, 3, 4, 5]. The structure and properties of the resulting nanocomposite can be conveniently mediated by controlling subtle guest-host interactions. Here, the focus is on mica-type layered silicates in which the polymers are confined in well-defined nanoscopically wide (0.87nm) slits which are formed by self assembly of negatively charged parallel stacks of alumino-silicate layers[6, 7, 9, 8, 10, 11, 12]. These inorganic crystalline layers can be naturally occurring or synthetic and are typically 0.97nm thick and several  $\mu$  in lateral dimensions.

In order to investigate the fundamental physics behind the experimentally observed phenomena, molecular dynamics(MD) computer simulations have been performed to directly observe the relevant atomistic motions. Here, we perform a molecular modeling study on PEO intercalated in clays of different inherent charges, so as to comparatively explore the effects of intercalation and the role of the counterbalancing lithium ions on the system properties.

## SIMULATION DETAILS

Molecular Dynamics simulations of fully atomistic models of PEO oligomers intercalated in mica type layered clays were performed. Full details of the simulation method, and the force fields employed are given elsewhere[9]. Simulations were carried out for four different lithium surface densities, corresponding to the different inherent charges of the confining surfaces, (varied by changing the partial charge of the octahedral aluminum layer, and changing the number of counterbalancing lithium cations in a commensurate manner to preserve electrostatic neutrality). This situation mimics the experimental systems formed by intercalation of PEO into 1nm slits in different mica-type silicate clays. In the crystal galleries of the confining clay surfaces, trivalent aluminum ions are substituted by divalent magnesium cations; due to these isomorphic substitutions, the silicate layers possess a net negative charge.

The different CECs that we present here correspond to the numbers of lithiums varying as 29, 21 and 13 for each gallery of our double slit simulation box, which are equivalent to lithium ion surface densities of 1.07, 0.78 and 0.48 li/nm<sup>2</sup> respectively. Studies were also carried out on a fully neutral wall surface, i.e., a theoretical intercalated system in which no counterbalancing cations are present. All simulations were carried out for 5ns, with a time step of 1fs; System trajectories were saved every 10ps for detailed analysis.

## RESULTS AND DISCUSSION

Nuclear Magnetic Resonance (NMR) experiments have revealed the coexistence of fast and slow relaxation times for the segmental dynamics, as represented by the C-H bond reorientation in nanoconfined PEO [7, 11]. To explore the molecular origins of this counter-intuitive behavior, in our simulations the temporal behavior of C-H bond direction vectors were studied, mimicking the experimental results [10]. The physical factors which influence the rotational dynamics are translational motion, local density inhomogeneities, and presence of adjacent lithium ions. To quantify this influence, the covariance between the rotational relaxation rate and the various physical factors were calculated for all systems and the results are shown in figure 1. The affect of lithium on system dynamics was enumerated by calculating the correlation between the presence of Li<sup>+</sup> and the relaxation rates of C-H bonds, and as seen in figure 1, this correlation is independent of the temperature and the total number of lithium ions in the system. The negative covariance indicates that the *greater* the number of Li<sup>+</sup> near a particular C-H bond, the *slower* is it's rate of reorientation, *i.e.* the *longer* is its relaxation time. This negative covariance arises because the lithium serves to pin the PEO chains to the wall, via its simultaneous coordination to oxygens of the polymer and oxygens of the silicate surface. The influence of the Li<sup>+</sup> on the PEO segmental dynamics is most visible in figures 2 and 3, which show the distributions of C-H bond relaxation times, calculated from the time autocorrelation functions of their C-H bond vectors [10]. Since the autocorrelation functions scale as  $acf(t) \propto \exp(-t/\tau)$ , the relaxation time for the rotational motion of each

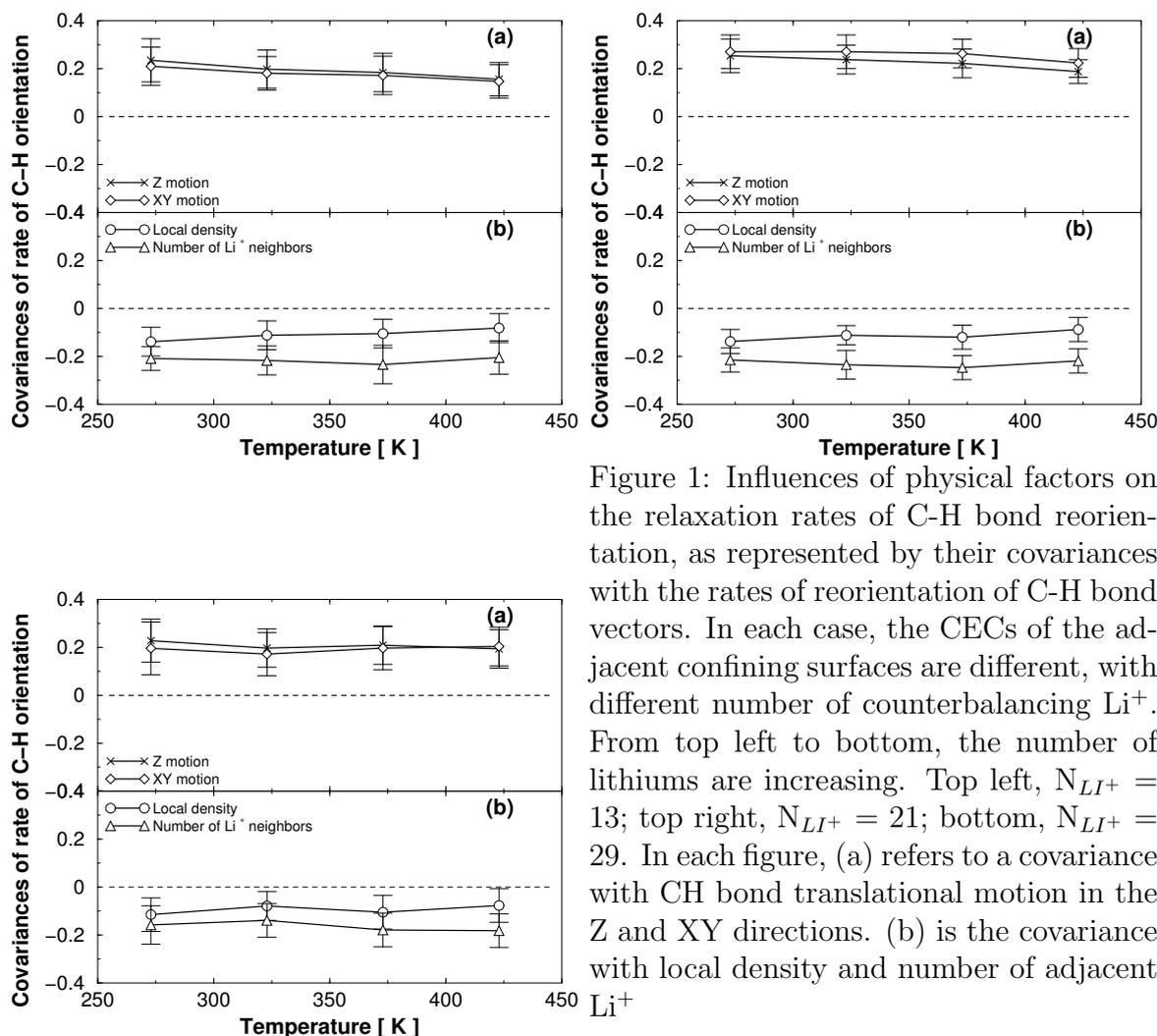


Figure 1: Influences of physical factors on the relaxation rates of C-H bond reorientation, as represented by their covariances with the rates of reorientation of C-H bond vectors. In each case, the CECs of the adjacent confining surfaces are different, with different number of counterbalancing  $\text{Li}^+$ . From top left to bottom, the number of lithiums are increasing. Top left,  $N_{\text{Li}^+} = 13$ ; top right,  $N_{\text{Li}^+} = 21$ ; bottom,  $N_{\text{Li}^+} = 29$ . In each figure, (a) refers to a covariance with CH bond translational motion in the Z and XY directions. (b) is the covariance with local density and number of adjacent  $\text{Li}^+$

C-H bond ( $\tau$ ) can easily be calculated from the slope of the natural logarithm of its autocorrelation function with time. As is evident, there is a drastic change in the distribution of fast and slow moieties corresponding to a change in the number of  $\text{Li}^+$  in the system. With decreasing presence of lithiums, the number of slow relaxing C-H bonds decreases, in agreement with the negative covariances of figure 1. Thus we see that the correlation value of  $-0.25$  present across all temperatures and all systems is sufficient to bring about a perceptible change in the relative populations of fast and slow relaxing species.

As seen in figure 1, there is also an appreciable influence of the local density on the relaxation behavior of C-H bonds. This is explained as follows: if the environment around a particular C-H bond is of a low density, then the ease with which the bond is able to reorient is correspondingly greater, since it is less hindered by adjacent species. This accounts for the negative covariance between the local density and the relaxation rate in confinement, which reveals that the *greater* the local density around a C-H bond vector, the *slower* is its relaxation. The reason that density is so important is because the extreme confinement serves to stabilize local density inhomogeneities in the slit-pore. Thus, in a bulk system where the lifetime of such density “ripples” is

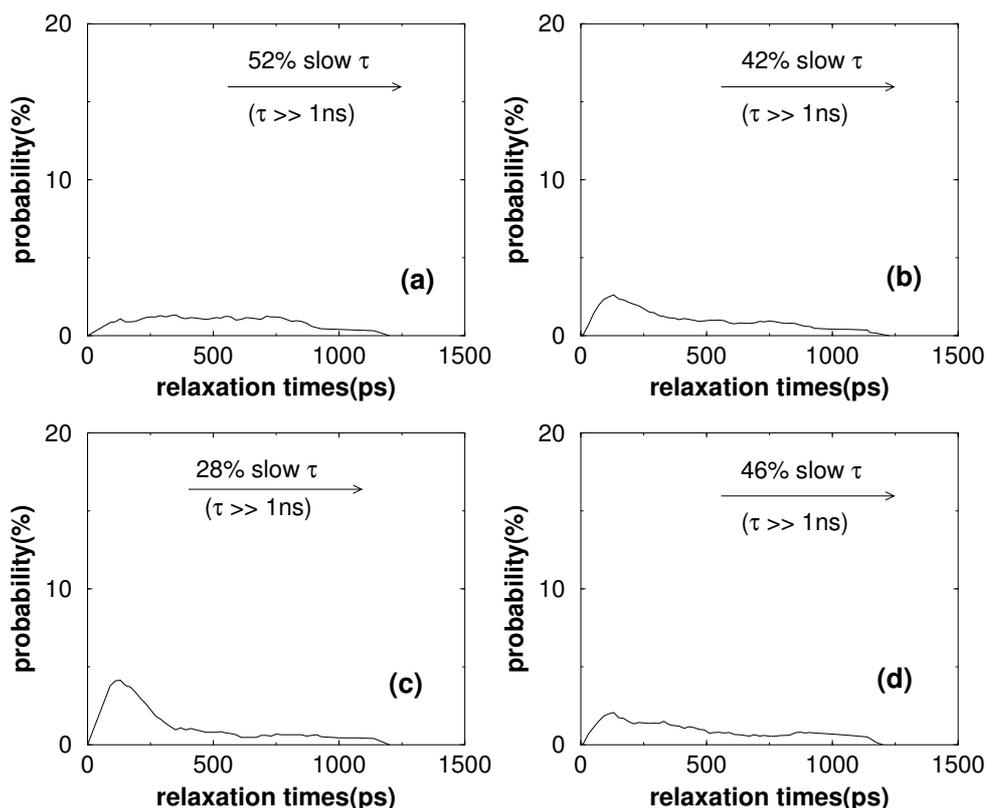


Figure 2: Distributions of fast and slow reorienting CH moieties calculated for all CH bonds in the system at 273K, with different numbers of lithium ions in the slit-pore. (a)  $N_{Li}=29$ , (b)  $N_{Li}=21$ , (c)  $N_{Li}=13$ , (d)  $N_{Li}=0$ . The influence of the  $Li^+$  leads to an increase in the number of slow relaxing species from (a) to (c). For (d), the number of slow C-H bonds is high because of the high local density which slows down the dynamics in the confinement.

of the order of a few picoseconds, for the confined PEO, the density inhomogeneities persist for the lifetime of the simulation run (a few nanoseconds).

The effect of local density is also apparent in other systems of nanoconfined polymers, like that of poly(styrene) intercalated in fluorohectorite [13, 14]. In contrast to the case of confined PEO where the dynamic behavior is influenced by different factors such as presence of  $Li^+$ , local density and lateral and/or vertical transport, the situation for confined PS is much more simplistic; the only influence on the dynamics of the styrene monomers is that of local density, and this is implicitly reflected in the higher value of the covariance of relaxation with the local density (absolute values of  $\approx 0.6$  for confined PS as opposed to  $\approx 0.2$  for confined PEO).

In the different systems studied, as we decrease the number of lithium ions in our systems to simulate the effects of the CEC, there is a corresponding decrease in the local density in the slit pore, leading to faster relaxation rates. This effect is most apparent in the system with no lithium present in the intergallery. Our initial results for this system revealed that the local density was so low, that at all temperatures,

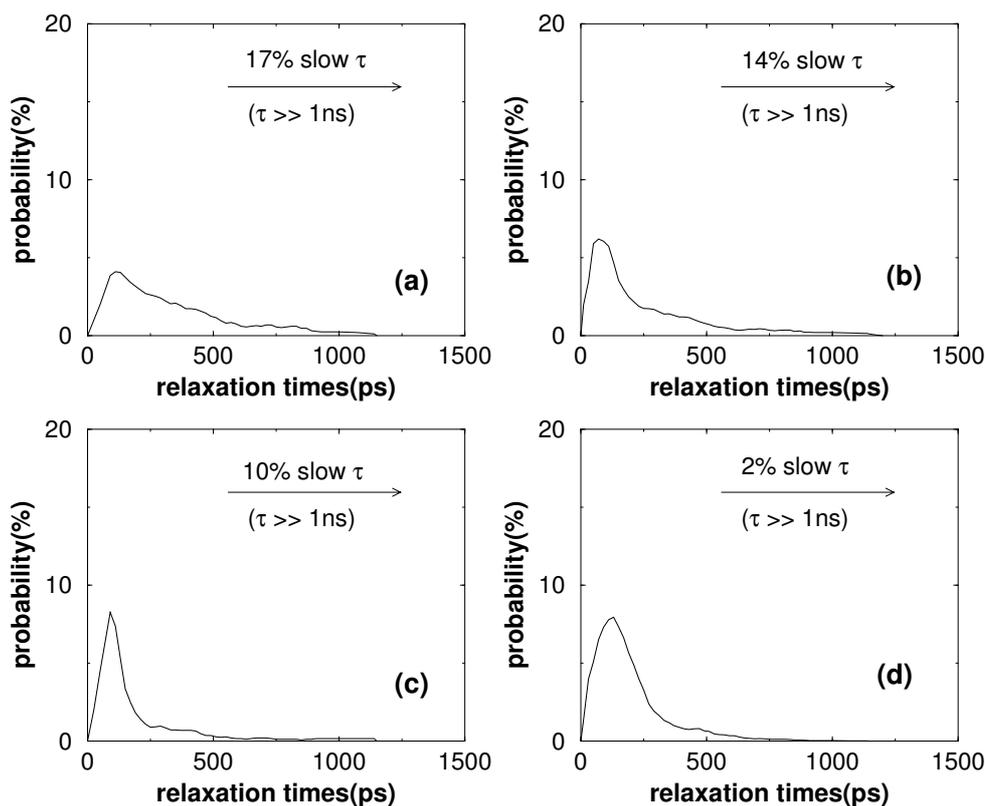


Figure 3: Distributions of fast and slow reorienting CH moieties calculated for all CH bonds in the system at 423K, with different numbers of lithium ions in the slit-pore. (a)  $N_{Li}=29$ , (b)  $N_{Li}=21$ , (c)  $N_{Li}=13$ , (d)  $N_{Li}=0$ . The presence of the  $Li^+$  leads to an increase in the number of slow relaxing species for all the systems.

only *fast* dynamics were established. Since our aim in this work is to illustrate the effect of  $Li^+$  presence on the dynamics of the system, it was necessary to de-link our results from the artifact created by the large empty spaces between chain segments. Thus, to circumvent the effect of local density on the segmental dynamics, MD simulations for the theoretical system absolutely devoid of  $Li^+$  were performed at a density equal to that of bulk PEO, which is approximately 25% higher than that of the original confined system for  $N_{Li}=0$ . At this “bulk” density, at 273K there is a broad distribution of relaxation times, with 56% slow moving C-H bonds. This number is higher than the corresponding numbers of slow moving bonds in the other systems, and clearly shows the effect of the local density on the segmental dynamics in confinement. At 423K, there are only about 2% slow bonds, which reveals that in addition to the density, the lack of the  $Li^+$  also strongly influences the reorientation behavior.

## CONCLUSIONS

Molecular dynamics computer simulations were used to study the effect of lithium surface densities on the segmental dynamics of severely confined poly(ethylene ox-

ide). The confining surfaces correspond to mica-type silicate clays of varied charge exchange capacities (inherent partial negative charges), and correspondingly varied lithium populations. Focusing on PEO/mica type intercalated systems, it is seen that the presence of  $\text{Li}^+$  ions in the interlayer gallery greatly influences the dynamic response of the system in confinement. This effect is due to the strong coordination between oxygen along the PEO backbone and the lithium cations, and is reflected in the distributions of C-H bond relaxation times for  $nm$  thin PEO films in the confinement. The proximity of lithium ions is responsible for the dynamic inhomogeneities exhibited by PEO segmental dynamics, because the lithium acts as an anchor for the PEO chain segments which are effectively “pinned” to the confining surface via their coordination with the  $\text{Li}^+$ . The negative correlation between the presence of  $\text{Li}^+$  and the relaxation behavior of the C-H bonds reveals that a decrease in the number of lithium leads to an increase in the number of fast moving C-H bonds in the system. With varied lithium ion populations, the distributions of relaxation rates for C-H bond reorientation show a dramatic change in the number of fast and slow relaxing species, which serves to delineate the correlation between the presence of lithium and polymer segmental dynamics.

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