

Computer Simulation of Li⁺ / Poly(ethylene-oxide) in Nanometer Confinements

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INTRODUCTION

The last few years have seen an increased interest in "hybrid" materials formed by combining organic and inorganic components. One of the most promising of such endeavors are those of polymers intercalated within inorganic layers, wherein the nature of the polymer is dramatically modified within or close to the layers. A variety of techniques exist with which to successfully probe the nature of these new composite materials.

Confined systems mimicking poly(ethylene-oxide) (PEO) intercalated between mica-type layers (montmorillonite) were simulated by molecular dynamics [figure 1], in order to obtain atomistic details of the structure and dynamics of these polymer nanocomposites. Comparative studies of bulk and nanoconfined poly(ethylene oxide) were performed to trace the confinement-induced mechanisms of ion dynamics in these complex systems.

Two different force-fields [1,2] for PEO were explored –for both bulk as well as confined systems– and both reproduced the structural details seen experimentally. The one chosen for final

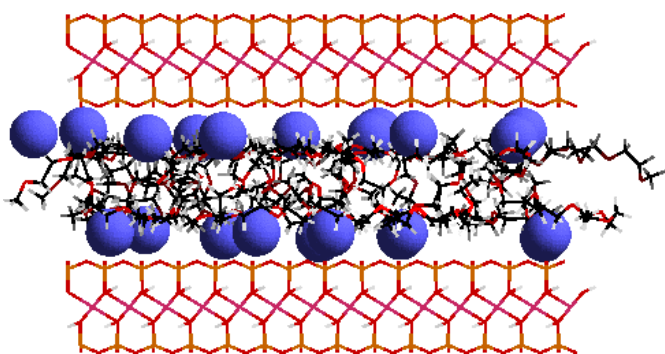


Figure 1. The simulated system: Li⁺/PEO confined –intercalated– in montmorillonite. The Li⁺ is represented by van der Waals spheres.

productive runs was the force-field proposed by Grant Smith et al. [2] as it reproduced more accurately the experimentally measured dynamics of the system. The PEO/montmorillonite interactions were modeled by the potentials of Hackett et al. [3].

RESULTS AND DISCUSSIONS

The structure of the intercalated polymer layers within the montmorillonite layers has been the subject of much debate [4,5,6]. The XRD derived electron densities show a non-crystalline bilayer structure, in agreement with earlier simulations and other experiments. An important aspect of the structural data that we present here concerns the positions of the Li⁺ ions. NMR experiments by Yang et al. have measured the lithium-layer [7]. Our simulations are in quantitative agreement with the NMR work, and moreover they reveal that Li⁺ reside in pockets formed by oxygen atoms on the surface of the montmorillonite.

Experiments have observed qualitative differences in the temperature dependence of conductivity between bulk and intercalated systems. In order to trace the molecular mechanisms of these differences we have evaluated the Li⁺ diffusivities (relating to the dark current) and analyzed Li⁺ trajectories in both our systems [figs 2,3,4].

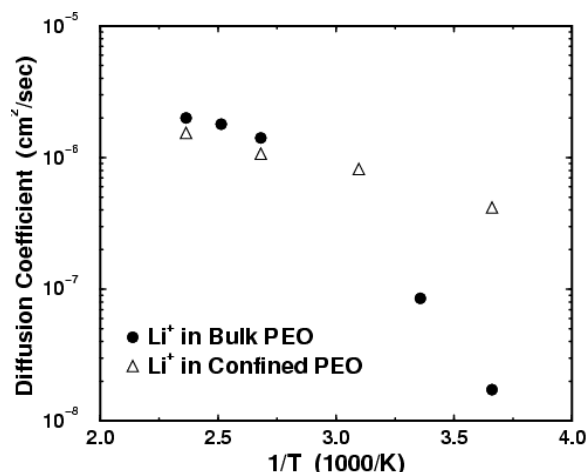


Figure 2. The diffusion coefficients of Li⁺ in bulk and nanoscopically confined PEO (0.7nm-thick films intercalated in montmorillonite)

The main focus of our simulation work was to provide an understanding of the Li⁺ dynamics in nanoscopic confinements, as well as the effect of the polymer reorientation on this motion. To this end, we performed simulations on both confined and bulk PEO systems to comparatively illustrate the different mechanisms operating in these systems, for the relevant range of temperature. Our data for the bulk system clearly shows a change in the mechanism of lithium motion from a hopping to an almost random Brownian-like motion with higher temperatures [fig 3]. At lower temperatures (i.e. below the melting point) the lithium ions vibrate around the equilibrium positions defined by the complexing PEO chains, in a crown like structure. The Li⁺ ions need a pathway for motion, which is created by the necking of the adjacent crown ring. There do not exist many such "openings" at low temperatures because the barrier for dihedral relaxation is high compared to $k_B T$. This is reflected in the low number of trans to gauche isomerizations and the hopping motion of the Li⁺. As the temperature increases, the number of changes is correspondingly greater, and numerous pathways for Li⁺ motion appear. At even higher temperatures, the lithium mobility is further promoted, resulting in trajectories that resemble Brownian motion. No longer do we see the hopping that characterizes the Li⁺ motion below the melting point.

In sharp contrast to the bulk behavior, the nanocomposite shows surprisingly little change in mechanism of ionic motion through the same range of temperatures [fig 4]. An analysis of the trajectories, similar to the one performed above for the bulk PEO, shows that the lithiums exhibit a hopping mechanism throughout the entire temperature range. This can be attributed to the strong preference of the ions for the "pockets of lower energy" formed by the oxygen ions on the surface of the montmorillonite walls. Thermal vibrations cause the Li⁺ to move slightly out of their pockets and then become coordinated by PEO molecules hovering just above the surface; wherefrom, the Li⁺ sometimes move to another low energy site on the inorganic surface. This entire progression of snapshots shows up as a hopping motion in the trajectory of the lithium during the course of the entire run. These sequences of events can be related to the qualitative change in ionic conductivity seen in bulk PEO around T_m , while for the confined systems there is only a VTF-like decrease with temperature.

An analysis of the correlations of lithium and of nearby polymer relaxations was done for both the bulk and the confined system over the temperature range. The bulk systems display a correlation between the motion of the lithium and the polymer dihedral relaxations (up to and slightly beyond the melting point), this correlation decreases as the temperature is raised further. For the confined systems there is a strong correlation throughout the same temperature range, suggesting that the polymer relaxations dictate how the ions escape from the pockets and move to other sites. Oftentimes, Li⁺ detach from the walls only to jump back into the same

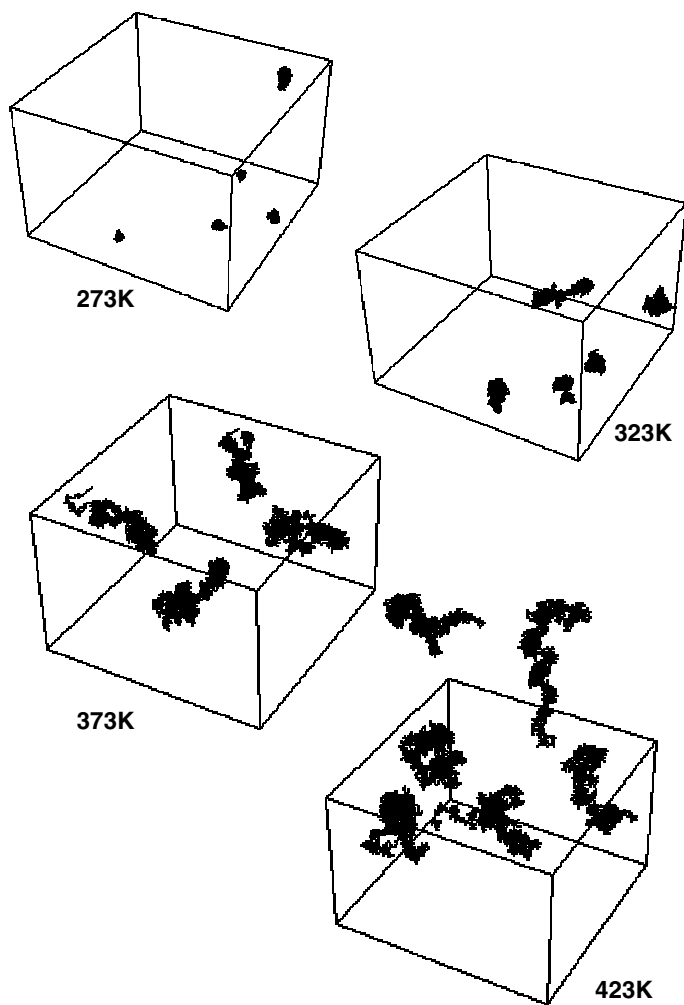


Figure 3. Li^+ trajectories at 273-423K in the bulk PEO systems.

surface pocket once again due to the non-availability of a free neighboring low-energy site.

CONCLUSION

We have carried out comparative simulations of bulk and nano-confined PEO/ Li^+ systems. The structure was found to be a non-crystalline PEO bilayer with the Li^+ located immediately adjacent to the surfaces, in agreement with N.M.R. structural data. For the bulk systems a clear change in the mechanism of ion transport is observed, from a hopping motion between PEO crowns (at low temperatures), to a random Brownian-like one at higher temperatures. In contrast, the nanocomposite displays a hopping mechanism, throughout the same temperature range, however, the "trapping" of the Li^+ is now by the wall. These observations determine the temperature dependence of the simulated Li diffusion coefficients, which capture the experimentally seen behavior.

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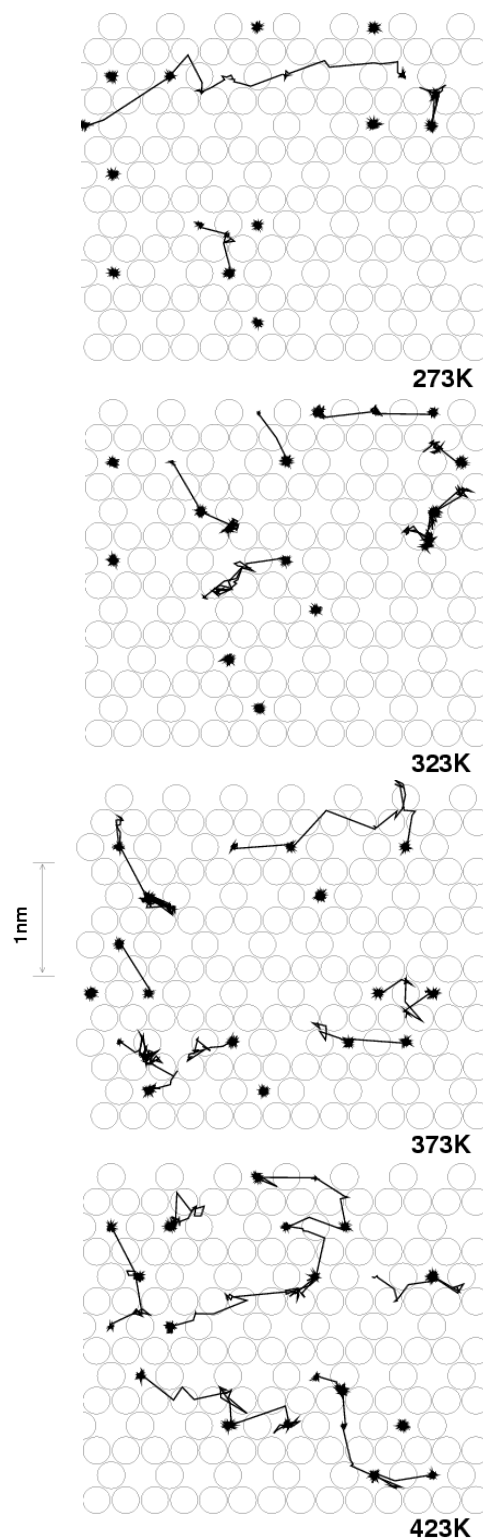


Figure 4. Li^+ trajectories at 273-423K for the confined systems.