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Segmental dynamics of polymers in nanoscopic confinements, as probed by simulations of polymer/layered-silicate nanocomposites

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Abstract. In this paper we review molecular modeling investigations of polymer/layered-silicate intercalates, as model systems to explore polymers in nanoscopically confined spaces. The atomic-scale picture, as revealed by computer simulations, is presented in the context of salient results from a wide range of experimental techniques. This approach provides insights into how polymeric segmental dynamics are affected by severe geometric constraints. Focusing on intercalated systems, *i.e.* polystyrene (PS) in 2 nm wide slit-pores and polyethylene-oxide (PEO) in 1 nm wide slit-pores, a very rich picture for the segmental dynamics is unveiled, despite the topological constraints imposed by the confining solid surfaces. On a local scale, intercalated polymers exhibit a very wide distribution of segmental relaxation times (ranging from ultra-fast to ultra-slow, over a wide range of temperatures). In both cases (PS and PEO), the segmental relaxations originate from the confinement-induced local density variations. Additionally, where there exist special interactions between the polymer and the confining surfaces (*e.g.*, PEO) more molecular mechanisms are identified.

PACS. 83.10.Rs Computer simulation of molecular and particle dynamics – 81.07.Nb Molecular nanostructures – 81.07.Pr Organic-inorganic hybrid nanostructures

1 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 [1,2]. One promising way to synthesize polymer nanocomposites is by intercalating polymers in layered inorganic hosts [3,4]. Graphite, transition metal chalcogenides, metal phosphates, complex oxides, oxychlorides and mica-type layered silicates are some examples of layered solids capable of intercalation. The structure and properties of the resulting nanostructure can be conveniently mediated by controlling subtle guest-host interactions. Here we focus on mica-type layered-silicates, *i.e.* 2:1 alumino-phyllosilicates; in these systems polymers are confined in well-defined nanoscopically wide (0.8 nm–3 nm depending on the polymer/inorganic system) slits, which are formed by self-assembly of parallelly stacked, negatively charged, alumino-silicate layers. These inorganic crystalline layers can be naturally occurring or synthetic, and are typically 0.97 nm thin and several μm in lateral dimensions (*e.g.*, natural montmorillonite clays have a distribution of sizes around 0.5 μm, synthetic fluorohectorite (FH) is $5 \pm 0.3\,\mu$m, vermiculite is tens of μm, and mica can reach lateral sizes of cm).

A variety of techniques has been employed to probe the chain and especially the segmental dynamics in these systems, aiming to elucidate the general behavior of polymers in nanoscopic confinements. Specifically, solid-state NMR, dielectric spectroscopy, X-ray and neutron techniques, have been applied to a wide range of polymers nanoscopically confined between layered silicates [5–11]. Although these experimental methods provide a detailed picture of the segmental dynamics, they cannot reveal the relevant molecular origins.

In order to investigate the underlying physics behind the experimentally observed phenomena, we performed molecular-dynamics computer simulations to directly observe the relevant atomistic motions. Towards this goal, we employed atomistically explicit models for intercalated systems, which mimic polyethylene-oxide (PEO) confined between montmorillonite (MMT) layers and polystyrene (PS) confined between organically modified fluorohectorite (FH), and we specifically focus on the short-time (tens of ns) dynamics of the monomers. In both cases,

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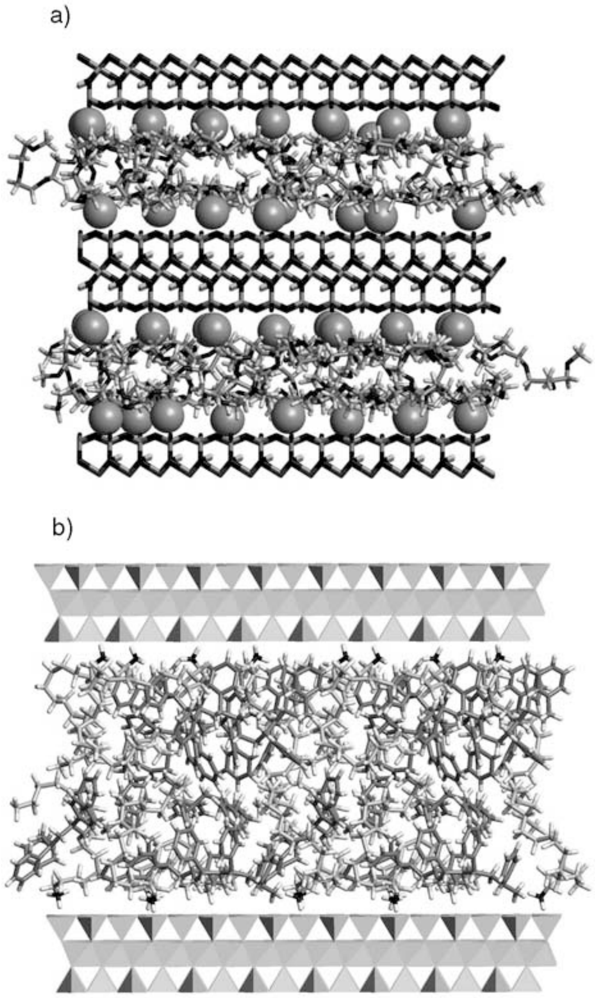

Fig. 1. The two simulation boxes used: (a) two PEO films (0.8 nm wide each) confined between two Li^+ montmorillonite layers [12]; (b) a PS film (2.05 nm wide) confined between octadecyl-ammonium fluorohectorite [13, 14].

the experiments report a striking coexistence of fast and slow segmental relaxations, spanning a very wide temporal range independent of temperature [7, 10]. Here we review our findings from molecular modeling studies of these two systems, and the comparison between the two provides clues on the "general" and the "system-specific" mechanisms underlying a seemingly common macroscopic behavior.

2 System geometries and simulation method

The two confined system geometries simulated are shown in Figure 1. The simulated systems mimic: a) polyethylene-oxide (PEO) hexamers [$H\text{-}(CH_2\text{-}O\text{-}CH_2)_6\text{-}H$] confined between Li^+ montmorillonite layers, with a nominal confined polymer layer thickness of 0.8 nm [8] (Fig. 1a); and b) polystyrene (PS) dodecamers [$H\text{-}(CH_2\text{-}C(C_6H_5)H)_{12}\text{-}CH_3$] confined between octadecyl-ammonium modified fluorohectorite (C_{18}-FH), with a nominal confined organic layer thickness of 2.05 nm [10, 15] (Fig. 1b). For both polymers, bulk —unconfined— systems were also simulated and compared against the confined ones shown in Figure 1. All productive runs were NVT molecular-dynamics simulations, with number of particles (N), volume (V), and temperature (T) kept constant. Periodic boundary conditions (pbc) were applied in all three directions, and a weak coupling to a reference temperature was realized via the Berendsen method [16]; the details of the methods, the force-field parameters, and discussion of the modeling approximations and choices are provided elsewhere (PEO systems [12], PS systems [13]). One comment that we can make here concerns the choice of a double-slit geometry for the PEO/Li^+-MMT systems, whereas a single slit was used for the PS/C_{18}-FH. The reason behind our choice of the simulation boxes is the importance of the electrostatics in the behavior of two systems. For the PEO, where the polymers are characterized by high partial charges, the segmental dynamics of the polymers are determined to a large extent by the system electrostatics, and are sensitive to the long-range Coulombic forces as repeated through the pbc [12, 17]. Thus, a single-slit simulation box (that would have had a z-dimension of only 1.8 Å) results in unrealistic segmental dynamics due to the periodic repetition of the Li^+-wall dipoles through the pbc [12]. On the other hand, the PS box is already wider in the z-direction and additionally, due to the small partial charges of the PS atom types, the PS segmental dynamics are not markedly sensitive to the electrostatics; the electrostatics are only important for the ammonium "tethering" on the silicate surfaces, which is not sensitive to long-range electrostatics either.

3 Results and discussion

The common feature in all experimental studies of polymers intercalated —confined— in 1-2 nm slits defined by silicate inorganic surfaces is a coexistence of fast and slow segmental dynamics, in a wide range above and below the glass transition temperature (T_g) of the bulk polymer. Spectroscopic techniques (NMR and dielectric) of intercalated/confined polymers report a very wide distribution of segmental relaxations throughout the explored temperature range, across polymer systems with varied T_g (from 223 K PMPS poly(methyl-phenyl-siloxane) [11], to 373 K PS [10]), in presence [10, 11] or absence [7] of alkyl-ammonium surfactants on the confining surfaces. These segmental relaxations span a wide range from ultra-slow solid-like dynamics, to very fast liquid-like motions, independent of temperature [18]. Our aim here is to review the molecular mechanisms responsible for these dynamics, and especially to distinguish between those mechanisms that are polymer/chemistry specific from those that are general across different confined polymers.

3.1 Slow segmental dynamics

In Figure 2 we show two simulation snapshots highlighting the "slow" moieties (carbons in the case of PEO, Fig. 2a,

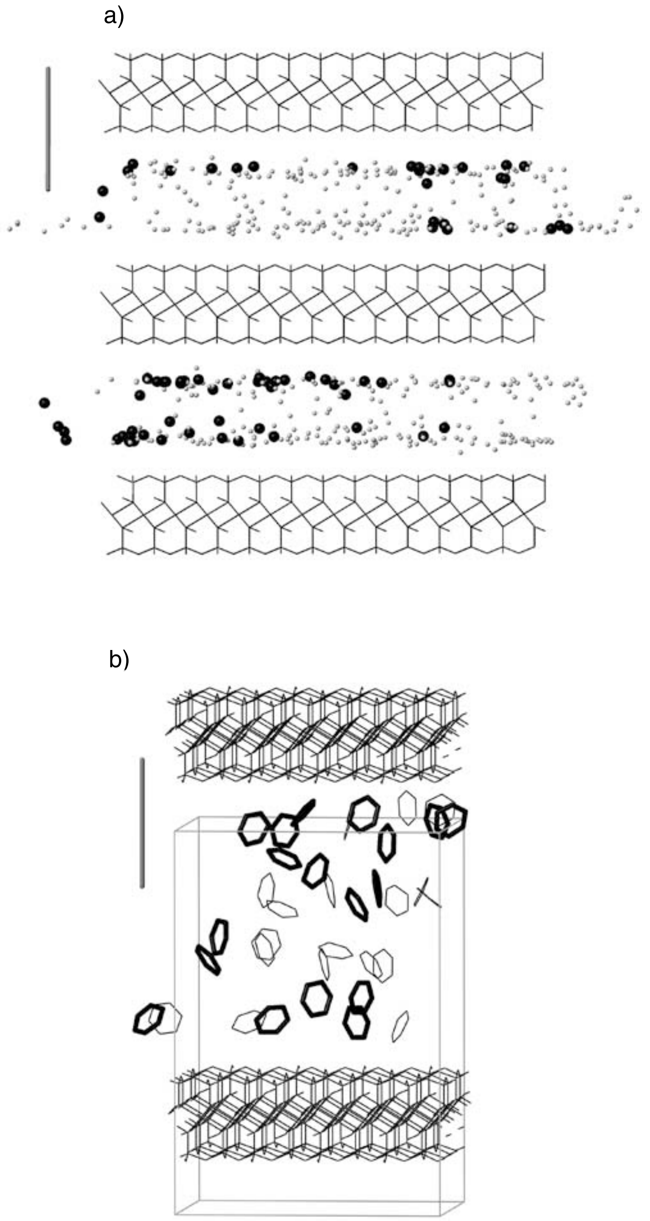

Fig. 2. (a) PEO immobile carbons $T = 423$ K; (b) PS immobile phenyls $T = 420$ K. All carbons in the PEO system (a) and all phenyls in the PS system (b) are shown, but the immobilized ones are highlighted.

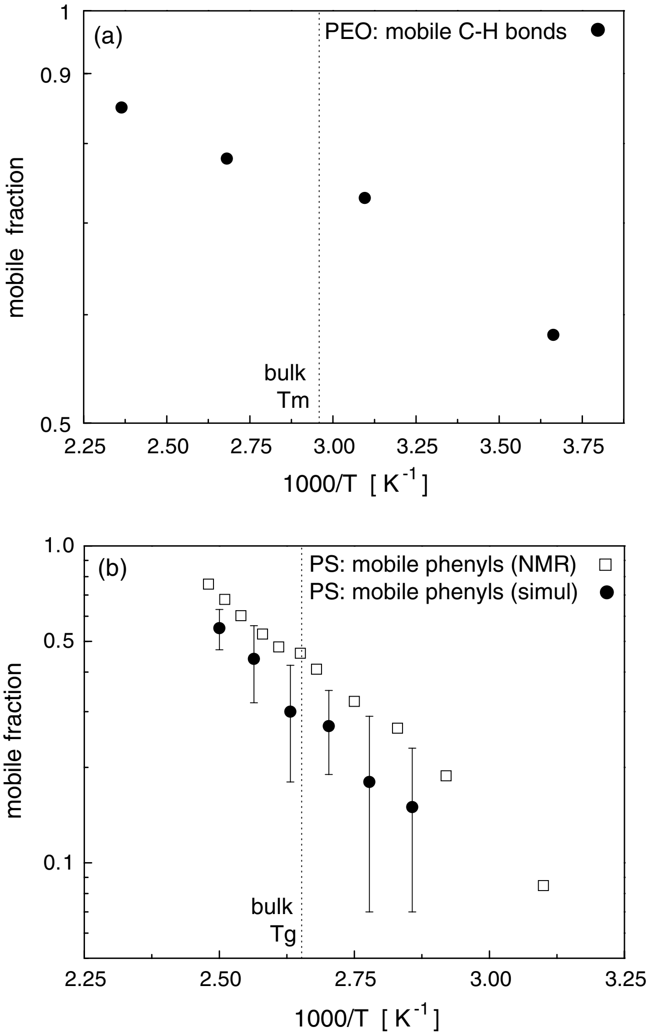

Fig. 3. Enumeration of the mobile moieties in the two nanoscopically confined systems as a function of temperature: (a) mobile PEO carbon-hydrogen bonds in 0.8 nm films [17]; (b) PS mobile phenyls in 2.05 nm [13]. For the PS systems we also show the mobile phenyls as enumerated by spin-echo NMR experiments (NMR data adapted from Fig. 5, Ref. [10].

and phenyls for PS, Fig. 2b). The criterion in both cases is the reorientational dynamics —of the C-H bond and the phenyl, respectively— and the highlighted moieties are immobile for the duration of the MD simulation, *i.e.* over several ns [17,13,14]. These are the same type of dynamics as investigated by the NMR studies, albeit NMR probes much longer times compared to our simulation trajectories. In both cases, the immobilized moieties are located mostly in the immediate vicinity of the confining surfaces, *i.e.* they belong to, or connected to, physisorbed polymer trains. This is not a new finding, it has been reported in many instances before by simulations (*e.g.* [19]) and by experiments (*e.g.* [20]), and is also predicted by theory. The more interesting physics relate to the origins of the "fast" moieties in these systems.

3.2 Fast segmental dynamics

The observation of very fast dynamics in these nanoscopic confinements is a striking finding, especially for very low temperatures below the T_g of the respective bulk polymers [7,10,11]. Although in those studies distinctly different polymers and silicates were utilized, the common characteristic is that the slit-width corresponds in all cases to about two monomers of the respective confined polymer. These self-assembled confined polymer bilayers are much thinner than what was studied by previous simulations [19], and by surface forces apparatus experiments [20]. Comparing the mobile [21] segment populations in the confined PEO and PS systems (Fig. 3), several common trends can be identified: a) The mobile segments are located throughout the confined film, including also inside the first layer physisorbed on the solid surfaces (Fig. 2; Fig. 5 in [17] and Fig. 3 in [13]). b) There seems to be a single Curie T-dependence [22] for the mobile — and thus the immobile— population under these confinements for each system across the T-range studied (Fig. 3); *i.e.* whatever the molecular mechanism(s) responsible for these dynamics, they remain in place above and below the bulk T_g or melting point (T_m). c) In these extreme confinements, there is no signature of a glass transition or a melting point in the segmental dynamics, for example, a sharp change of the temperature slope in the mobile segment population (Fig. 3); whereas the respective bulk —unconfined— polymers exhibit clear/sharp changes in their segmental dynamics under the same experimental conditions [10,23].

3.3 Molecular origins

In order to identify the molecular mechanisms affecting the segmental dynamics under confinement, we have analyzed the correlations between the segmental reorientation dynamics (of the C-H bond for PEO, and of the phenyls for PS) and various factors that could potentially affect them [13,14,17]. These correlations can be quantified through the definition of the covariance (*e.g.*, [24]) between two variables:

$$\mathrm{cov}(\tau, X) \equiv \frac{\langle\ (\tau - \langle\tau\rangle) \cdot (X - \langle X\rangle)\ \rangle}{\sqrt{\sigma^2(\tau)\ \sigma^2(X)}}\,, \tag{1}$$

where τ is a measure of the segmental reorientation dynamics, $\langle\tau\rangle$ is the ensemble average of τ, X is the factor whose effect on the reorientation we wish to measure and $\langle X\rangle$ is the ensemble average of X, $\sigma^2(\tau)$ and $\sigma^2(X)$ are the corresponding ensemble variances. Using this equation, we estimated the influence of different physical mechanisms on the *reorientation relaxation time* (τ) of the phenyls in the confined PS, and on the *reorientation rate* ($\mathrm{d}\phi/\mathrm{d}t$, [25]) of the C-H bond vector in the confined PEO.

The factors/molecular-mechanisms (X) for which we have identified effects on the reorientational segmental dynamics are: For the 2 nm confined polystyrene only the local density around the phenyl has a statistically important covariance; whereas the proximity of chain-ends to the phenyl, and the density of the alkyl-surfactant tails in the vicinity of the phenyl show some covariance trends, but are of much smaller statistical importance (see Chapt. 15, Fig. 7 in [2]). For the 1 nm confined PEO there is a synergy of several factors: a) the local density around the C-H bond, b) the translation —parallel and normal to the confining surfaces— of the C-H bond, and c) the proximity of Li^+ to the C-H bond.

For the confined-polystyrene systems, the relaxation time/local-density covariance for the mobile phenyls reveals the dominant effect (Fig. 4). For the lower temperatures simulated there exists a strong correlation between the local density around a phenyl ring and its the segmental relaxation. Namely, the *fast relaxing* phenyls are located in *low local density* regions; this behavior is independent of whether the phenyls are close to the walls, or in the center of the slit, and independent of whether the reorientation takes place through “flipping” or “rocking” phenyl motions. These density inhomogeneities are also present in the bulk —unconfined— polystyrene systems. The determinant difference between bulk and nanoscopically confined systems is the time scales over which these density inhomogeneities are stable [14]; namely, in the unconfined PS density fluctuations dissipate very fast (in less than 1 ns above the polymer T_g, and within 2–7 ns below 373 K), whereas in these extreme 2 nm confinements the density inhomogeneities are long-lived (more than 10 ns at $T = 390$ K). These confinement-induced long-lived density inhomogeneities allow for the phenyls to develop measurable fast reorientation relaxations [14].

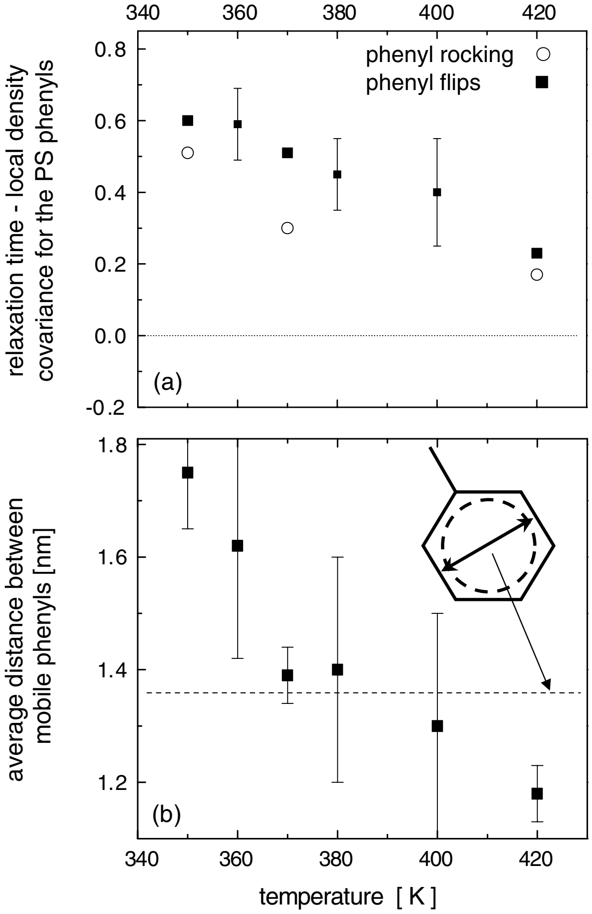

Fig. 4. Covariances for the *mobile* PS phenyls: (a) the covariance of the reorientational relaxation time of a phenyl *versus* the local density around this phenyl; (b) the average distance between mobile phenyls in the nanoscopically confined film. Data replotted from [14].

As the temperature increases, this correlation seems to decay in magnitude, although it still remains positive. In

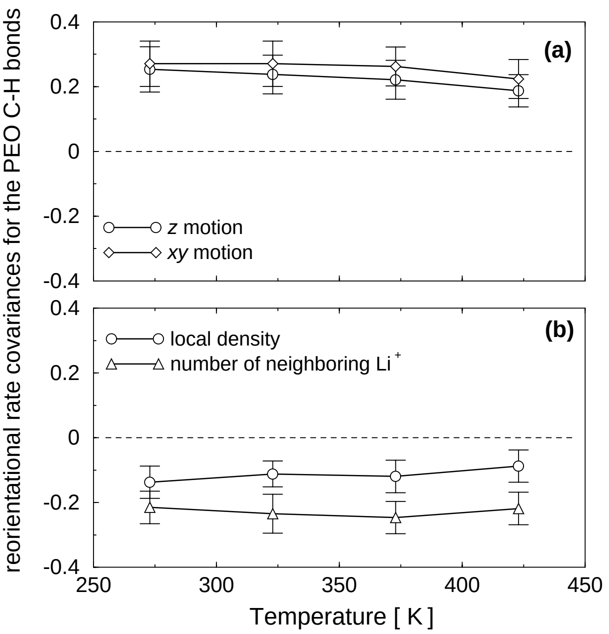

Fig. 5. Covariances for *all* the PEO C-H bonds: (a) Covariances of the C-H bond reorientation rate with translational motion of the respective carbon, both in the z-direction and in the xy plane; (b) Covariances of the C-H reorientation rate with local density around the C-H bond and with the number of proximal Li$^+$ ions. Figure adapted from [17].

fact, as the temperature increases, the number of mobile phenyls also increases to such a degree that large volumes in the middle part of the slit consists solely of phenyls with fast segmental dynamics (Fig. 7b in [13]). This reflects in a decreasing average distance between fast relaxing phenyls (as seen in Fig. 4b). This is also the reason for the apparent decrease in the relaxation-time/local-density covariance [13]. Furthermore, careful analysis of the MD trajectories reveals that at the lower temperatures there exist only a few segments with fast dynamics, which are isolated from each other inside the confined film. As the temperature increases, "clusters" of mobile phenyls are formed, especially in the center of the slit-pore (Fig. 7b in [13]); however, despite their proximity, the motions of the phenyls within the same "cluster" are not correlated nor cooperative. For all the temperatures simulated there exists a large number of immobilized phenyl rings in the immediate vicinity of the confining surfaces, where the organic film is locally densified by the silicate surfaces. The relaxation of these slow phenyls is markedly temperature independent, at least for the time scales that our MD simulations probe. This is in general agreement with the surface-sensitive cross-polarization NMR studies, which suggest that mobile styrene moieties are mostly in the center of the slits, while chain elements (phenyls, methylenes, and methines) in close proximity to the surfaces are dynamically inhibited [10].

Due to the existence of a large number of alkyl-ammonium molecules in our confined systems that can "plasticize" the polymer, it was not initially clear [10] whether these dynamical inhomogeneities arise from plasticization effects, or whether are confinement induced. Regarding this point, our simulations show that the fast segmental relaxations are not correlated to the surfactant proximity and/or dynamics (Chapt. 15 in [2]), but originate from the confinement-induced density inhomogeneities. This is further supported by experimental studies of the PEO/Li$^+$ montmorillonite systems, which do not contain oligomeric surfactants, but also exhibit similar dynamics associated with the same confinement-induced mechanisms. Specifically, in Figure 5 we show the statistically important covariances identified for the C-H bond reorientation dynamics of the PEO systems. Enumerating the same correlation, *i.e.* the covariance of the rotational relaxation of a C-H bond *versus* the local density around this C-H bond (Fig. 5b), 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, in agreement with the polystyrene behavior. 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. Probably, the simplest one conceptually is the connection between the translational displacement of a C-H bond and its reorientation behavior. We quantified two different covariances in this context, connecting C-H reorientations to translations parallel to the confining surfaces (xy) and perpendicular to them (z). As seen in Figure 5a, both are positive, which means that the *greater* the mobility of the C-H bond, the *faster* the rate of its reorientation. This behavior is not unexpected, since polymer segments that move in space are also more likely to undergo rotation around the carbons, as part of the polymer backbone flexing and trans-gauche isomerizations. For our simulation 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 xy motion covariance is comparable, indicating that motions in the plane parallel to the walls are as important for the C-H reorientation.

Perhaps the most interesting covariance identified for the PEO is the one between the reorientation rate of the C-H bond vectors and the number of Li$^+$ close to that C-H bond (Fig. 5a). Its negative value indicates that the *larger* the number of proximal Li$^+$ near a bond, the *slower* its rate of reorientation is. This behavior arises from the characteristic coordination of the PEO chains and Li$^+$ cations in the slit-pore. Earlier simulations [26] and NMR spin lattice relaxations studies [9] show that the lithium cations reside in close proximity to the wall surfaces, due to the strong electrostatic attraction by the negatively charged silicate layers. The PEO chains coordinated to the Li$^+$ cations with multiple oxygens [26], much like when salts are dispersed in PEO. Via this materials arrangement, the Li$^+$ cations, which are strongly coupled to the wall surfaces [12], mediate an indirect anchoring of the PEO chains to the solid surfaces. In this manner, reduced mobility is imposed on the chain fragments which are coordinated to lithiums, leading also to a lower rate of reorientation for the C-H bonds. This hindrance to motion —implicitly reflected in the negative value seen in our covariance— can be also directly seen in close observation of the system trajectories, for all the simulated temperatures (Fig. 6 in [17]).

Finally, the same confinement-induced fast dynamics are also reported for polymers in wider confinements, including polymers confined in zeolites, in nanoporous hosts, or amorphous polymer confined between its crystalline lamellae [27–29]; however, in those cases the experimentally observed relaxation times are much longer than the ultra-fast dynamics seen in the 1-2 nm silicate slits [7,10, 11]. In those wider confinements, bulk-like dynamics can develop in the confined polymers just two monomers away from the confining surfaces independent of the strength of the polymer-surface adsorption energy [19,30]. Consequently, the macroscopically observed dynamics in such nanoscopically confined systems have been proposed to be the weighted average of the confinement-induced response —occurring in the physisorbed monolayers— and the bulk-like response of the material two monomers away from the surfaces [27,30]. Thus, it is strongly suggested that measurable ultra-fast segmental dynamics is a direct consequence of the formation of an organic bilayer —two monomers wide confined films— between the silicates surfaces. A limitation of these intercalated polymer systems is that the confinement width cannot be easily tailored, and a bilayer almost always self-assembles between the layered silicates. If the interlayer spacing could be easily and reproducibly tuned, the importance of these systems as model two-dimensional confinements would have been inestimable.

4 Conclusions

Molecular-dynamics simulations of nanoscopically confined polymers, mimicking PS and PEO intercalated in layered silicates, are viewed as model systems to explore segmental dynamics in 1 and 2 nm wide slit-pores. The origins of the slow dynamics were summarily traced to the physisorption of polymer trains on the solid surfaces, as has been reported before and is intuitively expected. Additionally, for the PEO systems the characteristic interaction —coordination— between the ethylene-oxide and the silicate surfaces to the Li cations gives rise to more polymer specific mechanisms that promote immobilized PEO segments, with hindered translational and reorientational dynamics. The fast segmental dynamics, for both systems, are traced to local density inhomogeneities, and specifically to low local density regions that are stabilized by the confinement over long time periods (tens of ns). In the case of PEO, an absence of coordinated Li^+ is also necessary for the development of fast segmental dynamics.

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