

The origins of fast segmental dynamics in 2 nm thin confined polymer films

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Abstract. Molecular-Dynamics computer simulations were used to study 2 nm wide polystyrene films confined in slit pores, defined by inorganic crystalline surfaces. The simulated systems mimic experimentally studied hybrid materials, where polystyrene is intercalated between mica-type, atomically smooth, crystalline layers. A comparison between the experimental findings and the simulation results aims at revealing the molecular origins of the macroscopically observed behavior, and thus provide insight about polymers in severe/nanoscale confinements, as well as polymers in the immediate vicinity of solid surfaces. Pronounced dynamic inhomogeneities are found across the 2 nm thin film, with fast relaxing moieties located in low local density regions throughout the film. The origins of this behavior are traced to the confinement-induced density inhomogeneities, which are stabilized over extended time scales by the solid surfaces.

PACS. 83.10.Rs Computer simulation of molecular and particle dynamics – 68.60.-p Physical properties of thin films, nonelectronic – 81.07.Pr Organic-inorganic hybrid nanostructures

1 Introduction

The last few years have seen an increasing interest in organic/inorganic “hybrid” materials, as model systems to study confined polymers. One of the most actively explored class of such materials is that of polymers *intercalated* between mica-type, inorganic layers [1, 2]. 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, aluminosilicate 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 (mmt) clays have a distribution of sizes around 0.5 μm , synthetic fluorohectorite (FH) is $5 \pm 0.3 \mu\text{m}$, vermiculite is 20–100 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, with the goal of unveiling the general behavior of polymers in nanoscopic confinements.

Here, we report molecular modeling results of polystyrene (PS) intercalated between 2:1 aluminosilicate layers, with the emphasis on revealing the molecular origins of the confinement-induced fast segmental dynamics manifested macroscopically in NMR experiments [3]. Especially, we focus on the ultra-fast phenyl dynamics of

polystyrene, as probed by solid-state NMR methods in 2 nm thin confined films [3]. Through the comparison of our simulation results to these experiments, we aim at providing insight in the physics of polymers in nm thin slits, as well as of polymers in the immediate vicinity of solid surfaces.

2 System and simulation details

The simulated systems mimic experimentally studied nanocomposite materials, where PS is confined — intercalated — between atomically smooth, mica-type inorganic layers (namely fluorohectorite, a synthetic 2:1 phyllosilicate aluminosilicate). Since the surfaces are highly hydrophilic, an organic modification is necessary to render the inorganic surfaces organophilic and miscible with PS. The surfactants used for this reason are alkylammoniums, with an alkyl tail ranging from dodecyl to octadecyl for FH [3,4]. Careful choice of the organic modification leads to extremely well-defined confined geometries, with a slit-thickness of $2.0 \pm 0.1 \text{ nm}$, which spontaneously self-assemble when mixing the organically modified FH with the PS polymer above T_g [4].

The simulation geometries, force-fields, and methods are detailed elsewhere [5,6] and herein we will briefly mention some of the essential information.

Fully atomistic FH walls, alkyl-ammonium surfactants, and polystyrene molecules were studied. The sim-

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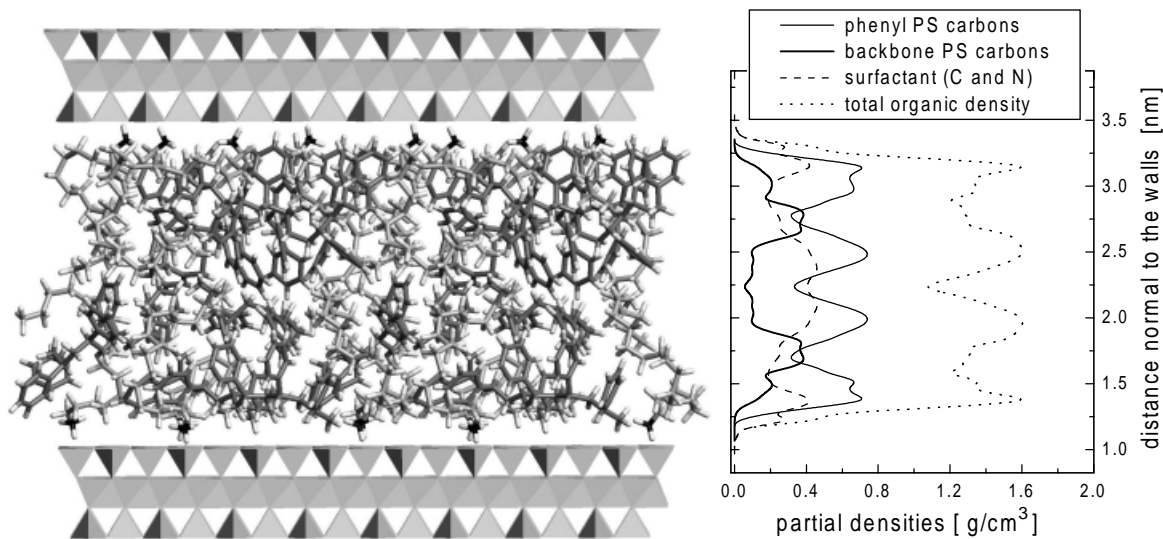


Fig. 1. An xz projection of the simulation box, and the corresponding partial densities of the various system components.

ulation system box was $4.224 \times 3.656 \times 3.05$ nm in dimensions, with periodic boundary conditions in all three directions (Fig. 1). A solid surface with the crystal structure of a synthetic 2:1 mica-type silicate is placed parallel to the xy plane, thus confining the organic molecules in the z -direction. The confined PS film thickness (2.05 nm), as well as the styrene (144 styrene monomers, in 12mers or 24mers of PS) and surfactant densities (32 octadecylammonium cations, at the FH grafting density of $\sigma_{\text{graft}} = 1/0.97 \text{ nm}^{-2}$), were selected to correspond to the experimentally measured quantities [3,4]. For some temperatures and the smaller PS molecules a smaller box of $2.112 \times 1.828 \times 3.05$ nm was also used [5]. Molecular-Dynamics simulations were done at constant NVT, with weak coupling to a heat bath [7]. Comparison of these studies to simulations at a constant N , zz -stress, and T , showed no differences on the results discussed herein, *i.e.* on the fast phenyl dynamics and the relevant molecular origins [8]. The force-fields employed for PS [5,9], reproduce faithfully the behavior of bulk polystyrene [9], as well as the structure [4] and dynamics [5] of FH-intercalated polystyrene. The wall interactions were modeled as per our previous work [10], which was tested for the hydration behavior of the inorganics, as well as for PEO and PS intercalated systems. A particle-particle/particle-mesh scheme with Ewald sums was employed for the Coulombic interactions.

Special attention was given in the way that we selected to sample the configuration phase-space [6]. Multiple, well-equilibrated initial configurations were created by a Monte Carlo scheme [6] for each temperature studied. Typically, we used 10 independent —well-separated in phase-space— initial configurations for each temperature and we followed each system for 100 ns at $T = 350$ K, 50 ns at $T = 360$ through 390 K, and 10 ns at higher temperatures. Thus, these MD simulations are aiming to follow the short-time (tens of ns) trajectories of the system in multiple —well-separated— points in phase-space, rather than a long-time

trajectory representative of the ensemble. Although these chains may be too short to capture the genuine response of long PS macromolecules, they are longer than the average physisorbed train size of PS in these systems, and also allow for the existence of bridges between the two solid surfaces. Consequently, all the possible *fast segmental* dynamics that can develop inside these slit pores can be explored for these chain lengths.

3 Results and discussion

3.1 The macroscopic picture

Polystyrene/fluorohectorite intercalates have been employed as model systems for experimental studies of nanoscopically confined PS films, focusing both on segmental dynamics [3], as well as on the polymer motion in the nm thin slits [4]; our simulations here focus on the former. A combination of surface-sensitive ^1H - ^{29}Si cross-polarization NMR and quadrupolar echo ^2H NMR was used to study the segmental dynamics of selectively deuterated, high-molecular-weight PS in 2 nm slit pores [3]. From these recent NMR studies a new and quite unexpected picture is emerging for the segmental dynamics in 2 nm thin confined polymer films. Before we discuss our atomistic simulation results, we outline the main experimental observations to be addressed:

- over a wide temperature range there exists a distribution of relaxation times, ranging from ultra-fast to ultra-slow dynamics (far below and above the relaxation times of the corresponding bulk films at the same temperature);
- fast relaxing moieties are found at large numbers — even below the bulk T_g ;
- the mobile PS phenyls are predominately in the center of the confined films, particularly at higher temperatures, while chain segments which interact with the

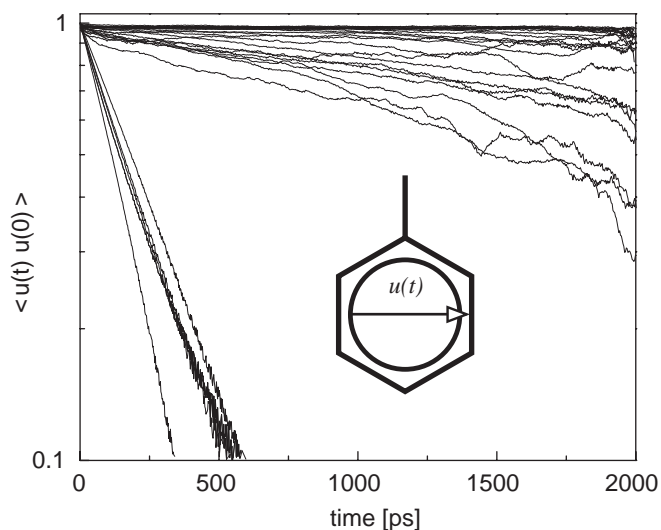


Fig. 2. The time autocorrelation functions of the orientation vector of each phenyl ring, for all the phenyls in the confined film ($T = 360$ K). The respective relaxation times correspond to the rotational relaxation of the phenyls (*i.e.* phenyl “flipping”).

surface are dynamically inhibited throughout the temperature range studied.

We should mention that all the above depict a general behavior of nanoscopically confined polymer films, that has been also reported for other systems which are distinctly different in nature. For example, similar response has been measured also in: a) Short-chain poly(methyl phenyl siloxane) confined in organically modified mmt and bentonite [11]; this system employs the same confining surfaces and similar confinement sizes as in the confined PS films, but the polymer used has a glass transition temperature more than 150°C below that of PS. b) Poly(ethylene oxide) in Na^+ or Li^+ montmorillonite, where the polymer is now more severely confined, in a 0.8 nm thin slit, and in absence of any organic surfactants grafted on the solid surfaces [12–14,10].

3.2 Atomistic simulation findings

Mimicking the solid-state NMR studies, which follow the $\text{C}-^2\text{H}$ bond reorientation, we can quantify the dynamics of the various styrene moieties by following their reorientation in time. From the MD trajectories, and focusing on the phenyl dynamics, we quantify the phenyl “flipping” *via* the time autocorrelation function (acf) of the phenyl orientation vector $\vec{u}(t)$ (Fig. 2). This function is defined by

$$C_{uu}(t) \equiv \langle \vec{u}_i(t_0) \cdot \vec{u}_i(t_0 + t) \rangle \propto \exp[-(t/\tau_R)^{\beta_{in}}], \quad (1)$$

where, $C_{uu}(t)$ is the time autocorrelation function, $\vec{u}_i(t_0)$ is the orientation vector of the i -th phenyl at time t_0 and $\vec{u}_i(t_0 + t)$ is its orientation after a time interval t , τ_R is the respective relaxation time (*i.e.* the rotational

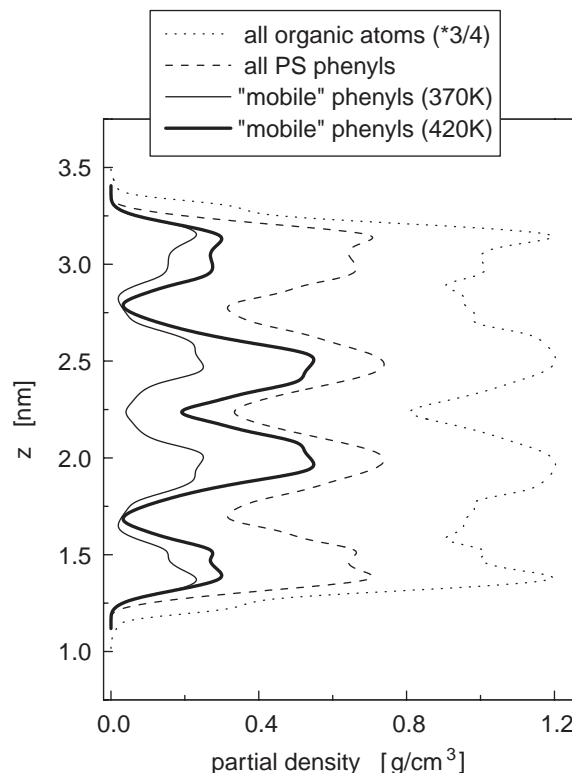


Fig. 3. Phenyl distributions across the confined film: The distributions of the “fast” phenyls at 370 K and 420 K are shown, also in relation with the total organic density and the distribution of *all* phenyls across the film (the last two are largely temperature independent).

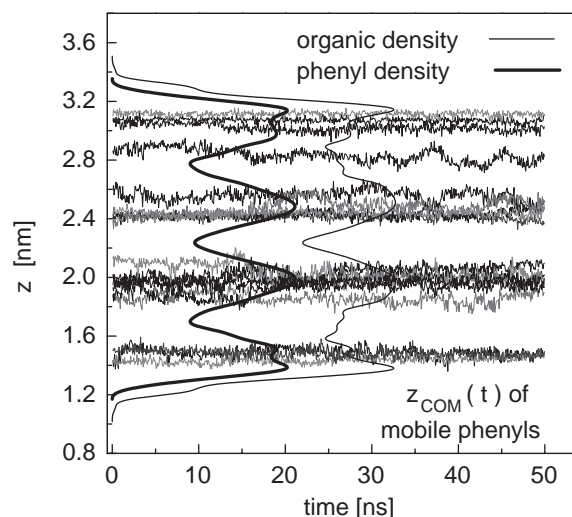


Fig. 4. The position of the phenyl center-of-mass (z_{com}) as a function of time, all “fast” phenyls are shown at $T = 390$ K. There is no marked adsorption/desorption for the simulated time scales (50 ns), both the “fast” and “slow” phenyls maintain their position relative to the confining walls.

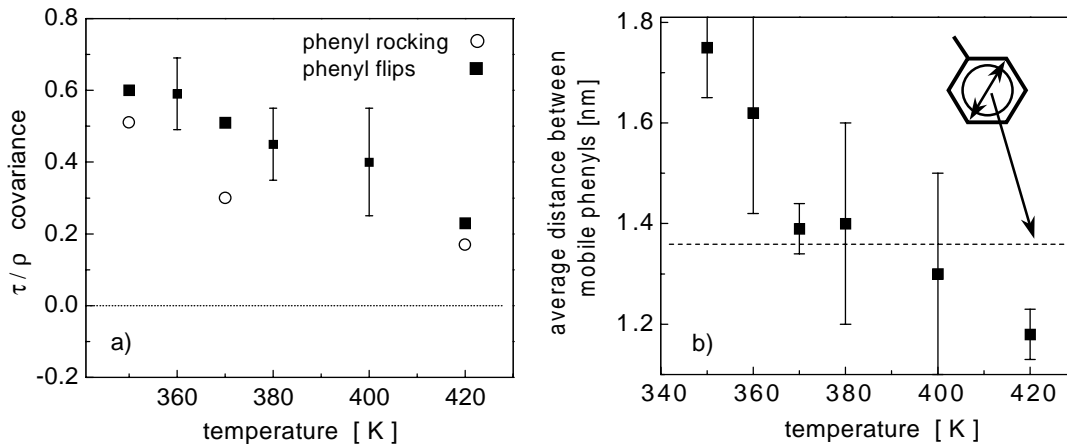


Fig. 5. a) The relaxation-time/local-density covariance *versus* temperature, for the phenyl dynamics. At the lower temperatures, there is a strong correlation indicating that the mobile phenyls are located at low local density regions [19]. The apparent decrease of the τ/ρ covariance with T , is due to the increased number of “fast” phenyls in the film, which results in multi-phenyl groups of “fast” phenyls, especially in the middle of the confined film [5]. In b) the average distance between the “fast” phenyls is shown. In both figures, the large simulation box was used for 320, 370, and 420 K, the smaller box was used for the rest.

relaxation time of the i -th phenyl), and β_{in} is the *intrinsic* Kohlrausch exponent [15] (for most of our phenyls $\beta_{\text{in}} \simeq 1.0$, whereas the lowest value used was $\beta_{\text{in}} = 0.9$). The ensemble average is over the trajectory time, and over multiple time origins (t_0) to improve statistics [16]. The data of Figure 2 were calculated from a trajectory of 50 ns at $T = 360$ K, by averaging over 100 time origins (t_0); the slope of the $C_{uu}(t)$ lines depicts the rotational relaxation time of the respective phenyl. A few of the $\langle \vec{u}(0) \cdot \vec{u}(t) \rangle$ in Figure 2 correspond to ultra-fast flipping phenyls, with rotational relaxation times (τ_R) of a few tens/hundreds of ps. These are characteristic of PS and are also observed also in bulk PS [9], albeit in much smaller populations. The confinement-induced dynamical inhomogeneities are seen in the family of curves with longer τ_R (smaller slopes correspond to longer τ_R). It becomes obvious that there is a very wide distribution of relaxation times, with τ_R ranging from 20 ns to “infinity” (*i.e.* lines with zero slope, that correspond to phenyl rings that are immobilized throughout the duration of the MD run). These immobilized phenyls persist even for the highest simulated temperature and make it difficult to quantify the exact width of the τ_R distribution. However, the relaxation time of the fastest rings is comparable (~ 20 ns) for all simulated temperatures (350–420 K). Thus we can qualitatively comment that the phenyl relaxation times associated with their orientational decorrelation span similar ranges of τ_R for all temperatures simulated. Although there are similarly wide distributions of relaxation times with T , the number of phenyl rings with faster τ_R is an increasing function of temperature; thus, the peak value of the distribution and the mean τ_R shift accordingly to lower times with T . The other modes studied [5] (phenyl rocking, backbone *trans-gauche* isomerization) have similar behavior as the one seen for the phenyl flipping. This distribution of relaxation times is actually confinement-induced, as discussed hereafter, and is in concert with the macroscopic response observed by NMR [3]. However, our simulations are not

aiming to “reproduce” the experiments, in the sense of a precise quantitative comparison. Our goal is to trace the molecular origins of the macroscopically observed behavior, especially the counter-intuitive ultra-fast segmental dynamics in 2 nm confinements, and on this theme we shall direct the course of the remaining discussion.

Dynamical inhomogeneities are typically associated with density inhomogeneities, and in our case confinement results in a very inhomogeneous density profile across the 2 nm film (Fig. 1). Focusing again on the phenyl ring dynamics, we show in Figure 3 the distribution of the carbons belonging to “mobile” (fast) phenyl rings, for two temperatures (370 K and 420 K). Paralleling the NMR definition [3], where “mobile” are moieties with relaxation times smaller than the NMR echo spacing (τ_{echo}), we define as “fast” or “mobile” those phenyls characterized by a measurable relaxation time in our simulations, as estimated from the time autocorrelation functions of Figure 2; however, we should emphasize that there is a considerable difference in the two time scales (*i.e.*, $\tau_R \ll \tau_{\text{echo}}$). With increasing temperature the number of mobile phenyls increases, and also these mobile rings are located increasingly in the center of the pore (Fig. 3). Since the mobile phenyls are located both near the surfaces —albeit in smaller numbers— as well as in the center of the slit pore, the fast segmental dynamics do not seem to originate from the location of the segments with respect to the confining surfaces, as is the case in wider confined films [17]. In those studies, Bitsanis *et al.* found that moieties that are physisorbed on the confining surfaces were dynamically hindered, whereas moieties more than one monomer-diameter away from the surfaces exhibited fast relaxations [17]. In our case, the films are so thin that a styrene bilayer develops, and all styrene monomers are physisorbed to one of the two confining surfaces (Fig. 1). However, fast relaxations —according to the NMR [3]— could also result when moieties are undergoing translation across the confined film, since translation is generally

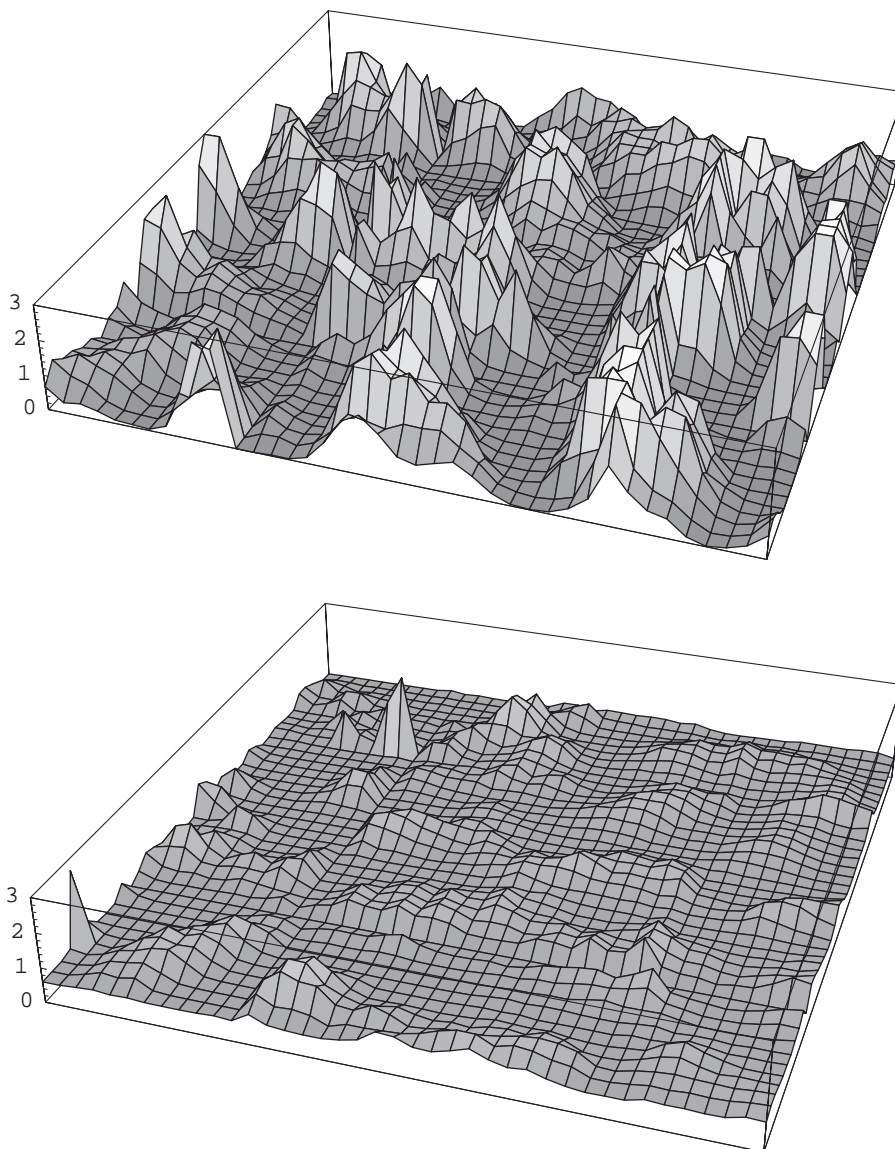


Fig. 6. The xy density in the confined (top) and the bulk (bottom) film, averaged over a 0.7 nm z -slice in the middle of the film for 10 ns (confined system $T = 390$ K, bulk system $T = 350$ K). The density scales are normalized by the corresponding average film density. The density inhomogeneities in the confined films are stabilized over extended periods of time, whereas density fluctuations in bulk PS are very fast dissipated by the thermal motions, even at a much lower temperature.

accompanied by C-H bond reorientation. This is not the case for the simulated systems: In Figure 4 we follow the position of the fast reorienting phenyls and we observe that there is no translation across the film. There exists only a local lurching motion of the phenyl center-of-mass around an average position, which results from the phenyl flips. Moreover, from Figures 3 and 4 it is obvious that the fast phenyls are not located in confinement-induced density minima *across* the film, but rather throughout.

Since there is no marked dependence of the fast phenyl dynamics on their position with respect to the surfaces, we subsequently explored the local environment. Inspired from MD simulations in glass-forming simple liquids [18], we checked the correlation between the *segmental dynamics* and the *local density* in the vicinity of each seg-

ment [19]. This can be realized through the estimation of the covariance of the segmental relaxation and the local density, defined as

$$\text{cov}(\tau, \rho) \equiv \frac{\langle (\tau - \langle \tau \rangle) \cdot (\rho - \langle \rho \rangle) \rangle}{\sqrt{\sigma^2(\tau) \sigma^2(\rho)}}, \quad (2)$$

where τ is the segmental relaxation time of a particular phenyl mode, $\langle \tau \rangle$ is the ensemble average over all phenyls, $\langle \rho \rangle$ is the average density across the slit pore, and ρ is the local density around the phenyl in question [19]. $\sigma^2(\tau)$ and $\sigma^2(\rho)$ are the ensemble variances of the respective relaxation time and local density. This quantity was defined for all phenyl and backbone modes, and in Figure 5a we show the relaxation time/local structure covariance for the mobile phenyls. Following this definition, complete corre-

lation between fast segmental relaxations and low local densities yields a value of $\text{cov}(\tau, \rho) = +1$, whereas no correlation between the segmental relaxations and the local density yields $\text{cov}(\tau, \rho) = 0$. For the lower temperatures simulated there exists a strong correlation between the local structure and the segmental relaxation. Namely, the fast relaxing phenyls are located in regions where the local density is low (independent of whether they are close to the walls, or in the center of the slit; and independent of whether the C-H reorientation takes place through “flipping” or “rocking” motions). As the temperature increases, this correlation seems to decay in magnitude, although it still remains positive.

In fact, as the temperature increases, the number of mobile phenyls also increases in such a degree that large volumes in the middle part of the slit consist solely of phenyls with fast segmental dynamics [5]. This reflects in a decreasing average distance between fast relaxing phenyls (as seen in Fig. 5b). 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. 7 in Ref. [5]). However, despite their proximity, the motions of the phenyls within the same “cluster” are not correlated nor cooperative. For all the temperatures simulated (even above 420 K) 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.

Density fluctuations also exist in bulk PS films [9]; however, in confinement these density inhomogeneities seem to be amplified and also stabilized over extended time periods: In Figure 6 we show the density in the xy plane —parallel to the confining surfaces— and in the middle of the film. We average over a z -slice of 0.7 nm (*i.e.*, one styrene monomer wide) and over 10 ns of the MD trajectory, and we normalize by the average density of the film. These long-lived density inhomogeneities in the confined films are not at odds with the existence of a large number of fast relaxing moieties in the same film. As the polymer is held together by strong covalent bonds, the relaxation of the chains is determined by the *slowest* moving segments along the polymer. Even though mobile segments do exist in large numbers, they are bonded to portions of the polymer that remain “frozen” for time scales vastly longer than the 50–100 ns simulated herein. Thus the immobilized segments —that are found mostly physisorbed on the solid surfaces— are responsible for stabilizing the inhomogeneous structure of the film, with local densities varying strongly from one region to another over tens of ns. In contrast, in a bulk PS film density fluctuations are very fast dissipated by the thermal motion: for example, the xy density —averaged over the same volume and time as in the confined film— seems to be smoothed out very fast (Fig. 6). Consequently, the dynamics of bulk

systems are also expected to be much more homogeneous, since the local environment around the various segments is essentially the same, when viewed at a time scale of 10 ns.

Similar density inhomogeneities are also expected to be created and stabilized in wider confined films, than the bilayers studied here, as well as near the solid wall of supported polymer thin films. In these cases, previous MD simulations have shown that the response of the wider —confined or supported— film, is the weighted average of the wall-induced and bulk-like behavior [17, 20, 21]. Thus, for supported thin polymer films it is expected that these effects will become measurable, when their thickness approaches a few monomer sizes. Earlier simulations [22] have also shown similar dynamic inhomogeneities near free polymer surfaces, however they were attributed to different molecular origins than herein.

3.3 Comparison to experiments

Finally, we would like to comment on the quantitative comparison between our molecular simulations and the NMR experiments. The spin-echo method as employed in the NMR studies [3], does not allow for the measurement of the relaxation times of the fast relaxing phenyls. Other NMR methods, *e.g.* T_1 measurements or 2d NMR, that can quantify the distribution of relaxation times, can provide a much better frame of experimental data to compare against. However, the spin-echo NMR can enumerate the population of the fast relaxing phenyls (“mobile fraction” [3]). The simulation enumeration of the mobile fraction underestimates the NMR measured one (Fig. 7), albeit capturing the correct temperature dependence. This discrepancy can result from several sources, such as the uncertainties in the relaxation time calculation, and phenomena that become important after the 50–100 ns probed by our MD runs (such as polymer diffusion or desorption, chain end-to-end relaxation). Although any of these two reasons could possibly account for the deviation between the experimental and simulation values, we believe that the cause of this difference lies in the organic —styrene and alkyl-ammonium— density used in our simulations, which must be higher than the ones in the experimental intercalated systems. Even though we based our densities on the TGA estimated quantities, the gravimetric method may also measure polymers physisorbed on the outside of the silicate stacks, *i.e.* not in the confined film. Since there exists a very strong dependence between the density and the fast segmental dynamics, minute deviations in density can result in large variations in the system dynamics. Nevertheless, the aim of our simulations is to provide relevant molecular-level insight to the system behavior recorded macroscopically by experiments. To this end, we believe that the findings depicted in Figures 2-6 bear a higher importance than the exact enumeration of the mobile fraction (Fig. 7).

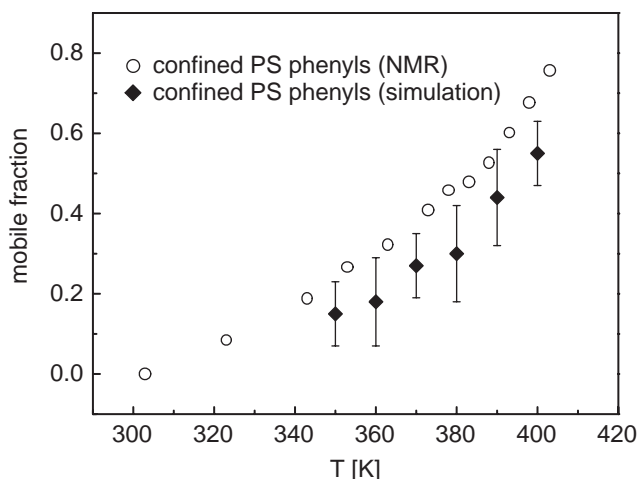


Fig. 7. Comparison of the simulation results to the NMR measurements. There is a systematic underestimation of the mobile phenyl fraction by the MD simulations.

4 Conclusions

MD simulations of ultra-thin confined PS between solid surfaces capture pronounced dynamic inhomogeneities across the 2 nm thin confined film, in concert with NMR experimental studies. Particularly, confinement gives rise to very fast segmental dynamics, throughout the temperature range investigated, which is very counter-intuitive and in contrast with the common belief that confined films are “dead” and immobilized, deprived of any dynamics. The molecular origins of this behavior are traced to the confinement-induced density inhomogeneities in the film, which are stabilized over extended periods of time near the solid surfaces. Since there is a strong correlation between local density and segmental dynamics, these long-lived density inhomogeneities give rise to a very wide distribution of segmental relaxations, with the fast relaxing moieties being located in low local density regions.

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