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Possible explanation of the Λ-shape anomaly in polymer surface diffusion

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We suggest an explanation for the anomalous behavior of the polymer surface-diffusion coefficient D reported by Zhao and Granick [J. Am. Chem. Soc. **126**, 6242 (2004)]: D first increased with increasing polymer surface concentration Γ, then suddenly dropped at a threshold value Γ^*. Our molecular dynamics simulations show the same behavior. We find that polymers form single-layered pancake structures for $\Gamma < \Gamma^*$, while double layers form for $\Gamma > \Gamma^*$. The double-layer structures allow the polymers to better adapt to the substrate corrugation. This increases barriers for lateral diffusion and is thus consistent with small values of D at larger Γ.

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Understanding the dynamics of polymers is a fundamental scientific problem with important technological implications. There has been a long history of studying the dynamics of polymers in the bulk [1–4]. Recently, there has been an increased effort to also elucidate macromolecular dynamics on surfaces [5–7] including that of DNA [8]. Of particular interest is the scaling of the single-polymer diffusion constant D with the degree of polymerization N [5,6,9,10].

A less investigated issue is the dependence of D as a function of surface coverage Γ at fixed N. A recent experiment found a surprising anomalous behavior in $D(\Gamma)$ [11]. When depositing poly(ethylene glycol) (PEG) onto fused silica surfaces with hydrophobic termination, D first increased with increasing Γ, and then, taking a Λ-type shape, decreased when Γ exceeded a threshold value Γ^* (which defines Γ^*). In these experiments, the polymer diffusion was measured with the help of fluorescence spectroscopy that detected the signal of fluorescent labels, which were attached to the PEG molecules. To the best of our knowledge, this nonmonotonic behavior, which we call a Λ-shaped anomaly, has neither been predicted nor explained convincingly.

One of the reasons why polymer diffusion on surfaces may be poorly understood is that theories (at least those known to us) focus on the conformations of the polymers and how the conformations may prevent the polymers from diffusing. The substrate is usually assumed to simply be an adhesive, hard-wall boundary without explicitly accounting for its corrugation. However, an ideally flat boundary would result in extremely large mobilities since there would be nothing to prevent the polymers from free gliding. Thus, addressing the question of how a substrate manages to exert frictional forces onto adsorbed layers in general [12] and polymers in particular is a key task if we want to understand polymer diffusion on surfaces. Indeed, once the surface corrugation is explicitly taken into consideration, [10] simple bead-spring models of polymers reproduce the correct scaling of D with N.

While simple bead-spring models are certainly inappropriate to describe the complexity of PEG, it is interesting to investigate whether they show similar anomalies in D with Γ. When analyzing the experiments, it would be presumptuous to state that the polymers are in thermal equilibrium. Indeed, the experimental data themselves provide arguments that the systems had not been in full equilibrium, despite the fact that similar values for D were obtained after 1 h of relaxation and after 12 h of relaxation: D shows an almost discontinuous dependence of Γ at Γ^*. In full equilibrium, such discontinuous behavior would not occur unless there was a phase transition point at Γ^*. If there was a second-order phase transition in the thermodynamic sense, one would not expect a dramatic change of a *local* observable such as D near Γ^*. If there was a first-order phase transition, it would be necessary to observe a hysteresis in order to know the full equilibrium state on both sides of the transition point. Therefore, it may be worth addressing the question, what are the metastable states that the polymers initially adapt when being deposited from solution?

Given these considerations, it is desirable to mimic "true dynamics" in the simulations rather than artificial dynamics, which are otherwise useful to quickly generate well-equilibrated (virtual) samples. For this reason, we will employ regular molecular dynamics (MD) simulations, in which temperature is imposed by weakly coupling a Langevin thermostat to the monomers. (Lateral diffusion in our samples is sufficiently slow so that the precise choice of the thermostat, which is only coupled in the direction normal to the substrate, has no detectable effect on D.)

A popular model for the investigation of generic static and dynamic polymer properties is a simple bead-spring model [13,14], in which monomer units interact with Lennard-Jones potentials $V_{\mathrm{LJ}}=4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^6]-V_{\mathrm{cut}}$ if the distance r between two monomers is less than a cutoff distance r_c. V_{LJ} is set to zero for $r > r_c$, and V_{cut} is chosen such that the potential is continuous at r_c. In poor solvent conditions, $r_c = 2\times 2^{1/6}\sigma$ is chosen, while good solvents are modeled with $r_c=2^{1/6}\sigma$. Adjacent monomers on a chain are additionally bound by a potential $V_{\mathrm{chain}}(r)$

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$=-(1/2)kR_0^2\ln[1-(r/R_0)^2]$, where $R_0=1.5\sigma$ and $k=30\varepsilon/\sigma^2$. The results presented below are expressed in units of the Lennard-Jones energy ε, the Lennard-Jones radius σ, and the mass m of individual monomers. Values that would be representative of hydrocarbons are as follows: $\varepsilon=30$ meV, $\sigma=0.5$ nm, and $t_0=3$ ps [13]. The thermal energy is set to 0.5ε, which makes the polymers stick to the substrate and to themselves, while still being sufficiently mobile to diffuse during the time scale of the simulation. In the simulations, we fix the degree of polymerization to $N=10$. This value is smaller than the experimental value of $N\approx 244$. However, given that the persistence length (in units of monomers) is probably smaller in the MD simulations than in the experiments, we expect to be in the correct regime.

The substrate consists of a (111) surface of a face-centered-cubic solid. The geometry is essentially square with a fixed linear dimension of 37.5σ and periodic boundary conditions are employed in lateral direction. Atoms in the substrate are confined to their lattice sites with a nearest-neighbor distance of 1.209σ. Monomers and substrate atoms interact with the same potential as that for monomers interacting with each other in poor solvent conditions. Due to the discreteness of the wall, corrugation barriers exist. They break the translational symmetry and hence prevent the polymers from freely gliding over the surface. This model has been used previously to study the diffusion of polymers between two walls, and the friction between two walls in the presence of polymers as well as in their absence [15]. Here, however, we will only consider one surface.

Initial configurations are generated by distributing the polymers randomly in the lateral direction and close enough to the substrate so that they are likely to feel the substrate's adhesive force. We believe that this procedure reproduces the experimental deposition from solution sufficiently well. We run the simulations for 5×10^8 MD time steps, that is, $2.5\times 10^6 t_0$ to equilibrate the sample, in some cases for longer times. The system is then observed over another few 10^7 MD time steps, during which observables such as the diffusion constant and the structure factor are measured. D is obtained from the time-correlation function $C(t)$

$$C(t)=\frac{1}{2N}\sum_{\alpha=1}^{2}\sum_{i=1}^{N}\langle[R_{i\alpha}(t+t')-R_{i\alpha}(t')]^2\rangle, \tag{1}$$

where $R_{i\alpha}(t)$ is the x or y component of the position of monomer i in a given polymer, by making use of the relation $D=\frac{1}{2}\lim_{t\to\infty}\partial C(t)/\partial t$. An average over time and all polymers is taken in Eq. (1). Moreover, in the evaluation of D, the limit $t\to\infty$ is replaced by fitting a straight line to $C(t)$ at the largest times. In all cases, the polymers were well in the diffusive regime when determining D. This means that local equilibrium was reached, which does not imply that the global, thermodynamic equilibrium was achieved.

The results obtained for D as a function of the coverage Γ is shown in Fig. 1. The functional dependence of $D(\Gamma)$ shows the same distinct Λ-type shape as in the experiment. The similarity is particularly striking for our poor solvent conditions. This may be surprising given that (bulk) water is a good solvent for PEG. However, the surface termination in the experiments is strongly hydrophobic [6,11], which dramatically reduces the dielectric constant of water within the first few water layers near the surface. This explains why water's solvation force for PEG would be reduced at the interface. In the following, we will focus on poor solvent conditions. All results are qualitatively similar for good solvents.

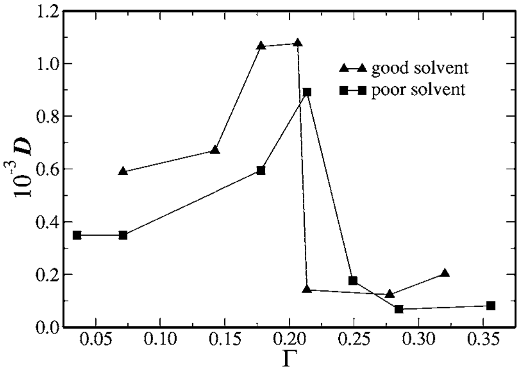

FIG. 1. Lateral diffusion coefficient D of individual polymers as a function of monomer coverage Γ, which is measured in number of monomers per unit surface area. Lines are drawn to guide the eye.

Having reproduced the experimentally observed features in $D(\Gamma)$, it is sensible to investigate whether the changes in the dynamics are accompanied by morphological changes of the adsorbed polymers. Indeed, when studying simulation snapshots, it becomes apparent that the polymers "spontaneously" formed single-layer islands for $\Gamma<\Gamma^*$, while double-layer islands formed at concentrations $\Gamma>\Gamma^*$ (see Fig. 2). To be more precise, when depositing five chains on the substrate, corresponding to $\Gamma=0.0356$, it took about 5×10^8 MD time steps for the five chains to form one single, single-layered island. Conversely, at the large deposition concentrations, for example at $\Gamma=0.356$, small double-layered islands formed after only 10^7 MD time steps. Even after 10^9 MD time steps, however, there were still disconnected islands, which, on large time scales, would certainly unite. It is important to point out that we can observe the formation of double-layered islands with relatively few polymers when Γ is large, while larger single-layered structures can form when the local concentration is initially small. Thus, the structures

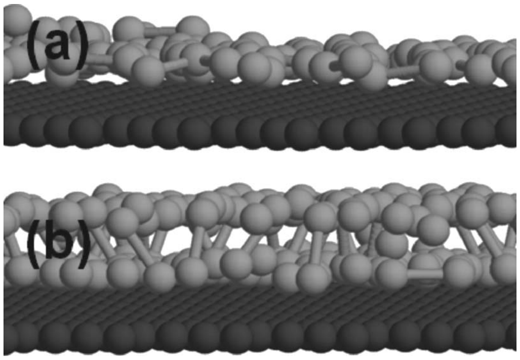

FIG. 2. Snapshots of structures for $\Gamma=$(a) $0.178<\Gamma^*$ and (b) $0.249>\Gamma^*$. Bonds are drawn between adjacent monomers in a chain.

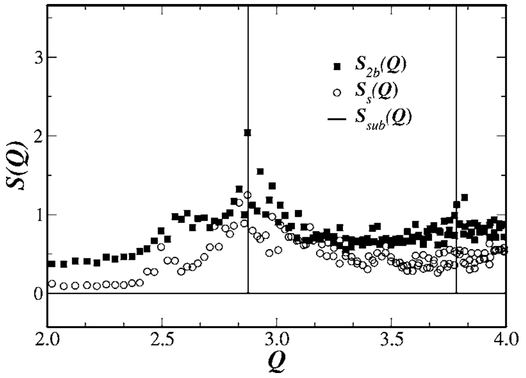

FIG. 3. Structure factor $S(Q)$ as a function of wave number Q for the substrate (line), the bottom layer of a double-layered structure $S_{2b}(Q)$, and a single layer $S_s(Q)$. All $S(Q)$ are normalized to yield the same value at $Q=0$.

initially formed (i.e., within the first few 10^6 MD time steps) appear to be extremely relevant for the long-time structure and ultimately for the (nonequilibrium) long-time dynamics.

It still needs to be understood (a) why the mobility increases when single-layer islands grow in size and (b) why the double-layered islands diffuse less than the single-layer islands. We cannot yet provide a striking argument for (a). However, we speculate that the increased fluctuations in the z coordinate for Γ less than but close to Γ^* assist the monomers to jump over the corrugation barriers. Simulations with fixed coordinates in z have to be conducted in the future to clarify this issue.

As for (b), two explanations seem plausible. (i) The second layer acts as an adhesive external load, pressing the monomers of the bottom layer deeper into the substrate's potential energy minima, thereby increasing the energy barriers and hence reducing mobility. We tested this idea by reducing the cutoff radius for the interaction between fluid and substrate atoms in such a way that only the bottom layer, but not the top layer, was attracted to the substrate. This alteration resulted in a mere 20% increase in D and hence does not explain the dramatic change of D at Γ^*. (ii) The two-layer structure gives the polymers more flexibility to adjust their geometry to the substrate corrugation. Indeed, in molecular snapshots of the bottom layer it becomes apparent that the atoms show the same local structure as the substrate. From simple adsorbed monolayers it is known that the substrate's ability to imprint its corrugation into the fluid decreases its slip time [12], which translates into a reduced diffusion constant. To make the analysis quantitative, we calculated the static structure factor $S_{2b}(\mathbf{Q})$ of the polymers in the bottom layer of a double-layer configuration for different wave vectors $\mathbf{Q}$ and compared it to the structure factor of a single-layered pancake $S_s(\mathbf{Q})$. In Fig. 3, we show the orientationally averaged results for the $S(Q)$'s and include the Bragg peaks $S_{sub}(G)$ from the substrate for comparison. These peaks are located at the substrate's reciprocal lattice vectors $\mathbf{G}$. One can see that the bottom layer of the double-layer structure has much more, i.e., more than twice as much, scattering intensity near the substrate Bragg peaks than the single layers do. We believe that this explains the much reduced mobility of the double layers in our simulations. In leading-order contribution, one can assume that the corrugation barriers ΔE_b, which prevent a slider from moving laterally with respect to the substrate, increase linearly with the structure factor [16]. Thus, the much increased values of $S_{2b}(\mathbf{G})$ with respect to $S_s(\mathbf{G})$ would be consistent with an exponentially reduced diffusion coefficient, in a simple Arrhenius-type activation picture, i.e., $D \propto \exp(-\Delta E_b/k_B T)$, or alternatively $D \propto \exp[-\alpha S_{2b}(\mathbf{G})/k_B T]$, where α is a proportionality coefficient. As the double-layer islands age, we observe a weak increase in $S(\mathbf{Q})$ near the $\mathbf{G}$'s. This increase is accompanied by a strong reduction in D. Our statistics are currently too poor to make a sufficiently accurate test of the $D \propto \exp[-\alpha S_{2b}(\mathbf{G})/k_B T]$ hypothesis.

To validate our claims related to the $S(\mathbf{Q})$'s in a real laboratory experiment, it would be necessary to measure the structure factor of the bottom layer independent from that of the top layer. This is because when we calculated $S(\mathbf{Q})$ of the full, double-layered structure, the signal had been dramatically reduced. We still believe that the $S(\mathbf{Q})$ argument may well be responsible for the experimental observations. The better interlocking of bottom layer and substrate is made possible by the additional flexibility of the polymers that they have when bonds connecting adjacent monomers can be out of plane rather than only within the plane parallel to the substrate.

It will certainly require more studies to validate our scenario. It may be particularly useful to work with realistic model potentials. However, one of the difficulties involved would be that the exact molecular surface structure will play a key role for prefactors. Unfortunately, the detailed roughness is hardly ever known to the desired degree. It may be important to emphasize that the crystallinity of the substrate is not important for the qualitative features of the mechanisms that we suggest to occur. The polymers need to (and do) match the surface corrugation only locally. Thus, we would have expected similar trends in our model in $D(\Gamma)$ if we had used atomically flat, but amorphous substrates, provided that the interatomic spacing in these substrates had been similarly large on average as in the crystalline surfaces.

Although this study was done based on generic potentials and simple face-centered (111) surfaces, it may yet be worth discussing the issue of the time scale separation between simulation and experiment. There are two relevant time scales, if our scenario is correct. First, the time t_1 it takes a polymer to diffuse one lattice constant on average. Expressing our dimensionless diffusion constant in the characteristic units mentioned above, we find that the experimental value for t_1 is about ten times larger than ours in the limit of vanishing Γ. Given that energy landscapes enter exponentially into diffusion coefficients, this can only be seen as a coincidentally close agreement. The other time scale is the time t_2 it takes for the double-layer structures to form. In our simulations, the double layers are energetically favorable over the single-layer structures. Therefore, we consider our single layers to be metastable. In experiment, the propensity to form double layers may be much reduced as compared to our simulations, which would result in an exponentially increased t_2. Something that speaks in favor of this argument is that the drop in D occurs in experiment at a surface coverage $\Gamma \approx 1$, whereas we observed the discontinuity at $\Gamma \approx 0.2$.

If our scenario is correct, it is possible to discuss the question whether the experimental observation of a Λ-shaped $D(\Gamma)$ dependence is universal. We would argue that it is not. If polymers in the dilute limit already have the tendency to form two or more layers, the effect would probably disappear in the current picture. This argument would probably also apply to macromolecules with complex side groups such as DNA, unless the surfaces are intentionally structured in order to favor our scenario. The Λ-shaped $D(\Gamma)$ should not be expected either if the polymers in a single-layered pancake were able to accommodate the substrate corrugation within, say, one persistence length. In this case, the single-layered structures would be strongly pinned already and allowing the polymers to further increase the interlocking with the substrate due to up-and-down geometries might result in marginally increased diffusion barriers only. In most cases, however, we would expect that polymers and substrate are sufficiently incompatible for this latest scenario to occur. Polymers with large persistance lengths would probably not be able to lock into the substrate even if a second layer were formed.

In conclusion, our MD simulations have reproduced the nonmonotonic behavior of the polymer surface-diffusion coefficient D as a function of surface coverage Γ. Both experiment and simulation show a very similar $D(\Gamma)$ dependence. Due to the complexity of PEG it may be that the mechanism for this anomaly is different. However, even with today's computational resources it would be infeasible to directly simulate the experiments.

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