Scaling Laws of Single Polymer Dynamics near Attractive Surfaces

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We present a molecular dynamics study of a generic model for single polymer diffusion on surfaces, which have variable atomic-scale corrugation but no artificial, impenetrable obstacles. The diffusion coefficient D scales as $D \propto N^{-3/2}$ with the degree of polymerization N for strongly adsorbed, linear polymers on solid substrates in good solvents. Weaker scaling, i.e., $D \propto N^{-1}$, is found if (i) the substrate is a fluid, e.g., a membrane, (ii) the polymer is a ring polymer, and (iii) the polymer is commensurate with the substrate. In poor solvents, diffusion on solids slows exponentially fast with N. Reptation is not observed in any of the simulations presented here.

The surface diffusion of macromolecules has attracted increased attention within the last decade [1–5]. These studies are motivated in part by the desire to obtain a fundamental understanding of the diffusion of linear macromolecules on surfaces, including that of DNA [6] and phospholipids [7,8] on lipid bilayers. Further motivation for these studies comes from existing or potential technological applications of adsorbed polymers such as they occur for surface coating, adhesives, and tribology [9]. Progress in measuring molecular diffusion coefficients of adsorbed single polymers [2,6] or of polymers in thin films [10] was made owing to the application of fluorescence spectroscopy. However, despite these advances, it is not yet possible to extract direct experimental information on atomic-scale structure and dynamics of polymers. For example, it is not possible to ascertain whether or not polymers are reptating.

A key question in adsorbed single polymer systems is how quantities such as the lateral diffusion coefficient D, the end-to-end chain relaxation time τ, and the in-plane radius of gyration R_g scale with the degree of polymerization N. While the scaling laws for the structural properties appear to be well established, e.g., $R_g \propto N^\nu$ with $\nu = 0.75$ [3,6,9,11] for planar geometries in good solvents, there is conflicting information on the dynamical exponents, in particular, in the $D \propto N^{-y}$ relation. Two experiments found $y = 1$ [6,7] for polymers adsorbed on lipid bilayers, while another study identified $y = 3/2$ for a polymer adsorbed on a fused silica surface [2].

Because of the difficulties associated with the analytical description of polymer dynamics, simulation has become the method of choice [1,3–5,11,12] to ascertain what determines the dynamical exponent y. Depending on the model and the simulation method, different results are obtained, e.g., $1/N$ in a Monte Carlo (MC) study of a bead-spring model on a smooth surface [11], a crossover from $D \propto 1/N$ to $1/N^{3/2}$ depending on the concentration of random obstacles on the surface in a molecular dynamics (MD) simulation [3], a crossover from an apparent

dynamical exponent $y = 1.7$ for $N \le 150$ to $y = 3/2$ for larger N in a MC simulation of a two-dimensional bond-fluctuation model where impenetrable obstacles were present on the surface [1]. Most recently, an MD study [5] of a bead-spring model found that $D \propto 1/N^{3/2}$ for surfaces that were called "solid" and either had impenetrable barriers or "sticking points," while $D \propto 1/N$ was identified on so-called "fluids," which, however, were sometimes modeled with the help of obstacles of small, albeit finite concentration, surface roughness, and density modulations. Finally, a polymer lattice model on a hexagonal lattice without obstacles was suggestive of the law $D \propto (aN + bN^2)^{-1}$, where a and b were system-dependent coefficients [12]. In many of the simulations, it was argued that reptation dynamics occur [3,5,12].

It is surprising that none of the computational studies discussed in the previous paragraph investigated what we consider to be the most generic model for polymer diffusion on surfaces, namely, a simple bead-spring chain adsorbed onto a *simple* but *corrugated* substrate [13] without diverging energy barriers, such as is obtained when a surface is modeled with discrete atoms. Corrugation (or more generally speaking, breaking in-plane translational Galilean invariance) is a necessary "ingredient" to exert shear forces. Lattice models usually neglect the way in which the substrate breaks translational invariance, and it is thus not clear if one can relate their predictions to experiments. In many models, where translational invariance is broken, it is typically done by introducing energy barriers having infinite height. One may argue that these obstacles are somewhat artificial and thus do not necessarily produce the generic features of smooth surfaces which have only atomic-scale roughness, as is the case for fused silica surfaces.

In order to avoid artifacts induced by infinitely large energy barriers and/or smooth walls, our analysis of single polymer diffusion shall be based on a model that includes an atomically flat but *discrete* surface. Because of the discreteness of the surface, *finite* (free energy) corrugation

barriers which prevent the polymers from free lateral sliding are present. For fluids, no static barriers or lateral heterogeneity exists.

We have shown previously that (static) surface corrugation appears to be a key factor in determining the dynamics of polymers at interfaces [13]. Simulating generic bead-spring polymers moving on surfaces that have only atomic-scale corrugation, we were able to reproduce the perhaps counterintuitive experiments by Zhao and Granick [10]: They had found that D first increased with deposition concentration Γ and then suddenly dropped to a small value at a threshold concentration Γ^*. Our simulations suggested that the sudden drop in D may be due to a structural transition from single to double layers and that the double layers have more geometric flexibility to lock into the substrate's registry, which increases energy barriers and thus reduces lateral mobility at large Γ [13]. In comparison to other work where either an ideally flat surface or a strictly two-dimensional polymer embedded in a plane containing random obstacles was used, we believe that our scenario mimics the generic features of the experiments more closely. Therefore, it would be interesting to revisit single polymer diffusion as a function of N with the same model that reproduced the nonmonotonic behavior of D with Γ. We will also investigate the effect of molecular structure (linear vs ring polymers) and initial conditions (flat adsorption vs crossings).

In this work, all simulations are based on the same empirical bead-spring model [14] as for our study of $D(\Gamma)$ [13]. Monomers interact with each other and with surface atoms through truncated Lennard-Jones (LJ) potentials, which are all identical except in good solvent conditions, when the cutoff radius for the monomer-monomer LJ potential is reduced from twice to one times $2^{1/6}$ times the LJ radius. As in our previous work, the thermal energy is set to half the LJ energy unit. Temperature is imposed through a Langevin thermostat that acts only on the motion normal to the surface. The coupling strength of the thermostat was varied by a factor of 10 without changing the results in any discernible fashion. We did not include explicit solvent in order to emphasize the damping of the polymers due to wall friction. Since our calculations are in thermal equilibrium and thus in linear response, damping due to wall friction and damping due to hydrodynamic interactions are linearly additive.

The configurations are equilibrated for a few 10^8 MD time steps (depending on the chain size) and then observations are carried out over another 15×10^6 MD time steps; this corresponds to $7.5 \times 10^4 t_0$, where t_0 is the LJ time unit. To illustrate our simple, albeit generic model further, typical equilibrated configurations on solids are shown in the auxiliary electronic material for both solvent conditions [15]. In some cases, we also considered ring polymers, in which case the first and the last monomers are connected by a covalent bond.

We wish to note that the dynamics of polymers shortly after deposition appears to be rather interesting, complex, and of relevance for the long-time dynamics, in particular, if the surface concentrations are higher than those used in the current work [13]. The relevance of initial conditions, however, appears to be less of an issue for single polymer deposition. For the same interaction potentials, single polymers, even longer ones, have a much lower propensity to form double layers or other multilayered structures than shorter chains at moderate concentrations, say at 50% surface coverage. For instance, when initial structures are prepared such that the polymers have single or double crossings, the crossings become unstable after a few 10^5 MD time steps within the parameter space investigated here. These observations motivated us to favor "flat" deposition of the polymers onto the surfaces. Of course, our initial conditions do not prevent the polymer from "piling up" at long times when the solvent conditions are poor.

Although the central interest in this Letter is the calculation of the in-plane diffusion coefficient D, we wish to point out that we provide evidence in the auxiliary, electronic material [15] that our model shows the right scaling for the in-plane radius of gyration. D is obtained by measuring the slope of the centroids' mean-square displacement at large times. The main part of Fig. 1 summarizes the most important results for good solvent conditions. The data for our default system (linear polymer, regular interaction between monomers and wall atoms) are consistent with the power law $D \propto N^{-3/2}$ predicted by Azuma and Takayama [1] and with the experiments on poly(ethylene
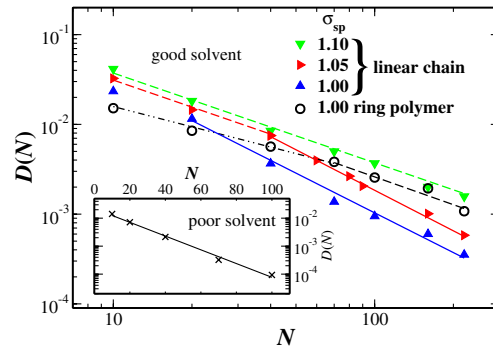

FIG. 1 (color online).   Lateral diffusion $D(N)$ as a function of degree of polymerization N for good solvent and both linear (triangles) and ring polymers (circles). Results are shown for different LJ radii σ_{sp} that are used for the interaction between monomers and wall atoms. Large values of σ_{sp} result in small roughness and vice versa. Triangles down, right, and up reflect high, medium, and small corrugation, respectively. Lines are guides to the eye. Solid lines (blue and red) indicate an $N^{-3/2}$ power law, long-dashed (green, red, and black) lines N^{-1}, and short-dashed (black) lines an $N^{-0.75}$ power law. Error bars are about symbol size. Inset: $D(N)$ for linear polymers in a poor solvent.

glycol) (PEG) near a fused silica surface [2]. It is surprising that introducing impenetrable barriers as done in Ref. [1] appears to have the same effect on the $D(N)$ scaling as finite barriers that can be overcome by thermal fluctuation. We certainly feel that our model is not only simpler, but as argued above, more general and natural than previously used models to describe the dynamics. Unfortunately, our results appear to be in partial contradiction to those of Qian *et al.* [5], who found that roughness and density modulation near the surface is not necessarily sufficient to obtain $y = 3/2$.

The result for our default system and its apparent contradiction with Ref. [5] invokes the question of whether a crossover to linear scaling would be found if N were distinctly larger than those values investigated here. An argument for this type of crossover would be that fractions of the polymers may move as uncorrelated domains and thus lead to Rouse dynamics at large values of N. We feel that this argument should be correct (at least) for dimensions equal to or above the upper critical dimension of the self-avoiding walk, i.e., for $d \geq 4$. However, investigating this issue in dimension four or above is beyond the scope of this Letter.

In order to investigate the possibility of a crossover in two-dimensional surface diffusion, the roughness of the walls was reduced. A reduced roughness should reduce the pinning and thus make the substrate more fluidlike. Roughness was reduced by increasing the LJ radius for the interaction between wall atoms and monomers, σ_{sp}, while keeping all other terms constant. This way the amplitude of the roughness is changed without altering the substrate's lattice spacing. When roughness is made very small, $D \propto N^{-1}$ is observed within the full range of N, which is to be expected for the diffusion on a fluid substrate (see discussion below). For intermediate roughness, a crossover from $1/N$ to $1/N^{3/2}$ scaling is observed with increasing N, in contradiction to the argument that the polymer should decompose into units that move in an uncorrelated fashion. Because of the observation of this crossover, we expect $D \propto N^{-3/2}$ at large N for any strongly adhering surface with finite, static barriers. Since the energy barriers are finite, no reptation is required for the polymers to diffuse on the surface. Indeed, when looking at movies of the MD simulations (see also a series of snapshots in the auxiliary electronic material) no indication of reptation can be identified [15].

An ideal flat surface (plus a linear-response damping acting on the monomers in the lateral direction due to collision with atoms in the substrate) automatically induces a damping that increases with N so that D should scale as $1/N$ or potentially faster if additional dissipation channels are present. In our simulations, we neither imposed external damping within the lateral direction nor did we include hydrodynamic interactions. However, due to the substrate's residual roughness, coupling of longitudinal, transverse,

and normal motion allows dissipating the kinetic energy associated with the polymer's in-plane center-of-mass motion to the normal degrees of freedom. This effect is sufficient to reproduce the same effect as hydrodynamic interaction with the substrate as long as the chain is fully adsorbed. This is why we abstained from incorporating hydrodynamic interactions directly and why we can observe an apparent exponent of $y = 1$ at small N and small roughness. A damping linear in N also occurs on flat substrates if the interaction between substrate and polymers is modeled with a dissipative-particle dynamics thermostat [5].

We can now explain why experiments (as well as some simulations) sometimes indicate Rouse dynamics ($y = 1.0$) instead of $y = 3/2$. The experiments favoring $y = 1.0$ were done on polymers adsorbed onto lipid bilayers [6,7]. These, however, are known to be in a fluid state. The polymers are thus "rubbing" against an on average uncorrugated, homogeneous fluid rather than against a solid with static corrugation, so that the damping (i.e., the inverse diffusion constant) of the polymers centroid is simply proportional to the number of monomers in contact with the fluid. For strongly adsorbed polymers the argument naturally leads to Rouse dynamics because each monomer is in contact with the lipid bilayer. The same argument explains why lattice models which do not explicitly include barriers find $D \propto 1/N$. MC dynamics are intrinsically overdamped, but the absence of any substrate-induced barrier does not add any (additional) resistance to sliding. The experiment suggesting that $y = 3/2$ was performed on a solid substrate. Our simulations indicate that finite, static (free) energy barriers, as they exist on solid substrates, produce dynamics with $y = 3/2$, at least if N is made sufficiently large. While this conclusion supports a similar conclusion by Qian *et al.* [5], we emphasize that our fluids do not have *any* type of heterogeneity, while our solids neither require impenetrable barriers nor sticking points.

The observation of a crossover from $y = 1$ to $y = 3/2$ for intermediate roughness suggests that the motions of the monomer units are highly correlated throughout the full chain (as argued above, if one could decompose the polymer into uncorrelated units, $1/N$ scaling should be observed). Thus, imposing a topological constraint, such as constraining the polymer to form closed rings, should have the potential to alter the dynamical exponent y, even though static properties such as the exponent ν may remain unaltered. When simulating ring polymers, we indeed find a different value for y, i.e., a crossover from $y = 0.75$ for short chains ($N \leq 70$) to $y = 1$ for long chains. The damping for long chains is probably due to the viscous damping force, which is an unavoidable consequence of the transverse-normal coupling discussed in a preceding paragraph.

In order to reduce the correlation between different monomer segments, we also investigated polymers that
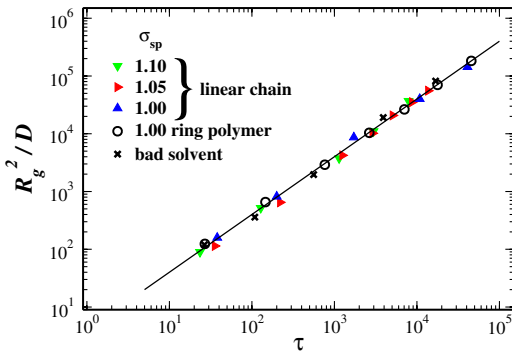
FIG. 2 (color online). Relation between R_g^2/D and end-to-end relaxation time τ for the various models. Symbols are consistent with Fig. 1. For ring polymers, τ is the relaxation time related to the motion of an arbitrary monomer with index n and the one with index $n + N/2$. The solid line has slope four and zero intercept.

were made locally commensurate with the substrate; i.e., the ideal bond length between two adjacent monomers in the backbone of the chain was made identical to the spacing between two potential energy minima of the substrate. Polymer segments can now locally rearrange without changing the net energy of the polymer. It had been argued that one possible reason for the $N^{-3/2}$ power law is that substrate-mediated forces may be correlated [2]. Our results are consistent with this conjecture: For commensurate polymers, D vanishes linearly with N; see [15] for more details. A very long commensurate chain thus diffuses faster than an incommensurate chain despite the better local locking of the commensurate chain.

As the chain's conformation in good and bad solvents is quite distinct, one may also expect different scaling laws $D(N)$ for good and poor solvent conditions. In fact, in the range of degrees of polymerization investigated, D decreases exponentially fast with N in bad solvents as can be seen in the inset of Fig. 1. There are two key factors that contribute to the slow dynamics in poor solvents: First, denser structures lead to more highly correlated motion of the monomers; i.e., in poor solvents, the longer the chain, the more monomers have to move at a given time when one monomer jumps from one favorable site on the substrate to the next one. Second, as the bonds between adjacent monomers in the polymer do not have to be quasi-parallel to the surface as soon as more than a single layer is formed, the polymers have more geometric flexibility to lock into the registry of the substrate. This locking then leads to exponentially increased barriers to diffusion. A similar argument was held responsible for the nonmonotonic dependence of D on surface coverage Γ [13], as mentioned above.

So far, we have considered only the chain's center-of-mass motion. It is worth noting that the internal relaxation dynamics follow the trends known from the bulk [16]; in

particular, the relaxation time of the end-to-end distance is inversely proportional to the chain's centroid diffusion constant. Specifically, for all simulations presented here we find that the equation $\tau = R_g^2/2dD$ holds within a stochastic error of about 6% (see Fig. 2). This shows that the polymers do not translate as rigid units.

In conclusion, our MD simulations support the observation that the exponent in the relation $D \propto N^{-y}$ is mainly determined by the phase of the substrate [5]; i.e., $y = 1$ for fluids substrates and $y = 3/2$ for solid substrates. However, we achieved these results by using discrete, solid surfaces with *finite* energy barriers and without sticking points, while our fluids did not have (artificial) heterogeneities. We could also show that strongly adsorbed ring polymers and locally commensurable polymers have weaker scaling with $y = 1$ and, moreover, predict an exponential decrease in D for poor solvent conditions.

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[1] R. Azuma and H. Takayama, J. Chem. Phys. **111**, 8666 (1999).
[2] S. A. Sukhishvili *et al.*, Macromolecules **35**, 1776 (2002).
[3] T. G. Desai, P. Keblinski, S. K. Kumar, and S. Granick, J. Chem. Phys. **124**, 084904 (2006).
[4] T. G. Desai, P. Keblinski, S. K. Kumar, and S. Granick, Phys. Rev. Lett. **98**, 218301 (2007).
[5] H.-J. Qian, L.-J. Chen, Z.-Y. Lu, and Z.-S. Li, Phys. Rev. Lett. **99**, 068301 (2007).
[6] B. Maier and J. O. Rädler, Phys. Rev. Lett. **82**, 1911 (1999); Macromolecules **33**, 7185 (2000).
[7] L. Zhang and S. Granick, Proc. Natl. Acad. Sci. U.S.A. **102**, 9118 (2005).
[8] T. Dertinger *et al.*, Langmuir **22**, 9339 (2006).
[9] E. Eisenriegler, *Polymers Near Surfaces* (World Scientific, Singapore, 1993).
[10] J. Zhao and S. Granick, J. Am. Chem. Soc. **126**, 6242 (2004).
[11] A. Milchev and K. Binder, Macromolecules **29**, 343 (1996).
[12] J. Klein Wolterink, G. T. Barkema, and M. A. Cohen Stuart, Macromolecules **38**, 2009 (2005).
[13] D. Mukherji and M. H. Müser, Phys. Rev. E **74**, 010601(R) (2006); Macromolecules **40**, 1754 (2007).
[14] K. Kremer and G. S. Grest, J. Chem. Phys. **92**, 5057 (1990).
[15] See EPAPS Document No. E-PRLTAO-100-068806 for supplementary figures and material. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[16] W. Paul, K. Binder, D. W. Heermann, and K. Kremer, J. Chem. Phys. **95**, 7726 (1991).