Auxiliary material: "Scaling laws of single polymer dynamics near attractive surfaces"

This electronic auxiliary material contains supportive evidence for claims made in the main text.

STRUCTURAL PROPERTIES

To give an impression of the various systems analyzed in the main part of our letter, a few snapshots are shown in Fig. 1.

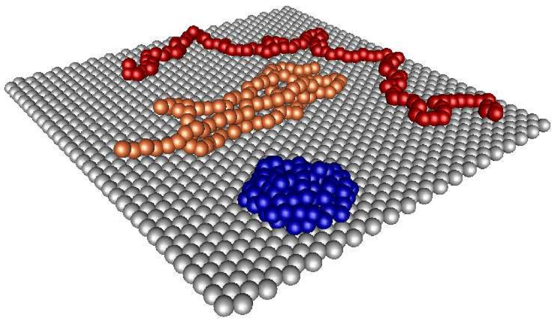

FIG. 1: Three investigated polymer configurations with $N = 100$ are shown. The (red) snake-shaped chain is a typical configuration of a strongly-adsorbed, linear chain in good solvent. The (orange) slightly self-entangled chain represents an artificially created knot, which becomes unstable after a few 10^5 time steps. The (blue) dense structure represents a single polymer in poor solvent conditions.

In the main part of our manuscript we claim that our model reproduces the correct static features of adsorbed polymers. As to be expected for a self-avoiding walk in $d = 2$ dimensions, the in-plane tensor of gyration, $R_{\mathrm{g,i}}$ for both linear and ring polymers scales with a power law $R_{\mathrm{g,i}} \propto N^{\nu}$ with $\nu = 3/(d+2)$ in good solvent conditions [P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, London, 1979)]. In poor solvent conditions, $R_{\mathrm{g,i}}$ scales with $N^{1/3}$ as one would expect from a dense structure. Evidence for this claim is presented in Fig. 2 in this auxiliary material. The height of the caps is consistent with an increase proportional to $N^{1/3}$, which we do not explicitly demonstrate here.

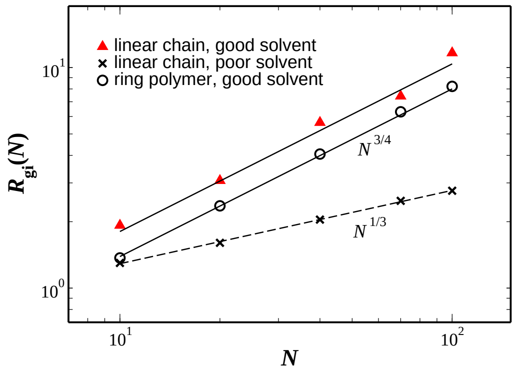

FIG. 2: In-plane radius of gyration R_{gi} as a function of degree of polymerization N for linear and ring polymers. Solid and broken lines reflect the power laws $N^{3/4}$ and $N^{1/3}$, respectively.

DYNAMICS

In the main text, we make the claim that the dynamics that are consistent with $D \propto N^{-3/2}$ can be obtained on solid surfaces, even when the linear chains do not reptate. While this claim can best be supported with a real movie, the sequence of configurations shown in Fig. 3 may reveal that the polymer does not show a motion along its backbone.

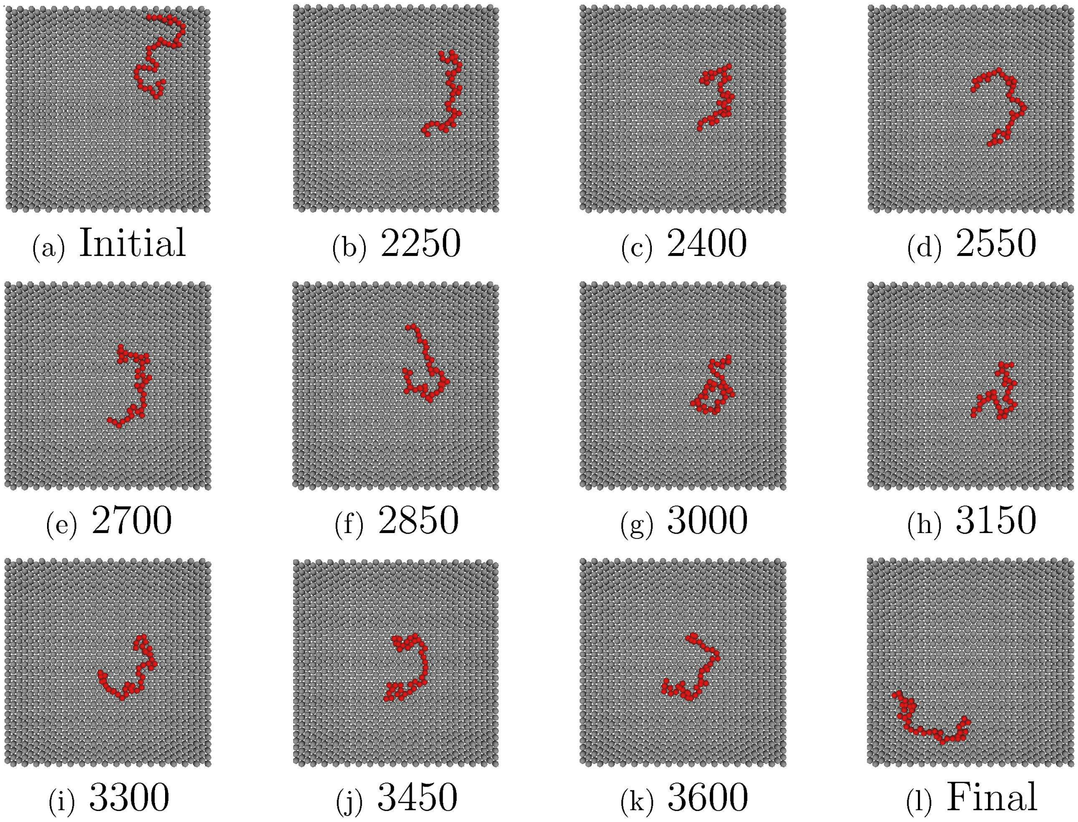
(a) Initial (b) 2250 (c) 2400 (d) 2550
(e) 2700 (f) 2850 (g) 3000 (h) 3150
(i) 3300 (j) 3450 (k) 3600 (l) Final

FIG. 3: Sequence of snapshots at different times - as measured in units of Lennard Jones time. The initial time would be $t = 0$, while the final time is $t = 5,000$.

In the main text, the claim is made that polymers that are locally commensurate show less weak scaling than incommensurate polymers. This leads to the counter-intuitive behavior that polymers that are locally commensurate with the substrate can diffuse faster than those that are incommensurate, even though their local dynamics must be slower, since all atoms can simultaneously sit in potential energy minima. However, presence of incommensurability results in a more correlated movement of monomers. In Fig. 4 we provide a schematic, graphical rationale why the motion for a commensurate chain is uncorrelated, i.e., individual segments can move without changing the potential energy of other monomers. For incommensurate monomers, a similar argument does not hold and thus correlation can exist over many different bond lengths.

The stronger scaling of incommensurate chains is demonstrated in Fig. 5. As argued in the main text, short commensurate chains diffuse more slowly because the local locking is better, however, for long chains, the incommensurate chain is slower.

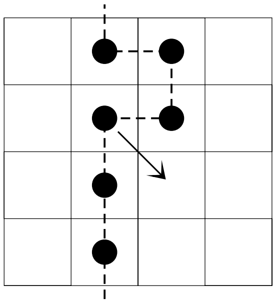

FIG. 4: It is shown that a monomer residing in a commensurate substrate (as indicated by the grid) can make a local move (as indicated by the arrow) without affecting the energy of other monomers. A similar sketch cannot be drawn if polymers and substrate are locally incommensurate. All monomers will have to readjust after a single monomer has been moved.

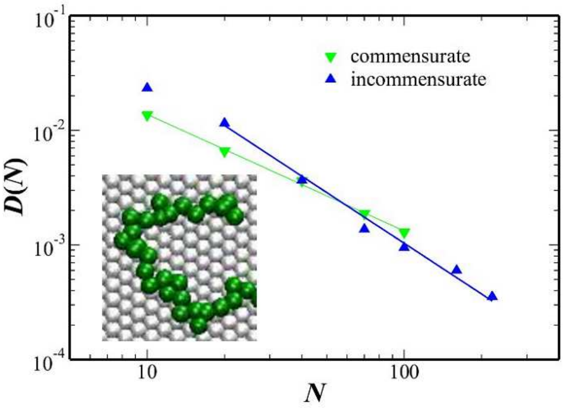

FIG. 5: Comparison of the diffusion coefficient for polymers that are locally either commensurate or incommensurate with the substrate. Incommensurate systems show $1/N^{3/2}$ scaling, while commensurate systems show $1/N$ scaling. The inset shows a snapshot of a part of an adsorbed chain that is commensurate with the substrate.

MODEL DETAILS

Our simulations are based on a well-known bead-spring model by Kremer and Grest [K. Kremer and G. S. Grest, J. Chem. Phys. 92, 5057 (1990)], in which monomer units interact with Lennard Jones potentials

$$V_{\mathrm{LJ}} = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^{6}] - V_{\mathrm{cut}} \tag{1}$$

if the distance r between two monomers is less than a cutoff distance r_{c}. V_{cut} is chosen such that V_{LJ} is zero for $r \geq r_{\mathrm{c}}$. In poor solvent conditions, $r_{\mathrm{c}} = 2 \cdot 2^{1/6}\sigma$ is chosen, while good solvents are modeled with $r_{\mathrm{c}} = 2^{1/6}\sigma$. Adjacent monomers on a chain are additionally bound by a FENE potential

$$V_{\mathrm{chain}}(r) = -(1/2)kR_0^2 \ln[1 - (r/R_0)^2], \tag{2}$$

where $R_0 = 1.5\sigma$ and $k = 30\varepsilon/\sigma^2$. The results presented in the main text and in the auxiliary material are expressed in units of the Lennard Jones energy ε, the Lennard Jones radius σ, and the mass m of individual monomers.

The thermal energy is set to 0.5ε, which makes the polymers stick to the substrate and to themselves in poor solvents. They are yet sufficiently mobile to diffuse laterally during the time scale of the simulation.

Temperature is imposed with the coupling of monomers to a Langevin thermostat which acts only on the *normal* to the surface. There is no implicit or explicit coupling to solvent particles. As argued in the main text, the translation-rotation coupling due substrate corrugation induces a weak effective damping in lateral direction, see also D. A. Aruliah, M. H. Müser, and U. D. Schwarz, Phys. Rev. B 71, 085406 (2005).

The substrate consists of a (111) surface of a face-centered-cubic solid. The geometry is essentially square with a fixed linear dimension of 75 σ 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 1.209 σ. In some cases we also performed simulations where nearest neighbor lattice spacing is made comparable to the effective bond length of polymer (i.e., 0.97σ). Monomers and substrate atoms interact with the same potential as monomers interact with each other in poor solvent conditions.

In figure 6 it is demonstrated qualitatively that roughness can be reduced by increasing the Lennard Jones radius for the interaction between monomers and wall atoms.

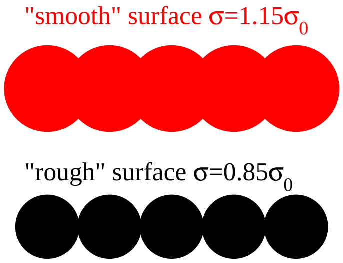

FIG. 6: Two surfaces are drawn in which the spacing between the surface atoms is identical. However the LJ interaction radiiσ differ between the two. The larger value of σ leads to the smoother surface envelope. The values are exaggerated with respect to those used in the simulations for demonstration purposes.