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Materials science

Diffusion of a polymer 'pancake'

Thread-like chains of flexible polymers that adsorb to a solid surface assume a flat 'pancake' conformation¹ when the surface coverage is low and are only able to diffuse in two dimensions because so many segments are adsorbed. Here we show that the centre-of-mass diffusion coefficient of the polymer chain, measured at dilute coverage to ensure minimal chain–chain interaction, has a strong power-law dependence on the degree of polymerization. This non-linear dependence of polymer diffusion on a solid surface contrasts with the linear dependence observed on a fluid membrane².

Our system consisted of polyethylene glycol (PEG) adsorbed from aqueous solution onto a monolayer surface of self-assembled octadecyltriethoxysilane³ coated onto a fused silica coverslip to render it hydrophobic (because PEG does not adsorb from aqueous solution to hydrophilic fused silica at high pH).

Diffusion was investigated by fluctuation correlation spectroscopy^{4–6} of a mono-end-labelled fluorescent probe after two-photon excitation. The focused two-photon beam creates an illuminated spot with a beam waist of about 0.3 μm. The small number of fluorophores contained within a given volume (typically 3–10) fluctuates as polymers diffuse in and out. The fit to the autocorrelation function determines the mutual diffusion coefficient (D_M) of the fluorescing species, and $D_M \approx D$, the centre-of-mass diffusion coefficient, because the system is dilute. Experiments were followed using a Zeiss microscope with a 63× Plan Achromat objective (numerical aperture 1.4).

We varied the PEG polymer chain length (Fig. 1 legend) by a factor of 15. Polymers were allowed to adsorb for less than 5 min from dilute (1–10 nM) solution in 0.01 M aqueous phosphate buffer, pH 8.4. To study bulk solutions, PEG samples were labelled with fluorescein 5-isothiocyanate, and for monitoring surface diffusion, we used an Alexa-488 label (from Molecular Probes), a

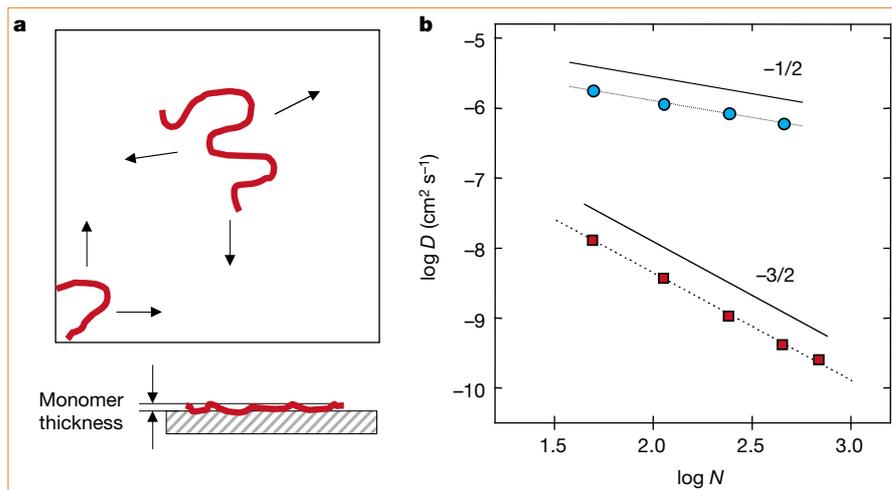


Figure 1 Comparison of polymer diffusion when adsorbed to a solid surface and in free solution. **a**, Flexible polymer chains that adsorb are nearly flat at dilute surface coverage ('de Gennes pancake'). The sticking energy for each segment is small, so no single segment is bound tightly, but the molecular sticking energy is large. **b**, Diffusion coefficients (D) in dilute solution (circles) and at dilute coverage on a solid surface (squares) are plotted on log–log scales against degree of polymerization (N) at 22 °C, for chains of weight-average molecular weights, M_w , of 2,200, 5,000, 10,800, 20,100 and 30,500 g mol⁻¹ and M_w/M_n values of 1.01–1.03 (where M_n is the number-average molecular weight).

derivatized rhodamine-green molecule. Control experiments demonstrated that unattached fluorescent labels did not adsorb, confirming that adsorption was controlled by polymer–surface attraction. At this dilute surface coverage, 0.5–2% of the saturating amount of polymer adsorbed.

We estimated the 'sticking energy' of the polymer as 0.5–1 $k_B T$ per segment, where k_B is Boltzmann's constant at T the absolute temperature. This emerged consistently from analysis of the Langmuir isotherm at low surface coverage, and from Arrhenius analyses of the very slow desorption rate and of the data presented below after extrapolation to the molecular weight of a single segment. Polymer chains thus adsorb, at low coverage, in a flat 'pancake' conformation¹ (Fig. 1a).

Measurements of D (Fig. 1b) reveal a power-law scaling with the number of chain segments (N), so $D \approx N^{-3/2}$. This is strikingly stronger than the $D \approx N^{-1}$ relation observed for charged, semi-flexible DNA obeying excluded volume statistics but adsorbed by Coulombic attraction on a fluid lipid membrane². The key difference is that adsorption sites on a solid surface are static, so the rate-limiting events concern the polymer rather than surface. For diffusion in solution, our results are consistent with standard hydrodynamic results for chains of moderate length, when $D \approx N^{-1/2}$ (refs 7,8).

Reptation (the diffusion of a chain, snakelike, along its own length) may explain this stronger dependence of D on N for polymers under our conditions. In this model¹, the terminal relaxation time scales as $\tau_{\text{rept}} \approx N^3$. Knowing that the radius of gyration (R_g) scales as $R_g \approx N^{3/4}$ in a good solvent in two dimensions^{2,9}, and arguing

that $D \approx R_g^2 / \tau_{\text{rept}}$, it follows that $D \approx N^{-3/2}$ for chains with excluded-volume statistics, as we find here. A simulation for a single self-avoiding chain diffusing among regularly spaced obstacles in two dimensions also gives $D \approx N^{-3/2}$ (ref. 10). But interpreting the value of scaling exponents is a problem, particularly as they seem to depend on obstacle density¹¹.

Reptation may be considered surprising in a dilute system where the physical origin of the static constraints that suppress lateral motion is unclear. But if there were some slack between sticking points — for example, loops of an isolated flexible chain might propagate with high probability along its length in a caterpillar-like fashion — the mathematics of the reptation model would then apply, despite the unconventional physical situation.

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