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# Shear-Induced Desorption of Isolated Polymer Molecules from a Planar Wall

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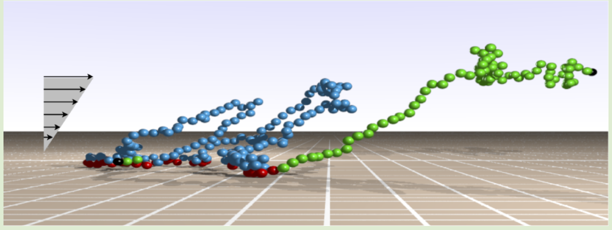
Supporting Information



**ABSTRACT:** We use Brownian dynamics simulations with hydrodynamic interactions to reconcile the apparent contradictions in experiments on the effect of shear flow on desorption of polymers. Our simulations show that desorption is governed by an interplay between chain-wall attraction and wall-induced hydrodynamic repulsion. When adsorption is weak, the chains form large loops and tails that generate stronger hydrodynamic interactions in the presence of the imposed shear flow, causing longer chains to desorb faster than shorter ones. In contrast, when adsorption is strong, the chains adopt a flattened conformation, weakening hydrodynamic interactions and resulting in shorter chains with fewer sticking points desorbing faster than longer ones.

The interaction between a single flexible polymer chain and an adsorbing wall is a classical problem in polymer physics with important technological applications in surface science.[1−7] The equilibrium thermodynamics of an adsorbed chain are well understood, balancing the favorable enthalpy from segmental attachment with the loss in conformational entropy of the chain due to confinement by the wall.[8−11] Unfortunately, even one of the simplest nonequilibrium perturbations (of practical interest) to the chain adsorption problem, an applied shear flow, is poorly understood. Experiments clearly show that desorption occurs in the presence of sufficiently strong shear flow,[12] but the literature is replete with mutually conflicting observations about phenomena as basic as the role of molecular weight.[13−16] In particular, experiments by Lee and Fuller[13] showed desorption to increase with an increase in shear rate for fixed molecular weight samples, but Soga and Granick[16] found minimal desorption, even at much higher shear rates. Moreover, Lee and Fuller also reported desorption to increase with an increase in molecular weight at a fixed shear rate, an observation not in agreement with later experiments by Chang and Chung.[15] In this Letter, we use Brownian Dynamics (BD) simulations to show that polymer desorption in the presence of flow is primarily driven by polymer-wall hydrodynamic interaction (HI), thereby resolving these apparently contradictory experimental results. By definition, HI cannot affect the equilibrium thermodynamics, which highlights the fundamental point of departure from the no-flow case.

The hydrodynamic interactions between a polymer chain and an adsorbing wall are tightly coupled to the chain conformation, so it is worthwhile to recall the key results for chain conformations in the absence of flow before proceeding to the nonequilibrium case. The conformation of an adsorbed chain is usually described in terms of three kinds of subchains: (i) *trains*, which have all their segments in contact with the surface, (ii) *loops*, which are sections of the chain between two trains, and (iii) *tails*, which are nonadsorbed chain ends. For an infinite chain, adsorption occurs only when the segmental adsorption energy $\varepsilon_w$ exceeds the critical adsorption strength $\varepsilon_w^c$. Adsorption is considered to be weak if the adsorption energy is close to the critical point, that is, $(\varepsilon_w - \varepsilon_w^c)/\varepsilon_w^c \ll 1$, and strong otherwise. The structure of weakly adsorbed chains is characterized by the presence of a number of large loops and tails, whereas strongly adsorbed chains have long trains interspersed by a few small loops. In the presence of shear flow, the loops and tails respond to the imposed flow field (see Figure 1) and give rise to HI-induced migration, whereas trains being bound to the wall inhibit migration.

Although it may appear obvious that increasing shear rate will lead to more desorption because of an increase in drag on the chain, the real cause for desorption is a consequence of HI between the polymer chain and the wall.[17−22] In the absence of HI with the wall, there is no mechanism forcing the chains to drift away from the wall other than diffusion. If an adsorbed chain does indeed unbind from the surface, it will readsorb and, on average, there will be no change in the amount of polymer adsorbed. In the presence of shear flow, the velocity gradient across a polymer chain causes a net stretching of the chain along the flow direction. The resulting entropic restoring force behaves as a pair of oppositely directed point forces acting on the solvent. Owing to the no-slip and the no-penetration

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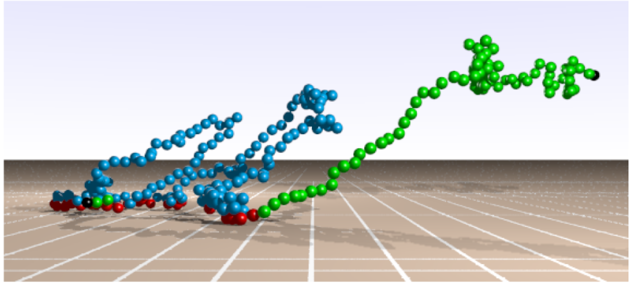

**Figure 1.** Snapshot from a BD simulation shortly after initiation of shear flow ($\dot{\gamma} = 0.5\tau^{-1}$) showing the conformation of a single (weakly) adsorbed chain of 256 segments near a planar wall. The flow direction is toward the right, parallel to the wall. The segment-surface interaction energy is $0.8kT$. The red beads represent segments in the train state, the green beads represent segments in the tail state, and the blue beads represent segments in the loop state. The chain ends are marked by black beads. The white lines on the plane are meant to give a sense of perspective and should not be misunderstood as representing a patterned surface.

conditions at the wall, the velocity field induced by these point forces possesses some component directed away from the wall (see the streamlines pointing away from the wall in Figure 2), leading to a net migration of the chain.

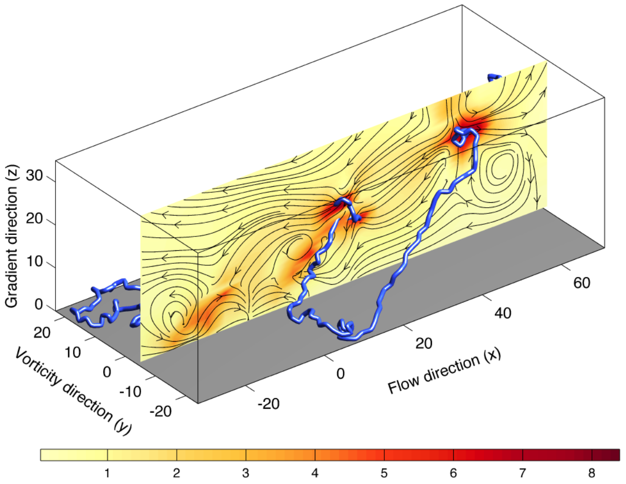

**Figure 2.** The same conformation as in Figure 1 (shown here as a blue tube), obtained from BD simulations shortly after the startup of flow, along with the perturbation velocity field **v** due to the presence of other beads at the plane $y = -5$ (along the vorticity direction of the imposed shear flow). The solid lines show the streamlines of $v_x$ and $v_z$ and the colors represent the magnitude of the velocity field, that is, $|\mathbf{v}| = [v_x^2 + v_y^2 + v_z^2]^{1/2}$, at the respective points in the plane. The spatial dimensions have units of $a$ and the magnitude of the velocity field is in units of $a/\tau$.

To study the desorption phenomenon in detail, we performed Brownian dynamics simulations with HI of a Kremer-Grest[23] bead−spring chain model of an adsorbing polymer in a shear flow. (The data appearing in Figures 1 and 2 were obtained from these simulations.) While some coarse insights into the problem can be gained by using a dumbbell model of the polymer,[18,19] the internal degrees of freedom embodied in the bead−spring chain model are critical to connecting the chain configuration and hydrodynamic interactions. Our polymer model and the implementation of the BD simulations are described in detail in the Supporting Information. In what follows, we use the bead diffusion time $\tau$ as the unit of time.

Even though the motion of the chain as determined from BD simulations is complicated, the underlying physics are readily explained. There are three major parameters of interest here: (i) the adsorption energy $\varepsilon_w$, (ii) the shear rate $\dot{\gamma}$, and (iii) the chain length $N$. The effects of changing the first two parameters are easily understood. Similar to the no-flow case, increasing $\varepsilon_w$ beyond $\varepsilon_w^c$ will lead to a more strongly bound chain; hence, it is obvious that desorbing such a chain will be harder and will require a much higher shear rate. The critical adsorption energy[11] for this polymer model and wall potential is $\varepsilon_w^c \approx 0.758kT$ (see Supporting Information for the details of this calculation). The role of shear rate is equally transparent: increasing the shear rate increases the desorption of the chain in the BD simulations (see Supporting Information), consistent with what is predicted from kinetic theory for a dumbbell model.[18,19] Note that the shear rate needs to be sufficiently high, as evidenced by the lack of any shear rate dependence on desorption in the experiments of Chin and Hoagland,[14] where the shear rates were nearly 2 orders of magnitude lower than those of Lee and Fuller.[13]

The role of molecular weight is considerably more interesting and provides the key insights to reconcile the disparate experimental results.[13−16] Figure 3 illustrates the effect of molecular weight on desorption at a shear rate of $0.5\tau^{-1}$ for different chain lengths. The top plot corresponds to a weakly adsorbed chain ($\varepsilon_w = 0.8kT$) and the bottom plot corresponds to a strongly adsorbed chain ($\varepsilon_w = 1kT$). In both cases, there is a monotonic decrease in the fraction adsorbed, and no steady state appears within the time range shown. Nevertheless, the transient behavior clearly indicates an inversion of the desorption order over a very narrow range of adsorption energies; the long chains desorb first in the weakly adsorbed case, where as the short chains desorb first in the strongly adsorbed case. The reversal occurs through intermediate states, for example, at $\varepsilon_w = 0.85kT$, when all the graphs appear to collapse before separating out in the opposite direction as $\varepsilon_w$ increases further (see Supporting Information for the entire set of plots). Note that there is negligible desorption in the absence of hydrodynamic interactions over this time scale, as shown for a similar model in the Supporting Information and the absence of a depletion layer thickness in kinetic theory.[18]

The origin for this inversion in desorption behavior as a function of molecular weight, described schematically in the Supporting Information, is the coupling of HI between the chain and the surface and the chain conformation. At low adsorption energies ($\varepsilon_w = 0.8kT$), the chains form large loops and dangling tails, as we saw in Figure 1. The perturbation flow caused by HI, illustrated in Figure 2, is substantial for segments of the chain that are not proximate to the surface. Since the polymer-wall HI leads to drift away from the wall by the shear-induced migration mechanism,[22] increasing the size of the loops and tails increases the shear-induced migration. For the molecular weights we studied here, longer chains form longer protrusions from the surface and thus desorb first. The desorption order is the same as in the experiments of Lee and Fuller,[13] which seems reasonable because the adsorption energy of polystyrene on chrome from those experiments is commensurate with thermal energy.

In contrast, at higher adsorption energies ($\varepsilon_w = 1kT$), Figure 3 shows that shorter chains desorb faster than longer chains. At higher adsorption energies, chain-wall attraction dominates; the

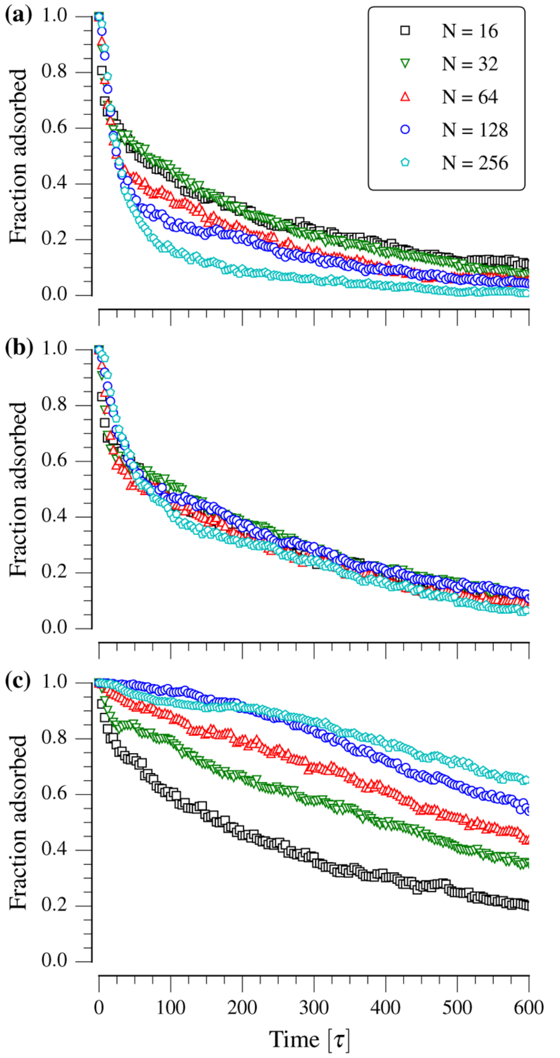

**Figure 3.** Fraction adsorbed vs time at a shear rate of $0.5\tau^{-1}$ for chains of different lengths for (a) weak adsorption ($\varepsilon_w = 0.8kT$), (b) moderate adsorption ($\varepsilon_w = 0.85kT$), and (c) strong adsorption ($\varepsilon_w = 1kT$) .

chains lie flat on the surface and chain-wall HI is minimal. But hydrodynamic drag still exists, and high shear rates aided by thermal fluctuations and excluded-volume interaction may lead to transient detachment of sections of chains from the wall. These detached portions can then be subject to wall HI, slowly peeling the chain away. Desorption occurring this way is easier for shorter chains, as they have fewer sticking points with the wall. Note that this mechanism is very different from the one primarily driven by wall HI in the case of low adsorption energies. The effect of stronger surface adsorption energy on the desorption order can be clearly seen from the experiments of Chang and Chung,[15] where lower molecular weight poly(vinyl acetate) showed more desorption compared to higher molecular weight samples. We speculate that the experiments of Soga and Granick,[16] which have a surface adsorption energy several times larger than thermal energy, would have exhibited behavior similar to that shown in Figure 3c if they had investigated the effect of molecular weight.

To summarize, chain desorption in shear flow is governed by (i) the size of the loops and tails of the adsorbed chain and (ii) the strength of chain-wall hydrodynamic interactions produced by such configurations. Our conclusions are drawn from simulations of relatively short chains under high shear rates (and thus high Weissenberg numbers, Wi). This is a computational necessity; experiments[13] and kinetic theory[19] indicate that steady-state requires around $10^5$ chain relaxation times, an infeasible time scale to simulate by Brownian dynamics. Nevertheless, we expect our conclusions will hold at lower shear rates. To a first approximation, the configurations of the adsorbed chain, that is, the size of the tails and loops, are governed by the adsorption strength rather than the flow. The primary contribution of the shear rate is to set the time scale for desorption by deforming the chain from its equilibrium adsorbed state and thereby producing the HI-induced drift from the wall. As a result, we expect the physical picture we have presented to apply to situations where (i) the effect of flow is strong compared to chain relaxation (Wi > 1) so that the chain is indeed deformed by the flow, and (ii) the chain is long enough to form protrusions that extend far from the surface. Both of these conditions are realized in experimental systems.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Simulation method and additional results showing the effect of shear rate, adsorption energy, and chain length on desorption. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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