Perspective: Kinetic and mechanical properties of adsorbed polymer layers

S. Granick[a]

Department of Materials Science and Engineering, University of Illinois, Urbana, IL 61801, USA

One of the ironies of polymer science is that the intense interest in the dynamics of flexible and semiflexible macromolecules in the bulk [1–3] is not yet of major enough concern regarding polymer surfaces, the preoccupation being with equilibrated conformations. The current situation is summarized in an authoritative treatise [4] and epitomized by important recent papers [5]. Drawing inspiration from the influential analogy by Guiselin between the burgeoning loops of adsorbed polymers and polydisperse polymer brushes, proposed 10 years ago [6], the interesting accompanying paper aims to explain the hysteresis of force-distance profiles in terms of the memory of an earlier state to which polymer layers were more highly compressed [7]. An even larger challenge will be to understand the *time* needed to *lose memory* of the previously adsorbed state. Polymer science does not yet have enough understanding of this question —the connection between rates, and surface-adsorbed states.

Another irony is that the intense concern with bulk polymer *crystallization* and *morphology* is so restricted to what happens in the bulk. Studies of short alkanes show that confinement at or between surfaces can promote crystallization at temperatures where the bulk fluid is in the fluid state [8,9], so it is reasonable to expect the same trend for polymers. The interesting suggestion by Johner and Semenov [10] that confinement promotes local crystallization of the sample, which amounts to an alternative explanation to that proposed in the adjoining paper, should therefore be considered seriously. It is a limitation of our field that the definitive answer is still speculative.

It is worthwhile to summarize some unsolved theoretical and experimental problems concerning kinetic and mechanical properties of adsorbed layers:

1) *Entanglements*. It is well known that long-chain flexible molecules exhibit special dynamic and elastic properties due to the fact that they cannot cut through
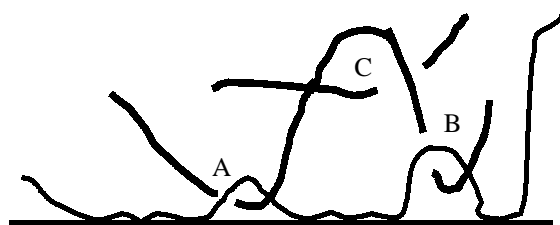
[a] e-mail: `sgranick@uiuc.edu`

Fig. 1. Hypothetical surface entanglements occasioned when flexible polymers thread through surface-attached loops. Entanglement is more severe at point A than at point B because the loop in the former case is tighter. Entanglement at point C illustrates that, hypothetically, surface-enhanced entanglements propagate in the direction normal to the surface. The decay distance to bulk behavior is not known.

each other. For fluids, the effects of these long-range correlated motions are transient in time and the intensity of entanglement, which determines the time scale of relaxation, has been described in various ways.

Evidence of unusually slow conformational relaxations in adsorbed polymer layers has been accumulating for a long time, and it is likely that adsorption can exacerbate entanglements. Figure 1 illustrates the entanglement presented to an unattached flexible polymer by the loop of an adsorbed polymer chain. It is reasonable to expect that the implied "tube diameter" and "critical molecular weight for entanglement" [1–3] will be reduced relative to those for the bulk, as the tube diameter in this example is dictated literally by the distance between adsorption sites that define the polymer loop. There is experimental support in favor of this idea; there is a strong topological influence on desorption kinetics, with the N^{-2} dependence on degree of polymerization N expected for flexible linear chains from concepts of reptation, and strong quenching when polymers are branched [11].

How to generalize this to an ensemble of flexible chains at surfaces? If polydisperse loops present a distribution

of effective tube lengths (as suggested in Fig. 1), what *average, effective* near-surface tube length results? It is even not clear if an effective tube diameter is relevant as (like the weakest link of a chain) the whole dynamics may be modified (if not controlled) by a single "A-type" entanglement (sketched in Fig. 1), assuming that this is an extremely tight one. In any case, the average may not be a simple linear average. If entanglements are enhanced near surfaces, as the cartoon in Figure 1 suggests, it helps to rationalize one reason why near-surface polymer dynamics are so retarded relative to those of the same polymer in the bulk.

Measurements of the shear spectra of confined polymer films (the linear viscoelastic shear responses as they depend on frequency) support this idea qualitatively [12, 13]. But for definitive interpretation in *molecular* terms of these ensemble-averaged force experiments, direct experiments at the molecular level are desirable. Probably the single most important foundation for understanding polymer dynamics in isotropic three dimensions —the single molecule in a sea of solvent, without interactions with neighboring macromolecules— has not seen yet a definitive theoretical or experimental counterpart in surface studies. The isolated macromolecule is the situation that is conceptually most simple and pure. It leads to landmark predictions, among which we may count the Rouse, Zimm, and reptation models of dynamics [1–3]. Experiments regarding the dynamics of isolated polymer chains at surfaces are at an early stage [14–18] and the consequences of finite surface coverage, leading to entanglement owing to overlap with other chains, are not understood.

2) *Monomeric friction coefficient, ξ_0.* The standard scaling laws for the dynamics of bulk polymers describe the overall relaxation time as the product of two independent quantities: polymer-specific items (*e.g.*, degree of polymerization and chain geometry, such as linear or branched), and chemically specific properties that express the resistance as the segments of polymers diffuse through their environment. This latter quantity, the monomeric friction coefficient, ξ_0, changes with temperature and pressure in ways that can be predicted phenomenologically [1], but its absolute value is, to date, a fitting parameter that cannot be predicted from first principles.

For example, a linear Rouse chain 25 segments long relaxes twice as fast as a linear Rouse chain 50 segments long, and one of the coefficients of proportionality is ξ_0. But there is much evidence that this differs near surfaces —it is the controversial "surface-T_g (glass transition) problem", reviewed recently in this journal [19]. If the segmental mobility of polymers near surfaces differs from that in the bulk, this implies that ξ_0 is different. There is much evidence that near-surface T_g is often (but not always) enhanced relative to the bulk; this helps to rationalize another reason why near-surface polymer dynamics are so retarded relative to those of the same polymer in the bulk. The details for chain dynamics are not enough worked out. Also the distance away from the surface, up to which chain dynamics are perturbed, is not understood.

3) *Near-surface gradients.* A peculiarity of near-surface dynamics is the ubiquity of gradients as compared to the bulk state.

The notion of a single ξ_0 probably oversimplifies the real situation. It has never been evident, even as concerns chains in the bulk, that the monomeric friction coefficient of segments near the end of a chain is the same as near the center. It is even worse when considering adsorbed chains; in Figure 1, it is reasonable to suppose that segments within the surface-hugging "trains" (in intimate contact with the surface) experience greater monomeric friction than segments in loops that dangle away from the surface.

At the solid surface itself, the controlling friction is believed to be a hopping process, the adsorption-detachment of individual segments when they physisorb, and the collective motion that results when numerous segments undergo this hopping in tandem. The intensity of adsorption, described by the parameter χ_s [4], is a stronger impediment than ξ_0, the friction as polymer segments glide past one another at positions removed from the surface. The near-surface T_g phenomenon suggests that ξ_0 varies with distance away from the surface; it probably decreases in cases where the near-surface T_g is reduced relative to the bulk, and vice versa. Quite independently, the near-surface entanglement phenomenon (item # 1) suggests slower near-surface mobility, for independent reasons.

4) *Time-temperature superposition.* The equivalence of time (frequency), and temperature/pressure, in describing the viscoelastic properties of polymers, was worked out by giants in this field [1]. The picture emerges that a single "master curve" underlies all dynamics regardless of the temperature/pressure —different windows on it are opened, depending on the monomeric friction coefficient ξ_0, whose value depends predictably on temperature and pressure. But, if ξ_0 at a surface must be reasonably described as a spectrum instead of a single number, it is not obvious that one can expect time-temperature superposition to hold.

Indeed, is it correct to describe the segmental sticking energy as a unit of $k_B T$ (though this is customary)? To do so implies that it scales with temperature, which is unlikely; it is a misleading convention, because these values are usually determined near room temperature.

From dynamic studies in which temperature was varied, there is some evidence that the relaxation times switch from diffusion-controlled, and exponential (far above the surface glass transition temperature), to adsorption-controlled and stretched exponential (close to the surface glass transition temperature, which for adsorbing surfaces exceeds the bulk glass transition temperature) [20,21]. The existing evidence is indirect, however, as it does not concern single-chain diffusion.

5) *Conformations —a parking problem; or equilibrated?* The adaptability of polymer shape at surfaces suggests that when chains encounter an initially bare surface, they spread on the surface to maximize the number of segment-surface contacts. Chains that arrive later, encountering a fewer number of potential adsorption sites, spread to have what Maria Santore calls a lesser
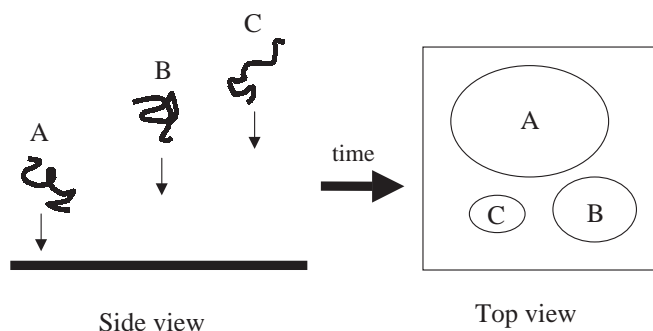
Fig. 2. Hypothetical case where chains encounter an initially-bare surface. The chains that encounter it first (A) spread to maximize the number of segment-surface contacts and the chains that arrive later (B, C) occupy smaller footprints on the surface. On the left, the surface and chains near it are sketched end-on. On the right, they are sketched from the top to illustrate the distribution of footprint size.

"footprint" on the surface. Though contrary evidence also exists [4,22], there is experimental [23–25] and theoretical [26–29] evidence in favor of this idea, which is sketched in Figure 2.

This picture, that the spectrum of polymer conformation in a surface layer is governed by the history of piecemeal surface deposition, contrasts strongly with the expected complete intertwining of polymers, which would occur at conformational equilibrium. The time scales to reach equilibrium may be so long that the applicability to typical situations comes into question. An interesting implication is that the chains that adsorbed later, finding fewer and fewer surface sites available, and hence becoming attached by fewer and fewer segments, should have center-of-mass located farther from the adsorption surface than those that arrived first. If this is the case, it follows that those chains would most influence the hydrodynamic thickness when fluid flows past the surface layer, and, more generally, stress transfer to the matrix nearby. That this can happen in at least one system was demonstrated recently [30].

This issue is fundamental when it comes to interpreting experiments that measure mechanical properties, such as the surface forces apparatus. The measurement generates a single number, the force, but although the surface separations are molecular, the areas of interaction are macroscopic, so this force comes from a macroscopic-sized ensemble of molecules. Under what conditions, and after what equilibration times, are the chain conformations equilibrated?

6) *How does an adsorbed layer respond when driven away from equilibrium?* The questions raised above emphasize what happens for systems at rest, with emphasis on unsolved questions regarding Brownian motion at rest. But many of the most salient experimental questions involve strong deformations away from equilibrium. For example, deformations in the accompanying paper were hardly performed in a quasistatic manner; instead, the adsorbed polymer layers were deformed severely relative to their undeformed dimensions [7].

The success of the tube theories of Doi and Edwards [2], relative to the earlier ideas about reptation [3], illustrates the additional level of complexity when seeking to understand nonlinear (as opposed to linear) responses. That distinction, well-known in the study of bulk viscoelasticity [1], is not often enough remembered when it comes to analyzing the mechanical properties of polymers at surfaces.

My primary aim in this commentary has been to highlight challenges, to argue that our understanding of kinetic and viscoelastic phenomena of flexible polymers at surfaces has not kept pace with its equilibrium counterpart, and to suggest several specific areas where focused experiments and theory would be desirable.

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