Molecular Motion at Soft and Hard Interfaces: From Phospholipid Bilayers to Polymers and Lubricants

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Key Words

diffusion, fluorescence, friction, solid-liquid interface, confined fluid

Abstract

Spatially resolved and time-resolved understanding of complex fluid situations compose a new frontier in physical chemistry. Here we draw attention to the significance of spatially resolving systems whose ensemble average differs fundamentally from the spatially resolved individual elements. We take examples from the field of fluid phospholipid bilayers, to which macromolecules adsorb; the field of polymer physics, when flexible chains adsorb to the solid-liquid interface; and from the field of lubrication, when two solids are squeezed close together with confined fluid retained between them.

INTRODUCTION

Complex fluid: a liquid comprising molecules with complex interaction potentials, often multiphase and multicomponent, with viscosity that depends on deformation rate

Although traditionally among the strongest themes in the study of bulk fluids (1–3), the dynamics of molecular motion is ironically not a major enough concern with regard to interfaces. The main preoccupation with interfaces is rather the understanding of their equilibrium structure. However, the confinement of fluids (ranging from water, hydrocarbon oil, polymer melts, and solution to DNA, proteins, and other biomacromolecules) can strongly modify not only their structure and the way they organize themselves, but also their motions and relaxations. Thus, the problem of surface and near-surface motion is fundamental to a wide range of synthetic materials and processes, as well as to almost all natural and living systems.

Experimentally, those scientists interested in these problems often take one of two approaches, with surprisingly little cross-fertilization between the communities. The community interested in motions at interfaces focuses on methods capable of studying single surfaces using the versatile method of force microscopy. As highly developed methods allow the measurement of forces with extreme sensitivity (4), this experimental approach is popular and increasingly is extended in the direction of measuring responses to linear (5) as well as nonlinear (6, 7) external perturbations. The information obtained is truly at the molecular level in cases in which single molecules are deformed, as when large molecules such as DNA are extended one at a time (8), but more commonly the experiments represent the ensemble-averaged outcome of how many molecules interact. A limitation for these experiments is that they require a theoretical model, from the raw data of force, to the desired output of information about the mechanisms of molecular motion. However, this approach to considering a single surface or the interactions between only two surfaces has the advantage that the chemical and topographical composition of the interface can potentially be controlled well.

The second major approach to the study of motions at interfaces is spectroscopic, by using vibrational spectroscopy (9, 10), dielectric spectroscopy (11–13), nuclear magnetic resonance (14), as well as nonlinear spectroscopies (15). Studies of this kind generally consider highly curved interfaces (such as micelles, emulsions, and porous media), perhaps partly because in these systems the surface-to-volume ratio is so high that the modest number of molecules in any single interface is small, and a large number of interfaces are considered at the same time. In this approach, however, the surfaces in question cannot be as precisely controlled as when dealing with a single interface. A further limitation is that many of these spectroscopic approaches average over a larger surface area (a large volume). Even in cases in which single surfaces are studied, as in some modern experiments using dielectric spectroscopy (12, 13), the experiments are not spatially resolved.

We can appreciate the desirability of a spatially resolved experiment from the following thought experiment. Suppose you survey the audience in a movie theater. Approximately half the audience wears eyeglasses (two eyes per person, usually); approximately half of the audience wears none. On average, the number of eyes bearing eyeglasses is one, but to take this average is too simple-minded. The naive average masks a bimodal distribution that carries physical significance.

Almost always, if one wishes to avoid sampling an ensemble average of many molecules, the experiment must be built on the use of fluorescence methods. Apart from important technique development and numerous applications in the field of biophysics (16, 17), the field of soft matter and materials study has seen few spatially resolved investigations at the single-molecule or few-molecule level. These have come mostly in the past five years and form the topic of this review, which is organized as follows. The following section discusses spatial heterogeneity when macromolecules adsorb to supported phospholipid bilayers. Then we review the related problem of polymer adsorption at the solid-liquid interface. We finish by contrasting friction with diffusion in molecularly thin films. Throughout, we emphasize unsolved problems and areas for useful future research.

Supported phospholipid bilayer: a phospholipid bilayer that conforms to a planar surface; useful for model microscopy and sensor studies

Dynamical heterogeneity: molecular mobility that, in a fluid or glass, is position dependent rather than homogeneous

FCS: fluorescence correlation spectroscopy

SLAVED DIFFUSION IN PHOSPHOLIPID BILAYERS

The presence within phospholipid membranes of molecules such as cholesterol produces heterogeneity; for example, lipid rafts and resulting nanodomains are well documented (18–20). However, the simple process of allowing macromolecules to adsorb also produces dynamical heterogeneity, even when the bilayers comprise one single type of phospholipid. We have known for some time that lipid diffusion depends on the chemical composition and phase state of the bilayer (21–23), but those studies dealt with naked bilayers (no adsorption). We have also known for some time that mixtures of phospholipids partition spatially after an encounter with an adsorbate (24), but those studies did not address the mobility of these lipids. Other diffusion-related studies—such as binding-induced mobility (25–27), anomalous subdiffusion (28), and the influence of obstacles in the diffusing plane (29–31)—have also been considered, but few of them involved macromolecule adsorption.

Dynamical Heterogeneity According to Spatial Position

The use of area-averaged methods to measure mobility suffers from the same potential liability as the naive eyeglass calculation described above. Methods exist to measure local mobility. Fluorescence correlation spectroscopy (FCS) enables one to measure the mobility of fluorescent molecules within the diffraction-limited focus of a laser beam, a diameter of ≈ 0.35 μm (32, 33). In experiments of this kind, it is convenient to design the experimental system so on average one sole fluorescent molecule resides within the area sampled. Then the fluctuations of emitted fluorescence, when fluorescent molecules diffuse into and out of this planar area, reflect their translational diffusion, and the method carries spatial resolution.

Spatially resolved measurements of lipid diffusion were made after macromolecules were allowed to adsorb to supported phospholipid bilayers at incomplete surface coverage (**Figure 1**). For simplicity, to avoid the complexity of having permanent electric charge, a system was chosen in which the lipids carried a zwitterionic head group, a dipolar head group that carries no net electric charge. Depending on where the laser was focused, the rate of fluorescence fluctuation switched; it varied

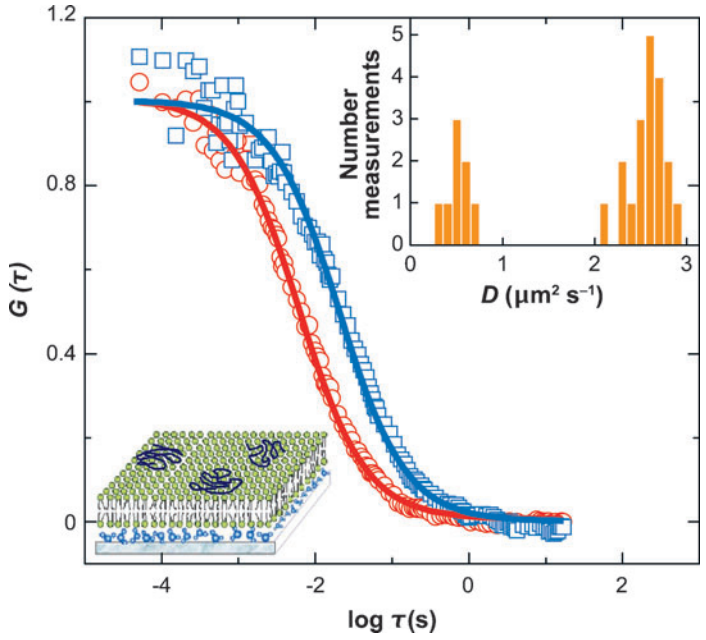

Figure 1

Fluorescence autocorrelation function $G(\tau)$ plotted as a function of logarithmic time lag τ for 1,2-dilauroyl-sn-glycero-3-phosphocholine supported lipid bilayer carrying adsorbed quaternized poly-4-vinylpyridine (QPVP) at the fractional surface coverage of 20%. The QPVP was 100% quaternized with a weight-average molar mass of 81,500 g mol^{-1}. (Fast and slow diffusion modes coexist depending on where the interrogatory laser spot was focused.) (*Inset*) Histogram of diffusion coefficients obtained from ≈ 30 different measurements on a number of samples. The mean D of the slow mode is 0.50 μm^2 s^{-1} with a standard deviation of 0.12, whereas the mean D of the fast mode is 2.62 μm^2 s^{-1} with a standard deviation of 0.18. Adapted from Reference 33.

from spot to spot on the bilayer, slower or faster, but not in between. Studies in the physical sciences rarely encounter this bimodal distribution. More usually, a heterogeneous distribution is evenly distributed around the mean, but it was not so here. **Figure 1** plots the intensity-intensity autocorrelation function computed from the observed fluorescence fluctuations against time lag after the cationic polymer, quaternized polyvinyl pyridine, was allowed to adsorb to partial surface coverage. The physical meaning of the autocorrelation function is to quantify the time for Fickian diffusion through the spot illuminated by the focused laser beam; then the translational diffusion coefficient D scales as the square of its linear dimension, divided by the time at which the autocorrelation function decayed to a given value. Quantitative elaboration of this idea, standard in using the FCS method, also takes into account the Gaussian shape of the spot illuminated by the laser beam (34). Analysis showed that the translational diffusion coefficient was described by a bimodal distribution, taking either faster value, or slower value, depending on where the laser beam was focused in space (33). This finding was robust; the bimodal distribution of diffusion

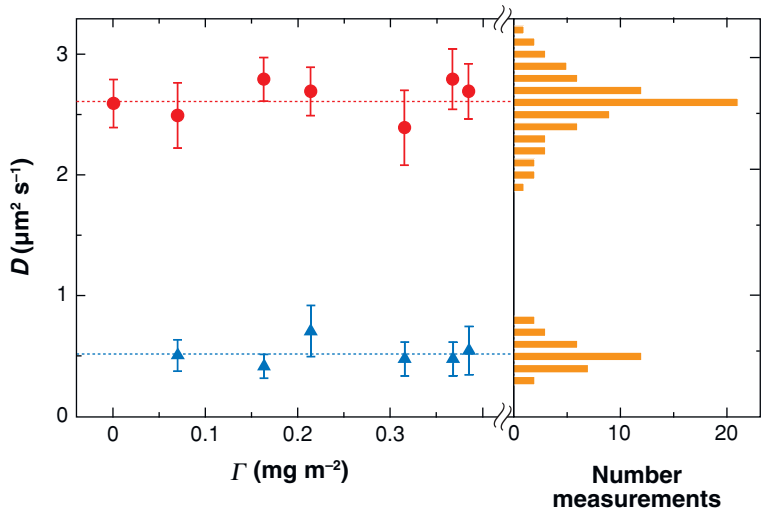

Figure 2

Surface-coverage dependence when surface coverage was <50% of saturated adsorption. (*Left panel*) Diffusion coefficients of the fast and slow modes of lipid motion plotted against surface coverage for the same system as in **Figure 1**. Error bars show standard deviation. (*Right panel*) Histograms of fast and slow diffusion coefficients obtained from ≈ 100 different measurements on a number of samples. Adapted from Reference 33.

coefficients held over a wide range of surface coverage, so long as the surface coverage was less than ≈ 50% of saturated adsorption (**Figure 2**).

This study investigated the influence of polymer molar mass. Always, a fast and a slow mode were observed, depending on where on the bilayer the focused laser beam was directed. The higher the molar mass of the adsorbate, the slower the diffusion. **Figure 3** plots the diffusion coefficient (D) inferred from the slow mode on log-log scales against the degree of polymerization of the adsorbed polymer (N); this chain length varies by nearly an order of magnitude, and the comparison is made at fixed surface coverage, 20% of saturated adsorption. The plot shows clearly an empirical power-law relation, $D \propto N^{-1}$.

Why does this relation exist? The most plausible interpretation of the coexistence of fast and slow diffusion in the same system, concluded from reflection and control experiments, was that macromolecular adsorption created nanodomains of lipid whose mobility was determined by the occluded area of adsorbed polymer (33). The multivalency of these nanodomains (i.e., the multiple potential adsorption sites to which lipid can bind when exposed to an adsorbate whose occluded area is large) caused lipids to remain segregated within separate nanodomains because the tendency to adsorb at any individual spot is amplified by the large number of potential binding sites.

For lipids trapped within these nanodomains, these arguments suggest that collective diffusion as a unit replaced the independent diffusion of individual lipid molecules. The translational mobility of a particle embedded in biological membranes has been

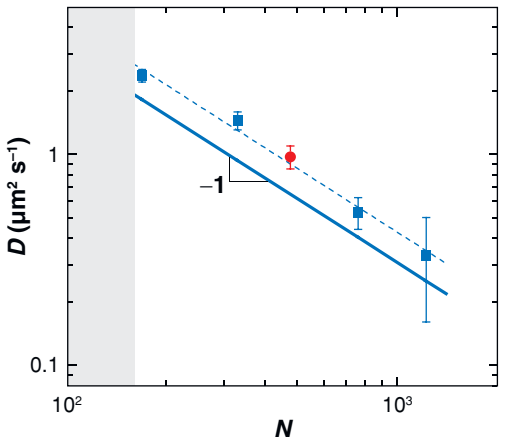

Figure 3

The slow-mode diffusion coefficient plotted against the degree of polymerization of the adsorbed polymer on log-log scales at the fractional surface coverage of 20%; the reference solid line has slope −1. The fully quaternized poly-4-vinylpyridine (QPVP) samples were prepared from parent PVP samples with molar masses M_w = 18,100; 34,200; 81,500; and 13,0000 g mol^{-1} (ratio of weight-averaged to number-averaged molar mass M_w/M_n = 1.11, 1.23, 1.18, and 1.24, respectively) (*solid blue squares*). The adsorbed poly methacrylic acid had M_w = 40,000 g mol^{-1} (M_w/M_n = 1.05) (*solid red circle*). These data extrapolate as N → 150 to D characteristic of the naked lipid (*shadowed area*), implying the slow mode disappears below a critical adsorbate size, a projected area of ≈ 80 lipid head groups. Adapted from Reference 33.

considered theoretically (35). These experiments show that lipid mobility, itself, is affected. Adsorption of macromolecular objects of variable size modifies the mobility of lipids underneath the adsorbed object. This leads to dynamical heterogeneity even though, chemically, the lipid comprises only one chemical species. The dependence on the adsorbed macromolecule's molar mass displays the same phenomenology as the diffusion of that same adsorbed macromolecule (36, 37); diffusion of the lipid appears to be slaved to it. The following section discusses in more detail those pioneering experiments by Maier & Rädler (36–37).

It may seem paradoxical to observe single diffusion processes at each laser focus spot (e.g., **Figure 1**); one may have expected to find a distinction so that lipid diffusion would fall into two populations, corresponding to the inner and outer leaflets of the bilayer. However, when arguments produce a paradox, one learns about the limitations of the model on which the argument is based. In their pioneering work, Bayerl and coworkers (38) studied phospholipid bilayers wrapped around spherical silica beads and concluded, using nuclear magnetic resonance, that lipid diffusion in the inner leaflet was slower than in the outer leaflet by a factor of two. The relevance of this study to planar-supported bilayers was uncertain, however, first because bilayers that coat a colloidal-sized substrate necessarily possess much higher curvature, and second because these colloids are typically rougher than planar surfaces. Using Langmuir-Blodgett methods to form supported bilayers one leaflet at a time, several groups used fluorescence recovery after photobleaching to discriminate between lipid diffusion in

the outer and inner leaflets (39, 40), but the generality of the conclusion was unclear because analysis was based on the assumption that lipid flip-flop between leaflets was slower than the experimental timescale of hours. However, recent sum frequency generation experiments questioned the validity of this assumption by finding lipid flip-flop to be considerably faster than this in the fluid state (41, 42). To further test this question, it seemed worthwhile to revisit it on planar solid supports using few-molecule fluorescence methods. Iodide quenching of dyes in the outer leaflet was used to distinguish diffusion in the inner leaflet from that in the outer leaflet and to confirm the generality of the findings; the bilayers were prepared not only by vesicle fusion, but also by Langmuir-Blodgett deposition. These studies concluded that regardless of whether the bilayers were supported on quartz or on a polymer cushion, translational diffusion in the outer and inner leaflets was the same within an experimental uncertainty of $\pm 10\%$, but with a small systematic tendency to be slower (by $<5\%$) within the inner leaflet (43). Theoretical arguments have interpreted such behavior as indicating that leaflet-leaflet coupling is stronger than leaflet-substrate coupling across an intervening thin water film or polymer cushion (44), but the precise nature of this strong coupling remains to be firmly elucidated at the molecular-mechanism level.

Much prior work considered the area-average mobility in phospholipid membranes, but these experiments show that mobility may vary from spot to spot on the membrane surface, in spite of the same lipid composition. These experimental findings complement the growing number of theoretical studies concerning membranes decorated with anchored or adsorbed polymers (45–50), from which the prediction emerges that adsorption modifies the local bending rigidity and the local spontaneous radius of curvature of the membranes.

This places into curious perspective a large amount of prior research. In the fields of polymer science and biomaterials, it is known that macromolecules adsorb prodigiously from solution because a small adsorption energy per segment adds up to a large adsorption energy per molecule (51). In the field of polymer science, this is traditionally considered to occur on surfaces having a frozen, unresponsive structure, and definitive treatises exist on this subject (51). This does not describe the situation in the previous section.

In contrast, in the study of phospholipid membranes, drug delivery, and gene therapy, interactions with polymers are known phenomenologically to have the capacity to make membranes leaky for the outflow of drugs from vesicles (52) or the inflow of encapsulated DNA into cells (53), for example. In those cases the membrane structure is clearly disrupted. Bacteriocidal action has even been demonstrated (54) by polymer disruption of phospholipid membranes. This said, when supported phospholipid bilayers are used in sensor and materials applications, macromolecules must adsorb heavily.

It is fascinating that these different communities developed with little cross talk. The adsorption and biology communities have focused on the extreme limits—the polymer side of the interface in the adsorption community, and the practical consequences, especially when membranes are disrupted, in the biology community. In fact, recent studies of surface equilibration dynamics at supported phospholipid bilayers

find patterns of dynamic physical behavior that differ remarkably from what is characteristic of adsorption onto frozen surfaces (51, 55–59). This has bearing not only from biological and biophysical standpoints (60), but also for formulating many cosmetics and pharmaceutical products (61). Although considerations of this kind have been known for many years in the field of surface science (62), they also are concerns for phospholipid bilayers, as the dynamics of adsorption and surface equilibration when the surface possesses reciprocal mobility is a largely unsolved problem.

POLYMER DIFFUSION AT THE SOLID-LIQUID INTERFACE

To place the above section into perspective, here we contrast polymer adsorption at the solid-liquid interface—the case in which the solid surface is frozen in place. In this case, the polymer adapts to being adsorbed, but the solid does not reciprocally adapt.

Curiously, little is known about this question, especially when one considers that the goal of understanding diffusion in the bulk composed a large part of the classical agenda of polymer physics (2, 3). To researchers in those early days, dynamics at the individual-molecule level surely underpinned fundamentally the macroscopic properties—viscoelasticity and other ensemble-averaged properties discussed below. Nowadays, study of the mechanisms and timescales of polymer diffusion in solution and in melts composes a developed field of study, summarized in textbooks (2, 3). Although one should never claim that understanding is definitive, polymer science has developed a rather mature understanding of how the dynamics of these molecules depends on chain length, chain architecture, and concentration—but not when interfaces are involved.

Why is this not the case for polymer dynamics at surfaces? Ultrahigh vacuum surface science has studied surface diffusion for many years; polymer science has not. One basic limitation is that the needed experimental tools have not been available. It is true that methods of dynamic-light scattering give insight into the global dynamics of polymer brushes (63, 64). It is also true that in the field of polymer adsorption, work has approached this question from the perspective of understanding surface on-off (adsorption-desorption) kinetics (65, 66). It continues to this day, going well beyond earlier work (67, 68). At the same time, it is also desirable to seek an understanding of in-plane polymer diffusion at surfaces, which is a distinctly different problem.

In the past, techniques imported from other fields of science enabled important advances. Researchers used secondary ion mass spectrometry and related methods from ultrahigh vacuum surface science to measure concentration profiles in multilayer thin films spin-coated onto solid supports, from which diffusion has been cleverly inferred (69–71). Lin et al. (72) used neutron reflectometry to study interdiffusion in thin films. Specular X-ray scattering allowed one to study capillary fluctuations in thin films (73). X-ray scattering was even used to assess segmental equilibration (74). These methods refer to thin melt films on solid supports.

Researchers often use atomic force microscopy and surface force apparatus to measure how friction and surface forces are perturbed when polymer films are very thin (75–78). Force measurements afford no direct measurement of diffusion, however.

A fundamental challenge has always been combining force measurements with spectroscopic information. The scanning-probe community is at an early stage of seeking to meet this challenge, using near-field scanning optical microscopy and surface-enhanced Raman spectroscopy, for example (79). These endeavors are mainly at the stage of technique development.

Apart from experimental difficulties, there are other reasons so little is understood about surface diffusion. So many variables come into play that the field is at an early stage in agreeing on the unifying general principles. For example, that dynamics of polymer chains at and near solid interfaces differs profoundly from the bulk is obvious physically. In the simplest imaginable case (a polymer without enthalpic attraction to the surface), intramolecular conformations must be anisotropic in the directions parallel and normal to a surface, and they also must vary with distance normal to that surface. Structure and dynamics may be further influenced by the attraction of segments to this surface. A large uncertainty concerns the possible effects that topographical and chemical heterogeneity of the surface may have. From this point of view, the interesting computer simulations of how chains diffuse in confined geometries (80–82) and in two dimensions (83–88) are difficult to put into perspective, in the absence of experiments for comparison. This is also related to the thin-film T_g (glass transition) problem, where even the sign of the effect is controversial. Controversies concerning the glass transition in thin polymer films show the impossibility, at the current state of understanding, of generalizing about even the case in which the polymer is attracted to the surface. Different chemical systems appear to behave differently (89–92).

From this perspective, we now discuss the known experimental information about polymer surface diffusion in the dilute regime of surface coverage. The above section introduces the elegant studies of Maier & Rädler (36, 37), in which they used fluorescence microscopy to image the conformations and rates of the lateral self-diffusion of DNA molecules when they were electrostatically bound to fluid lipid bilayers of opposite (cationic) electrical charge. The authors described these shapes perfectly as self-avoiding random walks, and they confirmed experimentally the long-predicted scaling result for chain conformations in a two-dimensional environment with excluded volume interactions. The translational diffusion was also visualized optically. They found the self-diffusion coefficient (D) obeyed Rouse dynamics, $D \sim N^{-1}$, indicating the friction between different parts of the same chain was uncorrelated. This confirmation of the predicted static conformations was pleasing, but presents a puzzle: Why were the chain conformations so strongly influenced by correlations between different segments along the chain, yet the self-diffusion was not? If the surface itself were mobile (in the sense that the rate-limiting event was determined by the motion of adsorption sites on the surface, itself, rather than by the adsorbed polymer), uncorrelated Rouse dynamics of the binding sites that anchor a macromolecule onto that surface would obviously be expected.

To test this idea, Sukhishvili et al. (93, 94) performed experiments in which they allowed a flexible synthetic polymer, polyethyleneglycol (PEG), to adsorb from aqueous solution onto a hydrophobic solid surface, a methyl-terminated self-assembled monolayer. They found the rate of self-diffusion measured by FCS scaled as $D \sim N^{-3/2}$

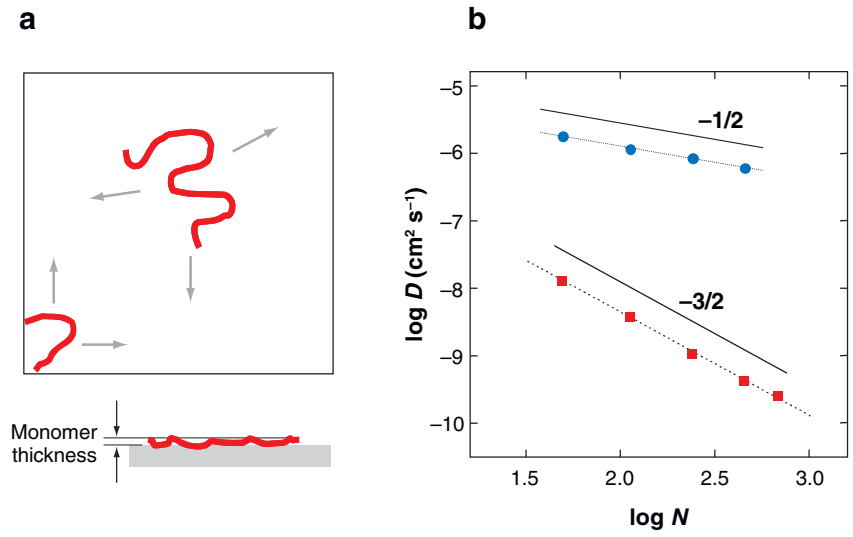

Figure 4

Comparison of polymer diffusion, polyethyleneglycol (PEG), when adsorbed to a solid surface and in free solution. (*a*) Flexible polymer chains that adsorb are nearly flat at dilute surface coverage (i.e., 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 (*blue circles*) and at dilute coverage on a solid surface (*red squares*) plotted on log-log scales against the degree of polymerization (N) at 22°C for chains of weight-averaged molecular weights, M_w, of 2200; 5000; 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-averaged molecular weight). Reprinted by permission from Reference 93.

(**Figure 4**). This nonlinear dependence when the surface is solid contrasts strongly with the linear dependence observed for a fluid membrane. Reptation may explain this stronger dependence on N. In this model, the terminal relaxation time scales in proportion to N^3, so it is easy to show that $D \sim N^{-3/2}$ for chains with excluded volume statistics (94), which is suggestively in agreement with the data.

But why, on these solid surfaces prepared to be as homogenous as the experimentalists could make them, did the experiments suggest strongly that diffusion was dominated by spatial heterogeneity on the adsorbing surfaces? Subsequent molecular dynamics computer simulations elucidated the obstacle density on the transport properties of dilute polymer chains in strictly two dimensions (88). The relevance of two separate factors, surface inhomogeneity and hydrodynamic interactions with solvent molecules, was critically examined. When heterogeneity was introduced by decorating the surface with impenetrable elements, chain diffusivity crossed from Rouse-like behavior to reptation-like with increasing surface coverage of obstacles. This transition in behavior occurred when the mean distance between obstacles was approximately twice the radius of gyration of the two-dimensional chain. In contrast, the inclusion of hydrodynamics had second-order consequences. This underscores the importance of surface disorder (not only literal obstacles but, by reasonable

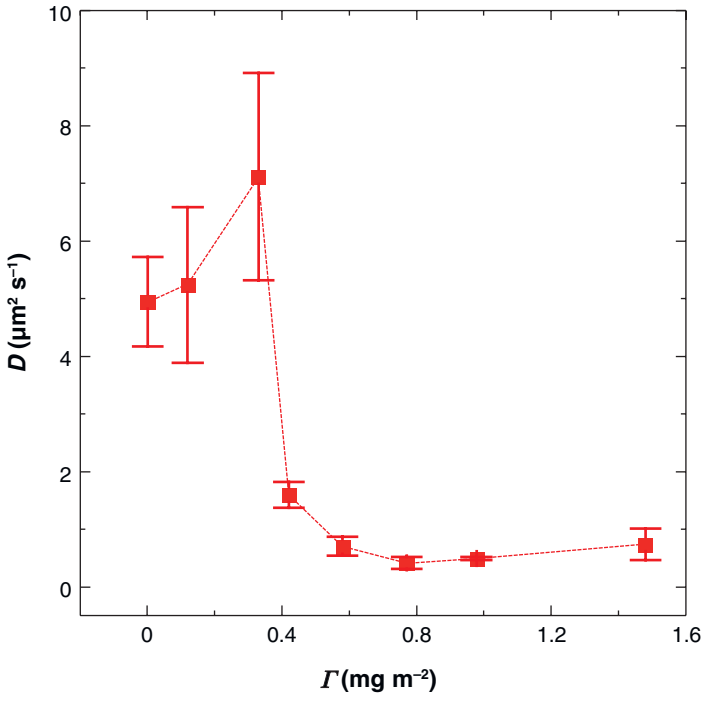

Figure 5

Lateral diffusion coefficient of polymer [polyethyleneglycol (PEG), $M_n = 10{,}800$ g mol^{-1}] at the solid-liquid interface in aqueous environment at pH = 8.4 plotted against adsorbed concentration. The error bars are the standard deviation measured in 10–20 repeated experiments at different spots on the test surface. Adapted from Reference 95.

extension, also other types of disorder) in determining the transport behavior of chains adsorbed to solids (88).

Later experiments on this same system varied surface coverage systematically, covering the full range from dilute to high surface coverage (95). **Figure 5** shows the translational diffusion coefficient (D) plotted against surface coverage. One observes that with increasing surface coverage, D at first increased moderately and then dropped suddenly, by an order of magnitude, at the surface concentration $c \approx 0.4$ mg m^{-2}, which is $\approx 40\%$ of full surface coverage by a monolayer. Reasoning by analogy with what is known for diffusion in bulk solution, we first seek to identify the regimes of dilute, semidilute, and concentrated surface coverage to interpret this data. The point of smallest surface coverage was certainly dilute—it was 240 × 240 nm^2 per molecule. The overlap concentration is estimated as the point at which the flat-pancake-adsorbed conformations first overlap. Supposing (by Occam's razor) the same persistence length as for PEG in bulk solution, and good solvent thermodynamic conditions so the radius of gyration scales as the three-fourths power of degree of polymerization [e.g., PEG in this three-dimensional bulk aqueous solution is in a good solvent (94, 95)], the estimate follows that $c^*_{2D} \approx 0.05$ mg m^{-2}, which is far on the low end of the concentration scale in **Figure 5**. Finally, it is tantalizing that the point of precipitous slowing-down in **Figure 5** is close to the expected close-packed density of two-dimensional chains (95), but whether this numerical coincidence is fundamental is not known.

When the surface coverage was less than a monolayer, modest speeding-up was observed. This may stem from a smaller number of potential adsorption sites as the chain conformations shifted from a flat pancake toward a three-dimensional loop-train-tail conformation. Subsequent (unpublished) experiments confirm this pattern when polystyrene adsorbs from chloroform (96). In this regime of high surface coverage, one may have anticipated adsorbed chains to diffuse more quickly than otherwise because they possess fewer adsorbed segments—but that was not the case. The influence of slowing-down owing to crowding by neighboring chains appeared to dominate instead. Recent molecular dynamics computer simulations are in striking agreement with these data (97). In the following subsections, we take stock and itemize a list of unsolved problems that constitute what we consider to be a worthwhile agenda for future work on these fundamental questions.

Entanglement: topological interactions between polymer chains that slow down center-of-mass diffusion

Entanglements

Long-chain flexible molecules exhibit special dynamic and elastic properties owing to their inability to cut through each other. For fluids, the effects of these long-range correlated motions are transient in time, and the intensity of entanglement, which determines the timescale 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 adsorption likely can exacerbate entanglements. **Figure 6** illustrates the entanglement presented to an unattached flexible polymer by the loop of an adsorbed polymer chain. The implied tube diameter and critical molecular weight for entanglement (2, 3) are likely 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 observed topological influence on desorption kinetics, with the N^{-2} dependence on the degree of polymerization N expected for

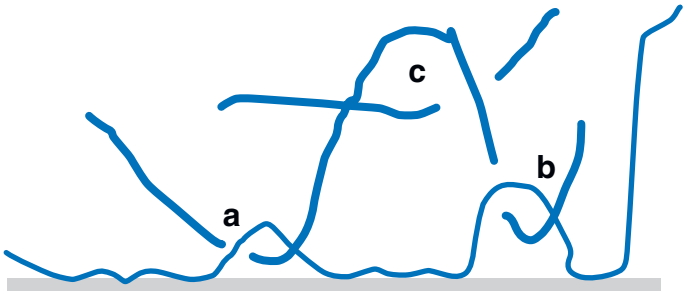

Figure 6

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. Reprinted with permission from Reference 106.

flexible linear chains from concepts of reptation, and strong quenching when polymers are branched (98).

How do we generalize this to an ensemble of flexible chains at surfaces? If polydisperse loops present a distribution of effective tube lengths (as suggested in **Figure 1**), what average, effective near-surface tube length results? It is not even clear if an effective tube diameter is relevant as (similar to the weakest link of a chain) the whole dynamics may be modified (if not controlled) by a single A-type entanglement (**Figure 1**), assuming 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 **Figure 1** suggests, it helps to rationalize one reason why near-surface polymer dynamics is so retarded relative to those of the same polymer in the bulk.

Monomeric friction coefficient: a parameter which, including the chemically specific aspects of macromolecular diffusion, separates these from the more universal physical aspects

Measurements of the shear spectra of confined polymer films (the linear viscoelastic shear responses as they depend on frequency) support this idea qualitatively (75–76). 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 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 (2, 3). Experiments regarding the dynamics of isolated polymer chains at surfaces are at an early stage (37, 57, 94, 95), and the consequences of finite surface coverage, leading to entanglement owing to overlap with other chains, are not understood.

Monomeric Friction Coefficient, ξ_o

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., the 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_o, changes with temperature and pressure in ways that can be predicted phenomenologically (2), 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_o. But there is much evidence that this differs near surfaces—it is the controversial surface-T_g problem (89–92). If the segmental mobility of polymers near surfaces differs from that in the bulk, then ξ_o 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 is so retarded relative to those of the same polymer in the bulk. The details for chain dynamics are not worked out enough. Also

the distance away from the surface, up to which chain dynamics is perturbed, is not understood.

Near-Surface Gradients

A peculiarity of near-surface dynamics is the ubiquity of gradients as compared with the bulk state. The notion of a single ξ_o probably oversimplifies the real situation. It has never been evident, even as it 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 6** 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 (51), is a stronger impediment than ξ_o, the friction as polymer segments glide past one another at positions removed from the surface. The near-surface T_g phenomenon suggests that ξ_o varies with distance away from the surface; it probably decreases in cases in which the near-surface T_g is reduced relative to the bulk and vice-versa. Quite independently, the near-surface entanglement phenomenon suggests slower near-surface mobility, for independent reasons.

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 (99). 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_o, whose value depends predictably on temperature and pressure. However, if ξ_o 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_BT, where k_B is the Boltzmann constant and T the absolute temperature (although 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) (55, 100). The existing evidence is indirect, however, as it does not concern single-chain diffusion.

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 "footprint" on the surface. Although contrary evidence also exists (51, 101), there is experimental (56, 102, 103) and theoretical (104, 105) evidence in favor of this idea (**Figure 7**).

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 timescales to reach equilibrium may be so long that the applicability to typical situations comes into question. An interesting implication is that the chains adsorbed later (finding fewer and fewer surface sites available, and hence becoming attached by fewer and fewer segments) should have a center of mass located further 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. A recent study demonstrated that this can happen in at least one system (107).

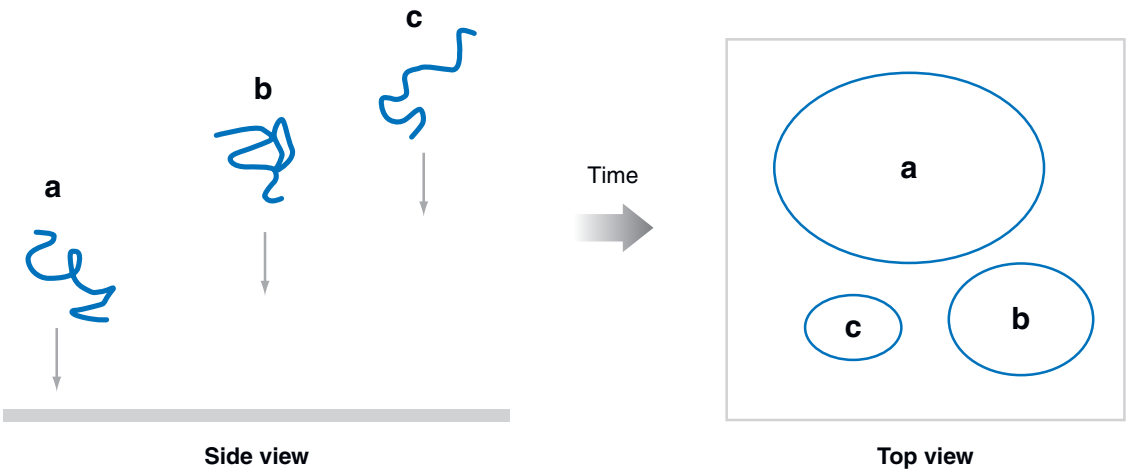

Figure 7

Hypothetical case in which 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* and *c*) occupy smaller footprints on the surface. (*Left panel*) The surface and chains near it are sketched end-on. (*Right panel*) The surface and chains near it are sketched from the top to illustrate the distribution of footprint size. Reprinted with permission from Reference 106.

LUBRICATION: SPATIALLY RESOLVED?

More spatially resolved experiments of the kind described above may help to resolve controversies in other related fields. For example, experiments on lubrication cannot distinguish beyond a single number: the friction. Incomplete equilibration and surface heterogeneity have been suggested to resolve the inconsistency between friction measurements obtained in various laboratories when molecularly thin nonpolar fluids are placed between atomically smooth single crystals and sheared (5). When researchers embedded nonadsorbing fluorescent dyes within fluids of this kind and measured their lateral diffusion by FCS, spatially resolved measurements showed that the diffusion rate differed by orders of magnitude within the same system, being slowest near the center of the contact (when previously curved surfaces were squeezed flat with fluid in between) and being more rapid near the periphery, not just under confinement at rest (108), but also while these fluids were deformed by shear (109). In these model systems in which to study lubrication, the diffusion of probe fluorescent dye molecules was shown to be massively heterogeneous according to spatial position. By inference, friction measurements (the ensemble average), which are more common in this field of study (110), represent ensemble averages that mask a previously unsuspected broad distribution of molecular motions whose origin is not fully understood. Spatially resolved (confocal) vibrational spectroscopy can contribute in this endeavor (111, 112).

PERSPECTIVE

This review summarizes recent investigations of molecular diffusion at soft interfaces and highlights some of the fresh problems and opportunities that emerge when such measurements are made in a spatially resolved manner. For future theoretical modeling, it is important to bear in mind that these measurements of motion necessarily raise ancillary questions of how molecules in these situations are oriented and arranged in space. The power of scattering techniques in this direction, especially X-ray diffraction and reflectivity methods, is evident (113) and advancing rapidly in capability. Another area of opportunity is to measure near-surface structure, as against the dynamics that forms the main subject of this review is vibrational spectroscopy (111, 114). A long-term goal during the next few years should be to bring the level of our understanding of liquids at interfaces toward the level of advancement already attained by studies in bulk systems. The studies surveyed in this review mainly involve monolayer or submonolayer situations, as this circumvents the difficulty of resolving motions and relaxations in the z-direction, normal to the surface. This review emphasizes the desirability to continue progress in these endeavors on the experimental side for studies that are spatially resolved, time resolved, and thickness resolved.

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