

VIEWPOINT

Open Questions about Polymer Interfacial Diffusion

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The goal of understanding diffusion in bulk has been a large part of the agenda in polymer physics from the start of our discipline. It seemed obvious to researchers, many years ago, that this and other aspects of dynamics at the level of individual molecules surely underpinned the macroscopic properties, such as viscoelasticity and other properties discussed in this viewpoint. Great names are associated with the seminal understanding of diffusion in the bulk: we have Rouse, Zimm, Doi, Edwards, and de Gennes on the theoretical side, but on the experimental side, important work has been done by so many researchers that to single out individual names would not be meaningful.

Nowadays, the study of the mechanisms and time-scales of polymer diffusion in solution and in melts is a developed field of study that is summarized in textbooks.¹⁻⁴ Interesting modern work does continue, for example, in understanding diffusion in blends and microstructured block copolymers. Although we should never claim that our understanding is definitive, polymer science has developed a rather mature understanding of how the dynamics depend on the chain length, chain architecture, and concentration.

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Why is the same not so for polymer dynamics at surfaces? Ultrahigh-vacuum surface science has studied surface diffusion for many years; polymer science has not. One basic limitation has been that the needed experimental tools have not been available. It is true that methods of dynamic light scattering have given insight into the global dynamics of polymer brushes. 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. 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 have enabled important advances. Secondary-ion mass spectrometry and related methods from ultrahigh-vacuum surface science have been used to measure concentration profiles in multilayer thin films spin-coated onto solid supports, from which diffusion has been cleverly inferred. Neutron reflectometry has been used to study interdiffusion in thin films. Specular X-ray scattering has allowed us to study capillary fluctuations in thin films. X-ray scattering has even been used to assess segmental equilibration. These methods refer to thin melt films on solid supports.

Atomic force microscopy and surface force apparatus are much used to measure how friction and surface forces are perturbed when polymer films are very thin.

Force measurements afford no direct measurement of diffusion, however. A fundamental challenge has always been to combine 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. These endeavors are mainly at the stage of technique development.

Apart from experimental difficulties, there are other reasons that 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 the dynamics of polymer chains at and near solid interfaces differs profoundly from that of 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 also must vary with the distance normal to that surface. The 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 and in two dimensions are difficult to put into perspective in the absence of experiments with which they could be compared.

This is also related to the thin-film glass-transition-temperature 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 even about an attractive case. Different chemical systems appear to behave differently.

This viewpoint calls attention to the potential of modern methods of fluorescence dynamics, developed mainly in the field of biophysics, which afford the needed experimental tools. These techniques include imaging the trajectory of single molecules; fluorescence correlation spectroscopy, which has single-molecule sensitivity yet, compared to single-molecule tracking, is not so much limited by the photobleaching problem; and fluorescence recovery after photobleaching in micrometer-sized spots within planar confined geometries. All these methods enable rates of diffusion to be spatially resolved, not just for polymers adsorbed from solution but also for polymers from confined polymer melts. In addition, Förster resonance energy transfer can be used to study polymer conformations.

Long-term scientific challenges include the following:

- What are the conformations of interfacial polymers? How does the polymer conformation at interfaces differ from that in the bulk and how does the conformation affect polymer diffusion?
- How does surface diffusion depend on the temperature and pressure, the fundamental variables with respect to bulk diffusion? How does it depend on the molecular weight? Does entanglement take the same form as that for polymers in bulk media?
- When does confinement alter fundamental properties characteristic of bulk media, such as the melting point or glass-transition temperature? Why are these raised upon confinement between flat surfaces but lowered if the confining surfaces are curved? What are the consequences for workaday ramifications such as tribology, groundwater transport, and adhesion?
- How do chemical reaction kinetics of polymers on surfaces and in confined geometries compare to these same chemical reactions in bulk media?
- In these questions, what is the role of the particular nature (flat or porous; chemically heterogeneous or homogeneous; dielectric or conducting) of the surface?
- What consequences result from the action of strong external fields (shear fields, electric fields, and temperature gradients)? Both the thermodynamics and kinetics can be modified.
- What happens in the case of preferential segregation of one component from a mixture, giving rise to a nonuniform distribution of components in the direction normal to the surface and possibly also in directions parallel to it?
- What are the technical consequences? How can the answers to these questions be usefully applied, by rational extrapolation, to assist the many related engineering disciplines? These systems are multi-component: lubricant formulations for oils in engines and clutches, filled polymers, groundwater transport through porous media, polymer alloys, and composite and nanocomposite materials.

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