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Scattering approaches to probing surface layers under confinement

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ABSTRACT

The confinement of soft materials between surfaces is central to the interactions that lead to adhesion, lubrication, and colloidal stability. Force measurements have long been able to describe the potential that exists between various coated surfaces, but it is only more recently that scattering techniques have permitted the detailed study of surface layers under confinement. By focusing on the characterization of interfacial layer structures, there is a growing understanding of the structural basis for the previously reported interaction potentials. Work to date has illustrated that the nanoscale confinement of adsorbed polymers, polymer brushes, polyelectrolyte multilayers, liquid crystals and lipid bilayers frequently leads to unexpected structural features. Approaches to probing interfacial structures with X-ray reflection and neutron reflection are described along with some of the advances in sample environment design that have facilitated these explorations.

1. Introduction

Many applications of soft matter utilize molecules at solid or fluid interfaces; commonly studied examples include the polymer layers that are found at the solid liquid interface in coatings, paints, and biomedical implants. Other practical surface layer systems include grafted polymer brushes, polyelectrolyte multilayers, and liquid crystals. Understanding the forces between surfaces and how these forces are mediated by the structures of the macromolecules is essential to ongoing efforts to predict and tune surface properties to make bespoke interfaces for individual applications.

The forces between two surfaces must clearly be different for the contrasting goals of adhesion and lubrication [1–3], yet these two attributes can both be obtained by coating the surfaces with polymer brushes [4,5]. The surface force apparatus and atomic force microscope have been extensively used to measure interactive forces of interfacial systems, but they cannot provide information on molecular structure. Going beyond measurements of forces and additionally measuring the near-surface structures has been an experimental challenge for a number of decades, with the answers to structure–force questions starting to emerge in recently reported work. The key experimental difficulty is that the surface layer structures are at their most interesting under confinement, while also being problematic to probe owing to the macroscopic solids creating the confined geometry. Obtaining sufficiently reproducible and accurate confinement is challenging, particularly when the restrictions of any given analytical technique are imposed.

Scattering techniques are very sensitive to surface structures, and properties such as layer thickness, layer density, and surface roughness can be explored [6]. In particular, neutron and X-ray reflectometry combine this sensitivity to supramolecular structures with highly penetrating radiation that can be used to probe what is happening between the two solid surfaces that are providing the confinement. The demands on a sample environment that can impose nanometric-confined geometries over a sufficiently large sample area for measurement by neutron reflection are strict; however, recent work has shown that a surface forces-type apparatus for neutron reflection is indeed able to probe interfacial structure under confined geometries [7].

Here, we will explore the ability of scattering approaches to probe confined soft matter and examine some of the interesting interfacial structures that have been found. We will see that current theory is unable to rationalize some of the effects that have been reported and that molecules in nanoscale-confined geometries can exhibit effects that differentiate these environments from the bulk.

1.1. Forces and confinement

The study of confined soft matter has its origins in the surface forces apparatus (SFA) and the atomic force microscope (AFM). These two

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instruments permit fine control over the forces and distances at which soft matter can be confined.

The first simple and direct measurements of attractive forces between surfaces and molecules were conducted by Derjaguin in 1956 [8]. The method involved bringing two surfaces close together and measuring the attractive force as a function of the separation. Most of these measurements were performed with glass surfaces and the forces were measured by deflection of a beam balance.

This type of experiment showed the changes in attractive van der Waals forces with respect to surface separation. The separation distances were typically between 80 and [2000] nm [9] and provided an experimental verification of van der Waals interactions.

In what will become a common theme in this review of confinement experiments, the roughness of the surfaces was the main constraint that prevented the separation distance going below [100] nm. Freshly cleaved mica, which can be molecularly smooth over a large area [10], later provided sufficiently smooth surfaces for Tabor and Winterton to reduce the surface separation to 5 nm using the now familiar crossed cylinder geometry. These pioneering designs were later refined into the surface forces apparatus [9] that has been widely used to confine systems and measure the forces involved in attraction, repulsion, friction, and lubrication across various systems such as adsorbed polymers and polymer brushes [11].

Another instrument that directly measures molecular forces is the AFM [12,13]. AFM force measurements frequently make use of a colloidal particle that is attached to a cantilever tip with known spring constant, and the deflection of the cantilever is measured optically [13]. By compressing the tip into a surface, the forces required to confine and then separate can be measured. The colloid probe is readily functionalized, and thus the forces of confinement of a range of materials have been studied [13,2].

1.2. Neutron and X-ray reflection

Although SFA and AFM techniques enable the direct measurement of forces between molecules or interfaces, they do not give information on the structure of the studied systems. When it comes to structural characterization, neutron and X-ray reflection have been used with liquid crystals, adsorbed polymers, lipid bilayers, and polyelectrolyte multilayers [14–16]. By analyzing reflection data, structural properties such as layer thickness, interface roughness, and layer density can be obtained [6,17].

For the study of confinement, specular reflection is the dominant technique, where elastic scattering means that the magnitude of the wave vector of the beam does not change after scattering, as illustrated in Fig. 1. For both X-ray and neutron reflection, the reflectivity is usually written in terms of the change in wave vector between the incident and the reflected beams. The scattering vector is given by $Q = k_1 - k_0$, where k_0 and k_1 are the incident and reflected wave vectors, respectively. For specular reflection, it is only the magnitude of this vector that is important and this is normal to the surface (by convention, the z direction):

$$Q = Q_z = \frac{4\pi \sin\theta}{\lambda} \tag{1}$$

where λ is the wavelength of the incident radiation and θ is the angle of incidence. Data are normally presented as either a reflectivity profile (R vs Q) or a reflectivity profile in which the Fresnel component of the reflection is removed (RQ^4 vs Q).

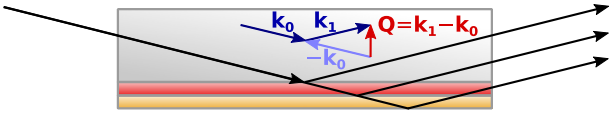

Fig. 1. In a reflectometry experiment, the incident beam approaches the interface at a shallow angle (exaggerated in this figure) and may reflect off each interface in a layered structure. For specular reflection, the incident and reflected wave vectors have the same magnitude k, and it is only the magnitude of the scattering vector, Q, that is considered.

As shown in Fig. 1, the reflection of the incident beam from different interfaces leads to a variation in the overall path length from source to detector. Thus, the refection profile describes the thickness of each of the layers in the structure in terms of an interference pattern, with Bragg peaks arising from structures with an internal periodicity and Kiessig fringes describing the overall thickness of the sample [6].

In the layered structure shown in Fig. 1, each layer is also constructed from different materials and so interacts differently with the beam. The scattering length density (SLD) of a material is a component of the refractive index for the beam in the material, and spatial changes in SLD lead to the observed scattering patterns. The beam is refracted as it passes through each interface, and steps in $\rho(z)$ can lead to total internal reflection at sufficiently low Q, giving a sharp feature in $R(Q)$ known as a critical edge. Overall, the $R(Q)$ profile depends on the SLD profile, $\rho(z)$, including both the SLD and the thickness of each layer. While this description has been developed in terms of discrete layers, it is readily generalized to smooth SLD profiles.

Neutron and X-ray reflection are similar techniques; however, the basic physics of the interaction is different: X-ray scattering is sensitive to electron density while neutron scattering is sensitive to the nuclei present. For each material, the SLD for X-ray and neutron beams is consequently different, and so quite complementary data are obtained from the two techniques. In both cases, it is $\rho(z)$ that is used in the data analysis; iteratively fitting plausible structural models to the experimental data provides the desired information, with a $\rho(z)$ being a necessary intermediate result.

A significant difference between X-ray and neutron scattering is that isotopic substitution provides a simple way to alter the SLD in neutron scattering, while the SLD is invariant for the equivalent X-ray experiment. Consequently, in neutron reflection, interfaces can be made invisible in an approach analogous to optical refractive index matching: matching the SLD of two layers and making $\rho(z)$ a constant across that interface hides the interface from view. The most common substitution is D (^2H) for H, with the prevalence of hydrogen in the solutes, adsorbates, and solvents used in soft matter systems, making this an extremely versatile approach to selectively highlighting parts of the sample. Contrast matching or contrast variation generates richer data sets that allow robust conclusions to be drawn from the data analysis.

2. Confining adsorbed polymers

The wide range of applications for adsorbed polymers has made these systems highly desirable subjects for confinement investigations, and a wealth of SFA and AFM force measurements underpin understanding in this field. Partnered with the experimental characterization of adsorbed polymers, the theoretical framework of Scheutjens–Fleer theory [18] provides a model to describe the polymer volume fraction profile in a solvent; this lattice model makes experimentally verified predictions for the volume fraction profiles [19–21] with NMR, small-angle neutron scattering (SANS), and neutron reflection playing important roles.

In probing the adsorbed polymers with neutron reflection, a significant technical limitation must be considered: a large neutron beam footprint (500 to [2500] mm^2) is required in order to finish one experiment in a reasonable time frame [7]. The confined interface needs to be uniformly distributed over a large area with a very low amount of roughness and excellent parallelism of the two surfaces. It was not until 1994 that Cosgrove and Zarbakhsh developed a thin film confinement apparatus in an attempt to measure the structures of confined adsorbed polymers [22,23]. The apparatus was equipped with two quartz plates between which the sample was placed and the upper plate was controlled by a hydraulic ram; a pressure as high as [130] bar could be applied to the upper plate.