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Biomolecules as soft matter surfaces

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ABSTRACT

Soft matter surfaces, such as organic layers or polymer surfaces, are dynamical and inhomogeneous (only in special cases crystalline). In contact with solutions, the situation becomes more complex, but still addressable with Surface Science methods. In single molecules and supramolecular assemblies, a large fraction of the molecule forms the surface. Can a single (bio) molecule be interpreted as a soft matter surface? A plant virus with a well-defined tubular structure demonstrates the problems, for which molecular dynamics simulations can give some answers.

1. Introduction

Surface Science is dealing with ever more complex surfaces. This concerns especially the surface chemistry: self-assembled monolayers (SAMs) of all types and adsorbed layers composed of rather complex molecules can be prepared in high quality, and also analyzed with great precision and control. Moreover, biologically functional entities such as adsorbed proteins have joined this research topic. For such cases, and whenever the thickness of adsorbed organic layers on solid substrates surpasses a certain limit of some nm, we can address the adsorbate as "soft matter". Soft matter surfaces with relatively simple structure and chemical properties, such as long-chain SAMs or bulk polymer surfaces, have been analyzed for many years. Concerning application, a main driving force is the widespread use of polymers, whose interfaces with air, water and various solids are of utmost technical importance. However, a soft surface has several important drawbacks for a detailed analysis, as we know it for defined crystal planes of inorganic matter: soft matter is usually nonconductive, hence poses problems for electron-based techniques, and it has a dynamic surface. This means that we have to give up the conventional thought of experimenting with homogeneous and immobile surfaces.

2. Bulk polymer and SAM surfaces

Let us first examine the classical case of flat surfaces of macroscopic extension. This might be surfaces of bulk polymers or of SAMs (Fig. 1) immobilized on flat substrates such as single crystal faces of gold or silicon or oxides. SAMs are one or a few molecular diameters thick, and polymers can often be prepared as thin layers [1]. For such samples, electron- and ion-based Surface Science techniques can be used advantageously (e.g. Auger spectroscopy, photoemission, ion scattering). SAMs show conformational changes in the molecular structure (Fig. 1a) [2] e.g. upon heating, while polymer and polymer surfaces become mobile above their respective glass transition temperatures, owing to the meandering motion of the chains, and aided by the available free volume. The Faupel group was able to show this elegantly by analyzing the penetration of metal particles into polymers [1]. For SAMs the penetration of metal atoms is well known [3], an effect based on lateral disorder: usually SAMs are very well ordered in the surface normal, but often this is not the case in the surface plane. This, together with the conformational defects, facilitates metal atom penetration. Thiol SAMs with amine and amide functional groups form dense layers, but exhibit high degrees of disorder in their carbon backbone; a phenomenon that depends on temperature, on surface charge (or electrochemical potential), and on the chemical environment (Fig. 1b), especially on the presence or absence of water [2,3]. Despite such structural disorder, SAMs with aine, amide and carboxylate groups can be used to construct well-defined metal islands [4] and even complete metal layers "on top", i.e. adsorbed on the chemically modified SAMs without contact to the substrate [5]. The driving force is here the interaction of the SAM end groups with either metal ions (precursors for the metal) or the metal itself.

For probing SAMs and thin organic films, a large part of classical Surface Science machinery can be used, e.g. X-ray diffraction, photoelectron spectroscopy, scanning probe techniques, or macroscopic wetting measurements (capillary forces). Ion scattering and secondary ion mass spectroscopy prove to be especially useful

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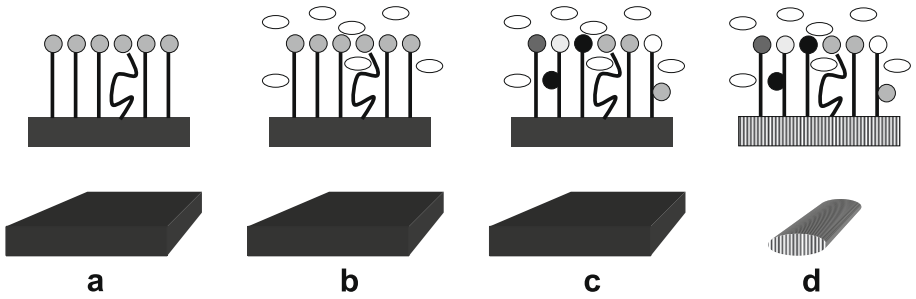

Fig. 1. Models of soft matter surfaces. The lines represent either short methylene chains as in organic monolayers, or polymer chains, or proteins. The ends of the chains carry a head group that binds to the surface, and a free end group (dark circle). (a) SAM or polymer layer with a defect, adsorbed on solid surface. (b) As (a), but interacting with a solvent (ellipsoids) in various places. (c) Adsorbed biomolecules with a variety of chemical groups (circles), surrounded by water molecules. (d) Biomacromolecule, e.g. protein assembly, with the same surface structure as (c).

for organic layers [6,7]. However, these techniques are usually slow in the sense that they are unable to follow the appearance of defects in a SAM or in a polymer layer, e.g. during buildup of a metal structure, or during any other chemical reaction. Thus the dynamical features of soft matter under such conditions are as yet not well known. Principally, optical techniques such as infrared or sum frequency spectroscopy are applicable here [2,3]. They are able to achieve good time resolution (ps to ns scale for changes of molecular conformation), e.g. by pump-probe approaches. One can expect that research into details of structural changes will be based on optical methods.

3. Biomolecules

Principally, the same arguments as for SAMs and polymers can be invoked for immobilized biomolecules (Fig. 1c), and the same Surface Science techniques can be used. However, most biomolecules require for preserving their shape and especially their functionality water or aqueous pH buffer, which renders many Surface Science methods not useful. While substantial progress has been achieved by working in a slab of ice, or with an ultrathin water layer, generally one should use in situ methods, where the molecules are in contact with bulk water. The best developed methods are based on X-ray and on scanning probe techniques, but as yet not many systems were investigated. One of the biggest problems is the control of orientation on the surface, and hence the often observed loss of functionality – e.g. when active sites of proteins bind to the substrate, or when protein adsorption causes large structural changes. It should be mentioned that the requirement of the contact to water extends also to calculations and simulations, where the molecule in question should be surrounded by a box filled with model water molecules [8].

4. Single molecules

From above arguments we can conclude that the Surface Science of soft and biological matter in thin layers is well developed, with the discussed restrictions and requirements [7–10]. In the following let us consider how to approach a surface that is curved and extends only over very small areas: Can we probe a single "soft object", in other words **a single (large) molecule or a single supramolecular structure** (Fig. 1d), and interpret the experiments in terms of a surface? As yet, this interpretation is rarely invoked in a Surface Science context [8]; notable exceptions are carbon nanotubes and colloidal particles [10] – chemical groups and soft matter layers on these materials are of great technological relevance for obtaining stable dispersions, or for bestowing chemical functionality.

Molecules are synthesized in parallel, i.e. a very large number of identical or at least very similar objects are obtained. Hence traditionally ensemble data (averages) rather than properties of single molecules are analyzed, e.g. the chemical composition by elemental analysis, the presence of chemical groups by nuclear magnetic resonance and infrared spectroscopy, the hydrodynamic diameter by light scattering, and the mass by electrophoresis. Measuring the properties of single molecules leaves us comparatively few experimental options, often related to nanoscale science, e.g. size by electron microscopy (if water can be evaporated without destruction), diameter (height) by scanning probe microscopy, chemical composition by nano optical methods. Many of these methods require some form of adsorption of the molecule on a solid substrate – and the interaction of the substrate with the molecule can change its properties. Despite this problem, the obtained data relate largely to the molecular surface, since almost all atoms are located at the surface [10].

In the case of single biomolecules, candidates for future research are especially those that are sufficiently stable in terms of temperature, mechanics and chemistry to sustain prolonged exposure to the measurement probe (light, electrons, and mechanical contact). In this respect, nucleic acids, sugars, and proteins assembled into cages, tubes and fibers are most valuable, while many non-assembled units (especially proteins) are stable only in a small range of temperatures and pH values. Simple viruses (nucleic acid with proteins) and various biological fibers (DNA, microtubule, spider silk) are prime examples. A problematic issue is the loss of biological relevance in two cases. First, neglecting dynamical aspects means overemphasizing static structures, while all biological processes are based on dynamics in the relevant molecules. A good example is the replacement of the "key-lock" interpretation of enzymatic catalysis (molecule fitting into adsorption sites on a protein surface) by the "induced fit" view (protein changing its structure to accommodate a molecule on its surface). Second, structure and the dynamics of a biomolecule usually depend heavily on water. For example, some water molecules are so tightly linked to proteins with hydrogen bridges that they can be detected by diffraction techniques. Their average residence time is hundreds of ps, as compared to loosely bound water with 5–50 ps (a typical vibration in a chemical group requires only tens of fs) [11,12].

5. Tobacco mosaic virus

In the following we will discuss three topics on experiments with Tobacco mosaic virus (TMV), a protein–RNA nanotube. This plant virus is the first detected virus, and the one characterized in greatest detail. Moreover, it is harmless for mammals, and tolerates a range of pH values (from <3 to >8) and temperatures up to