

Nanoscale Transport Phenomena at the Interface of Hard and Soft Matter

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Abstract

Hard and soft matter can be distinguished by the energy of chemical bonds in comparison with $k_B T$. At the interface of hard and soft matter, there exists a region of transition between strong (covalent/ionic/metallic) bonds in solids and weak (van der Waals/hydrogen/electrostatic) interactions in liquids and polymers. Transport of energy and mass at such interfaces is yet to be fully explored, but seems both rich in science and of technological importance. This paper discusses some fundamental issues as well as some technological implications.

Introduction

The purpose of this paper is not to present any new results, but instead to use the work of others from various disciplines and identify a common theme for future research that is both rich in science and could have significant impact on technology. This theme has to do with transport phenomena at the interface between hard and soft matter.

The hardness and softness of matter is essentially a comparison of the chemical binding energy of molecules to the entropic driving energy, $k_B T$. In solids, the bond strengths arising from covalent, metallic or ionic bonds are generally on the order of 1-5 eV whereas at room temperature $k_B T \approx 26$ meV. On the other hand, the binding energy in liquids due to van der Waals, electrostatic or hydrogen bond interactions fall in the range of 30-100 meV. Hence, entropic forces can lead to molecular mobility and transport properties such as viscosity. Polymers are a class of materials where some bonds covalent with binding energy of 1-5 eV but others are rather weak. This gives rise to flexibility and thereby fluctuations due to $k_B T$. Given this vast difference in the behavior of hard and soft matter, natural questions with regards to transport phenomena would be: How are heat and mass transported at their interfaces? Are there practical applications where such phenomena become important?

Before we go any further, let's first look at the interface between a solid and a liquid. In particular, I will focus on water in contact with a hydrophilic surface. Next, I will look at polymers in contact with solid surfaces.

Solid-Liquid Interfaces

Hydration Forces

Solid surfaces such as silica, mica or any other oxides or biological molecules such as DNA or proteins that contain a polar group, are hydrophilic and form hydrogen bonds with water. The H-

bond strength between water molecules and the surface can be so strong that the first few layers of water completely wet the surface and are often highly structured. Experimental evidence of such highly ordered 2-dimensional phase of water has been obtained by several investigators¹, as shown in Fig. 1, which suggest that the strong binding energy decays exponentially away from the surface with a characteristic length scale of 1-3 nm.

Electrostatic Forces

A solid surface or a biological molecule can be charged in two ways: (i) by ionization or dissociation of a surface group - for example, removal of H^+ ions from a glass surface; (ii) adsorption of ions from solution to a previously uncharged surface - for example adsorption of Ca^{2+} ions from solution to replace the K^+ ions in mica. When a surface or molecule is charged, a region of oppositely charged counterions in solution are attracted to the surface (see Fig. 2). The charge density of counterions decreases exponentially with distance from the surface and approaches the bulk value far away. The combination of surface charge and counterions in solution forms a region near the surface called the *electric double layer*. The length scale that characterizes the exponential decay of electrostatic forces is called the Debye length, ℓ_D , which can be expressed as

$$\frac{1}{\ell_D} = \sqrt{\sum_i \frac{\eta_{\infty i} e^2 v_i^2}{\epsilon \epsilon_0 k_B T}} \quad (1)$$

where ϵ is the dielectric constant of the medium, ϵ_0 is the permittivity of vacuum, e is the charge of an electron, v_i is the valence of the i th specie ion and $\eta_{\infty i}$ is the concentration of the i th specie ion far away from a surface. Typically, ℓ_D is on the order of 1-10s nm depending on the ion concentration in the bulk.

van der Waals Forces

Although not as strong as hydration or electrostatic forces, van der Waals forces are always present whenever a liquid is adsorbed onto a surface. They arise from interactions of induced dipoles between two or more atoms and are typically effective below 1-50 nm.

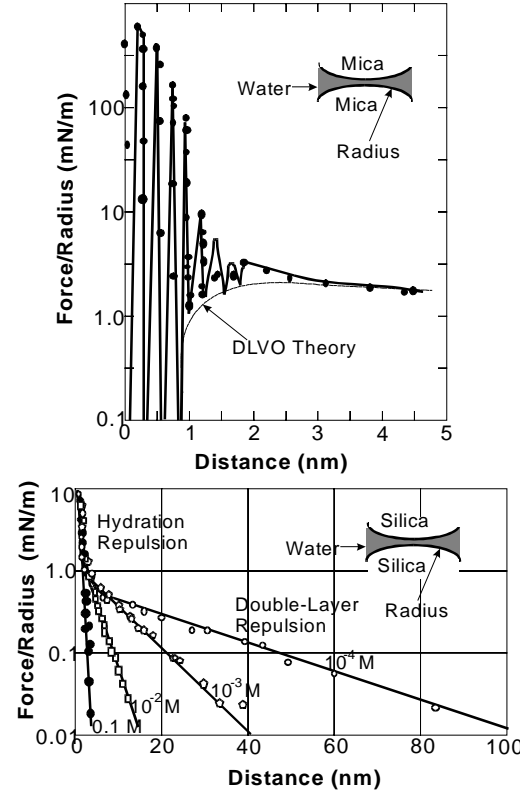


Fig. 1 Repulsive forces measured between two cylinders of (a) mica and (b) silica surfaces in the presence of water in a surface force apparatus [1].

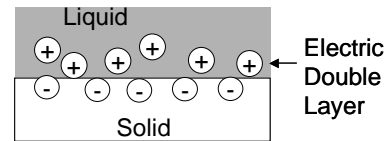


Fig. 2 A charged surface attracts counterions from solution forming an electric double layer. The ion density decays exponentially from the surface with a characteristic length scale of the Debye length.

Elastic Strain

The fact that water molecules are highly ordered in a two-dimensional ice-like structure close to a hydrophilic surface has been established through experiments and molecular dynamic simulations. Therefore, if the lattice constant of the substrate is not exactly equal to that of ice, the bonds between the water molecules will be strained. The fact that strain influences phenomena at the solid-liquid interface has been known for a while. For example, silver iodide (AgI) has been used to nucleate ice and it is commonly believed that it is the lattice match of the crystal structure of AgI and ice that promotes ice nucleation². Experiments have also shown that strain energy can play a significant role in nucleation processes, in particular for heterogeneous nucleation of ice from water on a solid surface^{3,4,5}.

Solid-Polymer Interfaces

Polymers are materials in which a sequence of chemical bonds are covalent to forms chains, but where the interactions between the chains are controlled by weaker bonds that are governed by van der Waals, hydrogen bonding, or electrostatic interactions. The stiffness of a polymer is often characterized by a length scale called the persistent length, ℓ , which is the length over which the motion of the atoms are statistically correlated. Hence, if the total length, L , of a polymer is much larger than its persistent length, $L \gg \ell$, the polymer is flexible and would rather form a coiled configuration than a straight chain one. This disorder in its structure is governed by entropic forces, which often determine its mechanical properties. Much has been studied about the structure and chemistry of polymers adsorbed on solid surfaces⁶. When end grafted on a solid surface through covalent bonds, the equilibrium configuration of the polymers are the ones that minimize their free energy, $\Delta G = \Delta H - T\Delta S$. Enthalpic interactions relate to chemical bonds between polymers and the surfaces as well as between neighboring chains, whereas entropic forces relate to disorder of the polymer chain itself as well as that of the ions and solvent molecules surrounding a charged or polar chain. Interchain interactions can be of many kinds: If the polymer is charged, counter ions from a solution could increase chain-chain repulsion due to osmotic forces which are entropic in nature. There could be chain-chain attraction due to van der Waals interactions and finally steric forces between closely spaced chain could be repulsive. As a result of all such interactions, the structure of polymers grafted onto a surface can be of many kinds depending on various interactions with their neighbors as well as chain entropy. Two possible scenarios are depicted in Fig. 3 for the cases — charged polymers with $L \gg \ell$ and uncharged polymers with $L \approx \ell$.

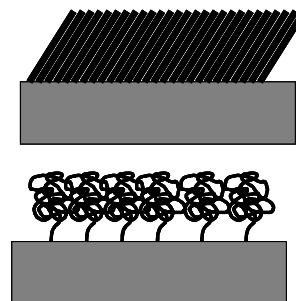


Fig. 3 Structure of polymers grafted on solid surfaces. (Top) Polymer chains on the order of persistence length align sideways to increase van der Waals interactions; (Bottom) Polymer chains much longer than persistence length coil up to increase their entropy.

Energy Transport at Solid-Liquid and Solid-Polymer Interfaces

The study of thermal boundary resistance was started by Kapitza in 1941 with the observation of resistance at solid-liquid He interfaces. Khalatnikov in 1952 explained the origin of the resistance through the development of the acoustic mismatch (AMM) theory. Much of the subsequent work focused on interfaces of non-metallic solids and solid-liquid He, which has been summarized in a comprehensive review by Swartz and Pohl⁷. In particular, it was shown that the AMM theory overpredicted the resistance for solid-solid interfaces. Swartz and Pohl

proposed a diffuse mismatch theory (DMM), which seems to underpredict interfacial resistance of non-metallic solids, although the discrepancy is not large. A recent review⁸ summarizes the work to date. What is interesting is that most of the work has dealt with non-metallic solids. Even metal-nonmetal interfaces have not been fully explored and there are several unanswered questions with regards to electron-phonon coupling in such interfaces^{9,10,11,12}. Besides solid-liquid He studies, there has been practically no work on solid-liquid or solid-polymer interfaces. Only recently, Wilson et al.¹³ made measurements of thermal interfacial resistance between metallic nanoparticles and fluids. In fact, in some cases the particles were coated with grafted polymers. Interestingly, they found the DMM theory to predict the thermal boundary resistance within a factor of 2. Despite this promising result, there are many questions still unanswered: (i) What is the mechanism of energy transfer between electrons in a metal, and vibrations/rotations in liquids? (ii) What is the mechanism of energy transfer between electrons in a metal and a non-conducting polymer that is covalently bound to the metal? (iii) How does the structure of the polymer relate to energy transport mechanism and dissipation? (iv) Can the interfacial resistance be controlled? Given the emergence and potential future proliferation of polymer-based micro/nanodevices and systems in various technologies (information, bio, energy, transportation etc.), a fundamental understanding of these issues is extremely important.

Mass Transport at Solid-Liquid Interfaces

It is clear from the previous discussion that all the surface forces in liquids operate at different length scales — some are near field and others far field. It is important to note, however, that regardless of their origin, they all operate in the range of 0.1-100 nm. Hence, it is only when a liquid is confined to 100 nm and below by solid walls or polymers that one should expect to observe changes in transport phenomena. In this paper, I will focus on nanoscale mass transport phenomena that is relevant in molecular biology.

One of the technologies that has revolutionized the way genomics research is performed nowadays is DNA microarrays. Figure 4 shows an image of thousands of spots where fluorescently labeled target single-stranded DNA (ssDNA) have hybridized with their complementary strand that is attached to a solid substrate (generally glass). Such gene chips allow one to simultaneously study the occurrence or mutations in thousands of genes. In addition, the expression of these genes in the form of messenger RNA (mRNA) can also be quantitatively measured, thus giving insight about the molecular machinery inside a cell. For mRNA in particular, quantitative analysis of how many copies of a certain gene is expressed is of prime importance. This is because over expression or under expression of genes can lead to disease. Such DNA microarrays are used not only in basic science but also in applications as

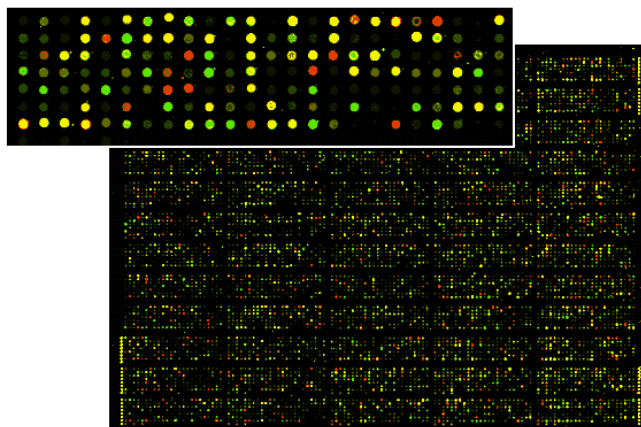


Fig. 4 Fluorescent image of a DNA microarray showing more thousands of fluorescent spots indicating DNA hybridization.

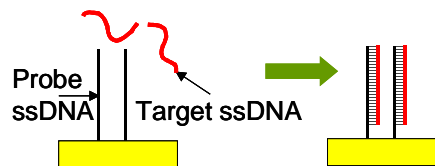


Fig. 5 Surface reaction of DNA hybridization occurs in DNA microarrays.

well, including forensics, drug discovery, diagnostics etc.

The fundamental process that occurs in such DNA microarrays is a surface chemical reaction, as illustrated in Fig. 5. The speed and efficiency of this reaction depends on a number of factors, namely: concentration of target ssDNA, density of probe ssDNA, length of probe and target ssDNA, and ion concentration. Although DNA microarrays are widely used, to a large extent their performance, although critical, is not well understood. Georgiadis and coworkers^{14, 15} have performed careful experiments to study the dependence on various factors. Figure 6 shows the effect of surface probe molecular density on the hybridization efficiency. The surface molecular density varies from 2×10^{12} to 12×10^{12} cm⁻², which relates to intermolecular distance of 3-7 nm. This falls in the regime of hydration, electrostatic and van der Waals forces, such that biomolecular reactions would be significantly altered in such confined regions over that in bulk fluid. The difference in the time taken as well as the efficiency of the reaction suggests that it would be very important to control the mass transport as well as reaction kinetics. Fundamental knowledge of nanoscale fluidic interactions through changes in intermolecular forces is the key to designing such biochips with optimized performance.

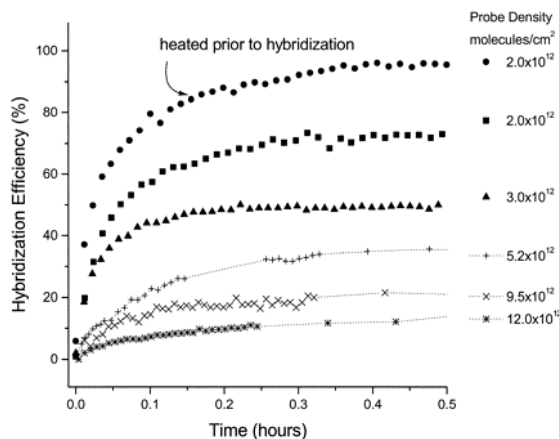


Fig. 6 Target hybridization kinetics as a function of probe density. The probe density, determined by surface plasmon resonance, varies from 2×10^{12} to 12×10^{12} molecules/cm². Heating of the probe film prior to hybridization increases the hybridization efficiency. All runs are 1 μ M target in 1 M NaCl with buffer.

While DNA microarrays are commercially produced and widely used, protein microarrays that utilize antibodies as probe molecules are starting to be developed. Here again the speed and efficiency of surface reactions would depend on the density of probe molecules, intermolecular forces between them and mass transport of target protein molecules to the surface. This would be an important and exciting area of research.

Conclusions

The interface between hard and soft matter provides a sudden change in chemical bond strength and molecular mobility. Examples include the interface between solids and liquids/polymers. The transport of thermal energy across such interfaces seems to be rich in science and is likely to have many practical applications in polymeric devices. Yet, in contrast with solid-solid interfaces, the topic is yet to be fully explored. This is perhaps because it requires an interdisciplinary approach with knowledge from solid state physics, polymer physics, statistical mechanics, physical chemistry. Mass transport and chemical reactions between biopolymers grafted on a solid surface seem to show significant dependence on the structure and density of the polymers. This topic is also rich in science because the free energy landscape of such reactions as well as diffusion in confined liquids is not yet well understood. Yet, this has important bearing on biotechnology.

Acknowledgments

I would like to thank John Lloyd (Michigan State U.), Katsuo Kurabayashi (U. Michigan), and David Cahill (UIUC) for discussions on energy transport at hard-soft interfaces.

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