

diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Molecular Motion in Thin Liquid Films near Surface Steps

Arne Schob, Frank Cichos

TU Chemnitz, Institute of Physics, Photonics and Optical Materials,
09107 Chemnitz, Germany, E-Mail: arne.schob@physik.tu-chemnitz.de

1. Introduction

The interaction of liquids with solids is one of the fundamental problems in physical chemistry. Processes like self-assembly at surfaces, lubrication, nanofluidics, catalysis or chromatography are influenced or completely ruled by solid-liquid interactions.

Within this study we employ for the first time a surface step to evaluate dynamics of molecular liquids at a surface. The use of a surface step together with single molecule tracking techniques provides a powerful tool to unravel the motion of dye molecules in-situ in a liquid at the surface. While common single molecule studies only rely on a tracking of molecular motion parallel to a solid surface, the use of surface steps allows direct access to the motion towards or away from the surface without losing the information on the diffusion parallel to the surface. Further the use of surface steps itself together with the results of this study provide details on how to employ surface steps to template molecular structures or to influence macromolecular conformation.

2. Results

In experiments with Rhodamine doped TEHOS (tetrakis(2-ethylhexoxy)silane) droplets touching a surface step on a cleaved mica substrate an enhanced probability to detect single molecules close to the step is found. A fraction of molecules moves along the step even for several 100 ms (see Figure 1) before leaving it. Further analysis of single molecule trajectories reveals that compared to a flat region the diffusion near the step is in general slowed down and strongly anisotropic. Molecular motion along the step is about three times faster than perpendicular to it.

Random walk-simulations as well as analytical calculations for a simple reflecting wall are carried out to model the experimental data. To study the spatial variation of the dye molecule mobility the local and angular dependence of the square displacement of molecules is calculated. Approaching the step reduces the square displacement of molecules in the direction of the surface step ($-z$ direction, see Figure 1) with both theory and experiment being in remarkable agreement. While the calculations predict only a weak dependence of the square displacement of molecules moving in z direction on the distance from the step, the

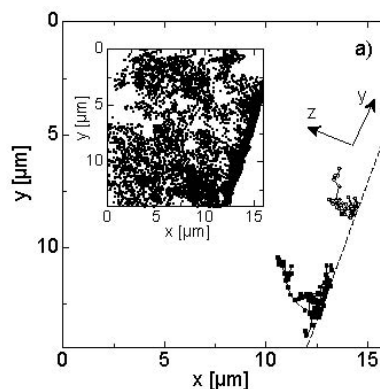


Figure 1: Two single molecule trajectories. Molecules diffuse along the surface step. Inset: Trajectory points of all molecules. Surface step in the lower right corner.

experimental data reveals a strong slow down directly at the surface step. This distinct difference is attributed to a temporal trapping of molecules at the surface step. The depth of this trapping potential can be calculated from our experimental results and was found to be about 600 meV(68 kJ/mol). Even though this trapping potential is strong, molecules are still able to diffuse along the surface step, which indicates a weakly corrugated potential along the step. Both findings suggest a confinement of molecular diffusion to a thin liquid layer parallel to the surface.

3. Summary

The interactions at the solid-liquid-interface were studied by observing the motion of tracer molecules within a liquid near a substrate surface step. The diffusion of molecules at the surface step was found to be slowed down and strongly anisotropic near the step. The results were compared to random-walk simulations and analytical calculations providing a simple model (reflecting wall). Differences between model and experiment are attributed to a trapping potential at the surface step.