

Discrimination Between Static and Dynamic Heterogeneities in Single Dye Diffusion in Ultrathin Liquid Films.

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1. Introduction

In single molecule experiments dye molecules are used to trace dynamics e.g. of diffusing DNA along membranes. We used Rhodamine B as a probe to study the microscopic mobility in an organic liquid (TEHOS) at the interface with a solid (Si wafer with 100 nm thermally grown SiO₂) via video wide-field microscopy. In previous experiments [1] we were able to show that diffusion within ultrathin liquid films is heterogeneous and drastically slowed down in comparison to bulk behaviour. Recent time series of 2 - 10 nm thin films revealed the influence of surface changes and of film thinning on the molecular mobility within such ultrathin films. It is well known that liquids show layering at interfaces with solids [2], therefore dynamic inhomogeneities in diffusion, caused by different dye mobility within different layers and by layer interchange of dye molecules during the observation, might explain the observed heterogeneities. Recent reports [3] as well as our own observations indicate additional static inhomogeneities caused by surface heterogeneities.

2. Observations and Discussion

In 2-10 nm thin films the dye molecules show periods of high mobility interchanging with extreme slow mobility along their trajectories. This behaviour can be understood by hydrodynamic and solvation forces causing the dyes to move towards the solid substrate, where they might adsorb e.g. to surface silanols [4]. Long time observations up to 220 hours reveal gradual changes in the overall dye mobility. Initially they stick quite often to the substrate and only some trajectories cover an area of more than 1.3 μm^2 laterally. Within 70 h to 150 h the fraction of immobile periods decreases and far more trajectories exceed the area of 1.3 μm^2 . Since we calculate diffusion coefficients by weighted mean squared displacements along the trajectories [5], the initially quite high fraction of immobile periods shifts the observed diffusion coefficients towards small values. This changes within 24 to 72 hours when

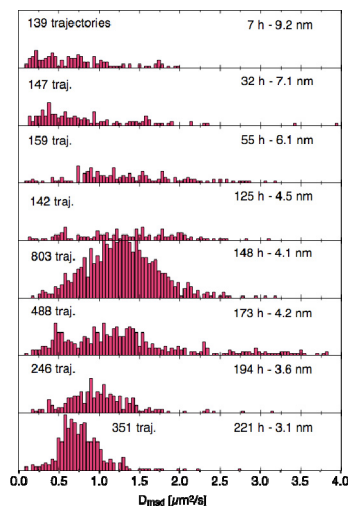


Fig 1. Long time observation of the distribution of diffusion coefficients.

the mobility increases probably due to physio-chemical changes at the solid-liquid interface, also yielding broader distributions of diffusion coefficients, as can be seen in Fig. 1 for one of the films. Afterwards the distribution narrows again accompanied by a decrease in its mean value. This can be understood as being due to decreasing film thickness, which forces the dye molecules closer to the liquid/solid interface where the diffusion is slowed down.

Further investigations of dye mobility recently led to the detection of very slowly diffusing molecules at certain areas on the substrate. Additionally we found some diffusing dyes which stopped at the same area on the substrate before continuing their diffusive motion. This hints to static heterogeneities on the substrate influencing the diffusive behaviour of the dyes. Since the diffusion is already influenced by dynamic heterogeneities, and since the detection of anomalous diffusion strongly depends on the time scales of observation, we need further analytic tools, e.g. to create local maps of mobility, and specially designed experiments to discriminate between the causes of heterogeneity in diffusive behaviour of dyes in ultrathin liquid films. These tools and also our models will be tested by recently developed simulations.

3. Conclusion

The correlation between film thickness and the gained distribution of diffusion coefficients confirms our previous results that the diffusion in ultrathin liquid films is influenced by dynamic heterogeneities due to layering. The initial increase in dye mobility can be explained by changes in surface chemistry leading to less adsorption sites e.g. surface silanols for the dyes.

To discriminate between dynamic and static heterogeneity in the process of diffusion further tools for analysis and specially designed experiments are needed.

References

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