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Investigations of Static and Dynamic Heterogeneities in Ultra-Thin Liquid Films via Scaled Squared Displacements of Single Molecule Diffusion

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1. Introduction

For analyzing the mobility of diffusing molecules, single molecule experiments are well established. Experiments in ultra-thin liquid films revealed a heterogeneous behavior of diffusion [1], which could be explained by a layering of liquids at solid interfaces as reported in [2]. Consequently, a layer model with layer-dependent diffusion coefficient was developed. Layer transitions of the observed molecules induce dynamic heterogeneities in the projection of their diffusion. They are strongly dependent on the dwell times in the layers. Additionally, experimental observations and recent research [3] indicate an inhomogeneous layer on the substrate. This results in domains which influence the local diffusivity and lead to static heterogeneities in the observation.

The objective of this research is an approach for the distinction between dynamic and static heterogeneities. Furthermore, a characterization of these heterogeneities should be achieved.

2. Approaches and discussion

The calculation of time-averaged mean squared displacements is widely used in single molecule tracking [4]. Therefore, especially long trajectories are necessary to calculate the mean diffusion coefficient. However, the involved averaging obscures the heterogeneities of the process. Hence, this method is not able to extract the involved diffusion coefficients of the underlying process. To overcome these problems, a new method in single molecule tracking is proposed. It is independent of the trajectories' lengths and therefore is insensitive against blinking and bleaching. First, along the detected trajectories, squared displacements are determined during a predefined observation time. Then the trivial time dependency is removed by dividing these squared displacements by the observation time. These scaled squared displacements (ssd) are proportional to the spatial and temporal local diffusivity.

A histogram of these ssd represents the probability density of the observed diffusion coefficients. Due to dynamic heterogeneities, this density reveals a non-trivial time dependency and a non-exponential relation between ssd and their relative frequency as depicted in Fig. 1. However, if the observation time becomes large compared to the dwell time of the molecules in the layers, the probability density will show an exponential relation. Then this resembles the special case of homogeneous diffusion processes.

Moreover, this probability density offers several possibilities for an analysis. It can be shown analytically that the first moment of the probability density yields the mean diffusion coefficient also obtainable by the mean squared displacement. Further, the probability density can be used to identify the contributing diffusion coefficients. It can be deduced that a multiple auto-convolution of the density results in a distribution where peaks evolve at the underlying diffusion coefficients. Thereby the number of auto-convolutions depends on observation time.

In case of static heterogeneities resulting from domains on the substrate, the probability density of the ssd becomes additionally dependent on the position where it was observed. This enables the construction of a map of local mean diffusion coefficients. According to dwell times and the observation time, the map discloses regions with different diffusion coefficients.

Finally, the proposed methods are evaluated with artificial data to verify their reliability and sensitivity on the parameters. Besides, investigations based on real experimental data are performed, and a comparison to previous analysis is drawn.

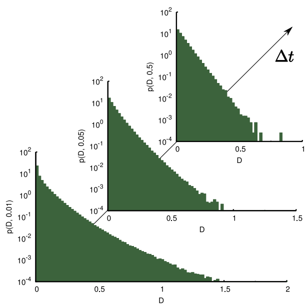

Fig. 1: Non-trivial time dependency and non-exponential relation of $p(D, \Delta t)$

3. Conclusion

The determination of scaled squared displacements offers an advantage for experimental data since short trajectories are sufficient. Further, the establishment of a time- and region-dependent probability density of these values seems to be a promising approach to detect and analyze both dynamic and static heterogeneities. It also features an efficient calculation of well-known quantities as obtained by the mean squared displacement.

References

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