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Diffusion in ultrathin liquid films

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Abstract

Inhomogeneous molecular diffusion in layered structures of thin liquid films deposited on solid surfaces is observed via wide field single molecule microscopy. The fluorescence dyes Rhodamine 6G and Oregon Green 514 are used to probe the diffusion in tetrakis(2-ethylhexoxy)-silane and polydimethylsiloxane. A broad distribution of diffusion constants is observed which can be attributed to diffusion within distinct layers of the liquid. Comparison with computer simulations shows that diffusion is normal but depends strongly on the distance of the molecules from the solid surface. Diffusion within layers is faster than between the layers and additional temperature activation is necessary to speed up interlayer diffusion.

Keywords: Diffusion

1. Introduction

Due to the extreme sensitivity optical single molecule or single particle experiments offer the possibility to investigate diffusion processes in ultrathin films, on surfaces or in restricted geometries. Moreover and even more important, experiments allow to follow the individual diffusion behaviour of single quantum objects, which might be subject to variations in dynamic properties induced by an inhomogeneous environment on a nanometer scale. Diffusion of single molecules in liquids has been extensively studied by confocal microscopy using fluorescence correlation spectroscopy [1,2] or fluorescence burst analysis [3,4] and real time wide field microscopy [5–7]. During the last several years single molecule real time (video) microscopy has become an important tool to track and image single molecules in various environments [5–9]. Recently we have performed single molecule diffusion experiments in surface wetting droplets [10] and ultrathin liquid films [11].

Liquid films exhibit a layered structure when close to smooth solid surfaces as detected by ellipsometry [12], surface force measurements [13,14], desorption studies [15] and X-ray diffraction [16,17]. Such structures imply that dynamics of liquids in thin layered films have to be different from the behaviour in the corresponding bulk liquid. Single molecule techniques allow for an analysis of the expected anisotropic diffusion. In combination with recently developed single molecule spot size analysis techniques [18] we were able to show that the diffusion of various dye molecules in liquid films of a few nm thickness behave indeed inhomogeneously when deposited on quartz surfaces [11]. In this communication we like to focus on the heterogeneity of diffusion processes, the effect of material variation, temperature, and the comparison of experiments with numerical simulations using Monte Carlo (MC) and Molecular Dynamic (MD) techniques.

2. Experimental

Experiments have been performed using a home-built fluorescence microscope consisting of a 100×/0.9 NA

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(Zeiss Epiplan Neofluar) objective and a lens (focal length 250 mm) to image the sample on an intensified frame transfer camera (Pentamax, Roper Scientific). Dye molecules are excited through the same objective by the 514 nm line of an argon ion laser in a wide field illumination scheme. Excitation light is focused to a spot of 20 μm diameter yielding an intensity of about 1 kW/cm^2. A holographic notch filter in front of the detector is used to remove the excitation light from the fluorescence. A microscope cryostat (Oxford) with a cold finger was used to adjust sample temperatures from 230 to 310 K.

The liquids used in the experiments are tetrakis (2-ethylhexoxy)-silane (TEHOS) and polydimethylsiloxane (PDMS). As fluorescent tracers we use Rhodamine 6G (R6G) and Oregon Green 514. Samples are prepared on quartz cover slips or silicon wafers with a thick oxide layer (about 100 nm), which are carefully cleaned before preparation. The deposition of thin films of TEHOS is carried out by dipping the substrates into a solution of TEHOS and R6G in hexane (details can be found in [11,16]). Wetting droplets of TEHOS and PDMS are prepared by depositing a small droplet of the liquid/dye solution directly on top of the substrate. The thickness of the TEHOS films is determined by measuring the surface plasmon resonance curve for a liquid layer deposited on a 50 nm gold film. Droplet profiles are measured by interferometric techniques. Additional ellipsometric measurements confirmed the determined thickness of TEHOS films. The films described in the following have a thickness between 1 and 17 nm. Most of the experiments have been done on 4(±1) and 17(±2) nm thick films. Details of the data evaluation are reported in [11].

MD simulations have been performed by using the DL_POLY packet [19] and are run on a Compaq XP 1000 computer.

3. Results and discussion

3.1. Heterogeneous diffusion dynamics

Typical single molecule diffusion trajectories consist of 20–400 snapshots with a total average of 40 snapshots. Lateral diffusion coefficients are obtained in two ways from the trajectories.

For each trajectory the mean square displacement (MSD: $\langle r^2_{\mathrm{MSD}}(\tau)\rangle = \langle[\vec{r}(t) - \vec{r}(t+\tau)]^2\rangle = 4D\tau$) is calculated as a function of time. Some examples of MSD for individual molecules of R6G in TEHOS films, deposited on quartz substrates, are shown in Fig. 1(a). What looks at first glance like "anomalous" diffusion is due to the finite trajectory length L_T since the linear dependence of the MSD on time τ is only valid for $\tau \to \infty$. This is also seen in computer simulations (Fig. 1(b)) assuming normal diffusion but final L_T. Given a finite trajectory length L_T, the value of $\langle r^2_{\mathrm{MSD}}(\tau)\rangle$ can be calculated only with an uncertainty Δ which grows with τ as is illustrated in Fig. 1(b). Thus it can be misleading to assume a distinct diffusion type (i.e. normal or anomalous diffusion) from $\langle r^2_{\mathrm{MSD}}(\tau)\rangle$ without knowledge of the uncertainty of the actual experiment which depends strongly on L_T (see

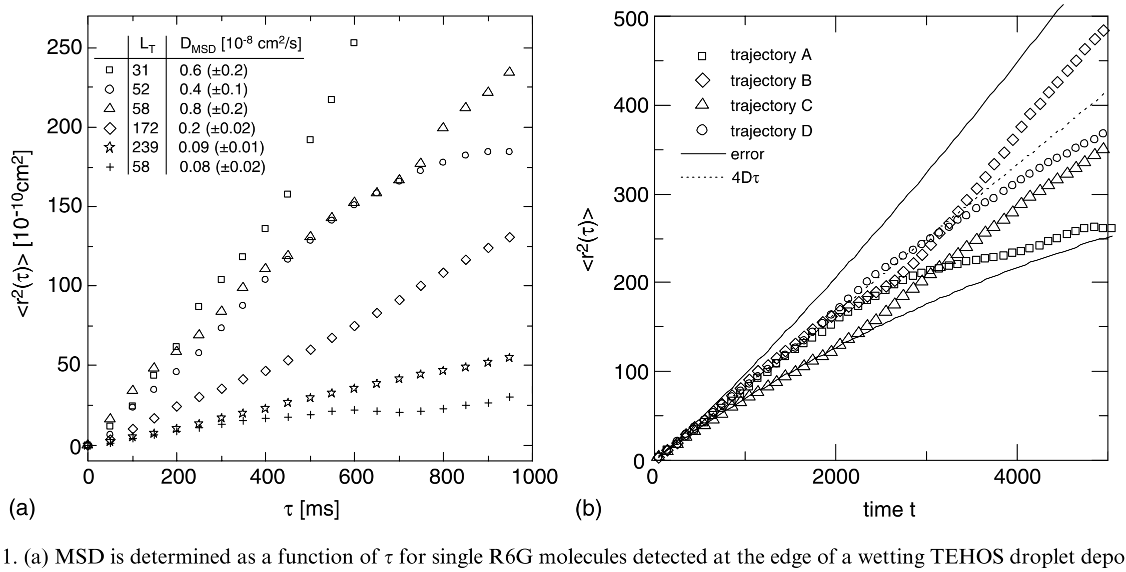

Fig. 1. (a) MSD is determined as a function of τ for single R6G molecules detected at the edge of a wetting TEHOS droplet deposited on a quartz cover slip. Trajectory lengths and diffusion coefficients deduced from MSD-functions are shown in the table. (b) MSD as a function of τ is calculated via Monte Carlo simulations of diffusing molecules (trajectory length $L_T = 500$). The broken line shows the function $4D\tau$, as it would be expected for infinite long trajectories. The solid lines indicate the variance due to a finite trajectory length according to [20].

[20] for details). This behaviour has already been analyzed by Saxton [20] and Quian [21] for diffusion processes in biological relevant systems and was proven in our case on the basis of computer simulations.

A weighted linear fit of our $\langle r^2_{\mathrm{MSD}}(\tau)\rangle$-data yields one diffusion coefficient per single molecule trajectory. The weights are chosen to reflect the variance in the diffusion coefficient as derived from measurements with limited trajectory length as described in [20,21]. In all cases we could show that when applying the corresponding weights only normal diffusion is observed in the presently reported systems and all deviations are within the experimental error.

Besides the MSD analysis we applied a new method named spot size analysis (SSA) developed recently which determines an optical spot size of each single molecule image and relates it to a diffusion coefficient [18]. This method allows for the first time to follow the time dependence of the diffusion coefficient along a single molecule trajectory. It is an additional tool to determine changes in the diffusion coefficient, which are usually hidden by the extensive averaging of the MSD technique.

A comparison of the results obtained either by MSD or SSA is shown in Fig. 2 for liquid TEHOS films of 17 and 4 nm thickness, respectively, deposited on quartz cover slips. Both analysis techniques result in a broad distribution of diffusion constants D which can be uniquely related to the different properties of 17 and 4 nm thick films. From each of the individual trajectories (748 for the 17 nm film and 148 for the 4 nm film) diffusion constants D_{MSD} are deduced and their relative probability is plotted. In comparison, the SSA technique results in a series of D_{SSA} for each diffusion trajectory. Averaging over all D_{SSA} for the corresponding trajectory should result in the same value of D as for the MSD analysis. However, this is not the case as can be seen in Fig. 2. The corresponding distribution of D_{SSA} is shifted to larger D-values as compared to the one of D_{MSD}. The over all molecular trajectories averaged $\langle D_{\mathrm{SSA}}\rangle$ are by a factor of 2 (1.5) larger than for $\langle D_{\mathrm{MSD}}\rangle$ for 17 (4) nm thick films. Fig. 3 shows the results for D_{SSA} from all trajectories obtained from the 17 nm thick film in comparison with different averaging procedures (five points averaging and total trajectory averaging, respectively). It is evident that the averaging procedure has at most an influence of 10% on $\langle D_{\mathrm{SSA}}\rangle$.

Comparing the results for D as a function of film thickness we obtain $\langle D_{\mathrm{MSD}}(17\ \mathrm{nm})\rangle/\langle D_{\mathrm{MSD}}(4\ \mathrm{nm})\rangle = 1.4$ and $\langle D_{\mathrm{SSA}}(17\ \mathrm{nm})\rangle/\langle D_{\mathrm{SSA}}(4\ \mathrm{nm})\rangle = 1.8$ showing the same trend for an increase of $\langle D\rangle$ with film thickness. For comparison we obtained a diffusion coefficient of 3.7×10^{-7} cm^2/s for bulk TEHOS and 5×10^{-9} cm^2/s for an about 1 nm thick droplet edge. This shows that on average diffusion is slowed down with decreasing film thickness. Additionally, the width of the distribution of diffusion constants increases with sample thickness reaching maximum values which are by a factor of 10

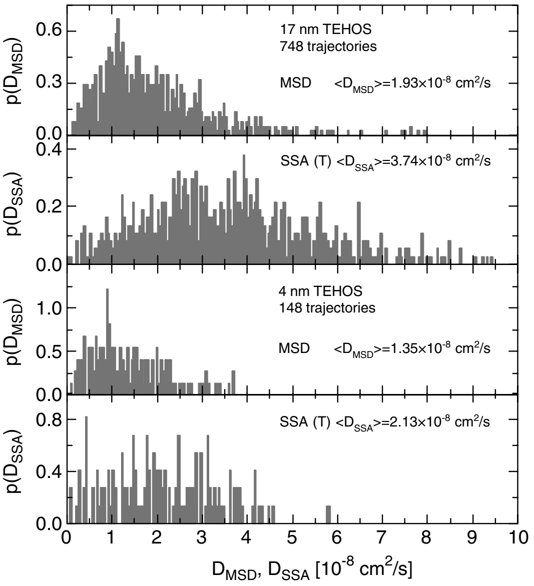

Fig. 2. Distributions of diffusion constants of R6G obtained for a 4 and a 17 nm thick TEHOS film from spot size analysis (trajectory average) and from MSD analysis. Additionally the number of trajectories and the ensemble average of the diffusion coefficient are given.

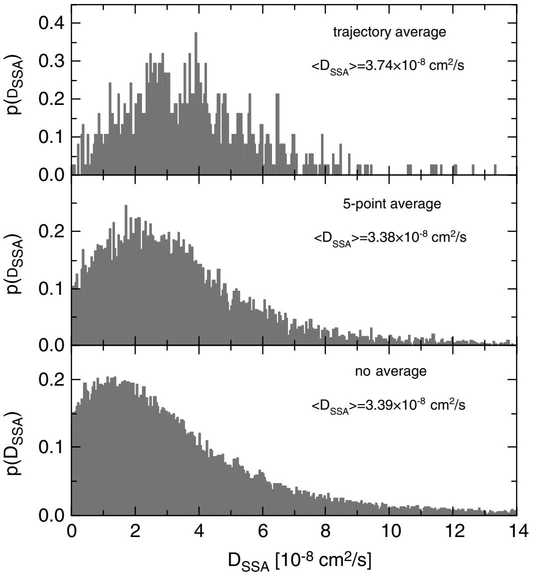

Fig. 3. Distributions of diffusion constants obtained from spot size analysis for the same set of measurement (R6G in a 17 nm TEHOS film) but different ways of averaging (from top: trajectory average, 5-point average, no average).

(see Fig. 2) smaller than for diffusion in bulk material. In comparison with simulations (forthcoming paragraph) it becomes evident that the measured distributions of D are influenced by interaction potentials of the liquid TEHOS layers with the solid surface, whereby the concentration of diffusing dye molecules will increase close to the interface due to "freezing" of diffusion.

Comparison with Monte Carlo simulations of the diffusion process and analytical expressions given in [20] shows that the width of the distributions is not limited by experimental accuracy, but is governed by the heterogeneous distribution of diffusion constants. In previous reports we have concluded [11] that layering of liquid films close to a solid surface gives reason to such heterogeneous diffusion processes.

An additional observation is concerned with the fact that D_{SSA} and D_{MSD} are independent measurements with respect to the kind of averaging. Whereas D_{SSA} describes the diffusion within an approximated ellipsoid (see [18]), D_{MSD} describes the diffusion of the center of gravity of the spot. $D_{\mathrm{SSA}} > D_{\mathrm{MSD}}$ seems to indicate that diffusion on a microscopic scale ($\leqslant$100 nm) is faster than diffusion on a length scale of several 100 nm to μm as determined via the MSD. This might suggest a kind of "caging" effect in the vicinity of the tracer molecules. Diffusion in the cage is thus faster than out of the cage. Further experiments and data analysis will show whether this argument holds.

The increase of D with film thickness indicates that "bulk diffusion" will only be obtained at a distance of more than 150 nm from the surface. Recent experiments on the homogeneous optical line width of single dye molecules in hexadecane crystalline matrices have shown that line broadening effects due to local or surface phonons are observed up to a distance of 150–200 nm from a silica surface [22]. Although this system is completely different from the present one the comparison merely shows that organic/inorganic interface effects can extend to distances from the surface of up to 100 nm and more.

3.2. Variation of tracer molecules and liquids

Using dye molecules as tracer molecules to determine diffusion properties of liquids such as TEHOS always imposes the question of the influence of the probe molecules on the diffusion process. To test this influence we have chosen Oregon green 514 (non-ionic dye) instead of R6G (ionic dye) as a probe molecule. The results for the diffusion coefficients at an edge of a TEHOS droplet (i.e. within the precursor layer) which is deposited on a quartz cover slip are shown in Fig. 4. The film thickness in the so called precursor layer at the edge of the droplets is measured to be about 1 nm [12]. Both probe molecules behave similar with respect to D_{MSD} and the width of the distribution of D_{MSD}. Similar results are obtained for the diffusion of R6G at the edge of a PDMS droplet.

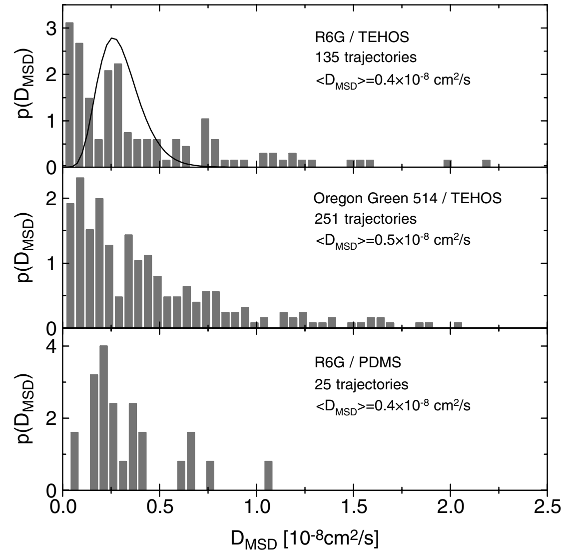

Fig. 4. Distributions of diffusion constants obtained from MSD analysis at the edges of wetting droplets (precursor layer, about 1 nm thick) for different dyes and liquids. The solid line illustrates the width of the distribution of diffusion constants due to the experimental error.

Estimating the diffusion coefficient of R6G in TEHOS and in PDMS via the Stokes–Einstein relation with given $D = 2.8 \times 10^{-6}$ cm^2/s in water [1] yields diffusion coefficients of 3.7×10^{-7} cm^2/s for TEHOS and 5×10^{-8} cm^2/s for PDMS. The viscosities of TEHOS and PDMS are by a factor of 7.6 and 56.2, respectively, larger as compared to water. The diffusion in PDMS will be more complex due to the nature of the polymer melt (crystalline and glassy behaviour). However, the close analogy of the results observed in ultrathin films of PDMS and TEHOS indicates that the diffusion in such films is not so much influenced by the chemical composition of the liquid but rather by the liquid structure which is modified due to the interaction with the solid surface.

3.3. Temperature variation

In addition to the results mentioned above we managed for the first time to record single molecule trajectories for different sample temperatures. Fig. 5 shows the results for the diffusion of R6G-molecules in a 16 nm thick TEHOS film, deposited on a silicon wafer with a 100 nm thick oxide layer in dependence on temperature. It can clearly be seen, that the distributions of the D_{MSD}-values become broader with increasing temperature but the minimum values of D_{MSD} are not shifted with temperature. $\langle D_{\mathrm{MSD}} \rangle$ averaged over all trajectories also

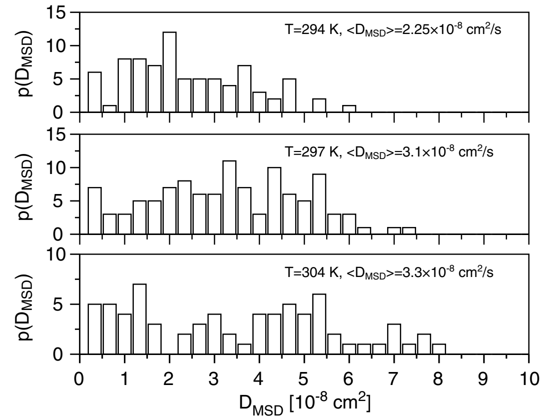

Fig. 5. Temperature dependence of distributions of diffusion constants obtained from MSD analysis for R6G molecules in a 16 nm thick TEHOS film. Average diffusion constants (ensemble averages) are given additionally.

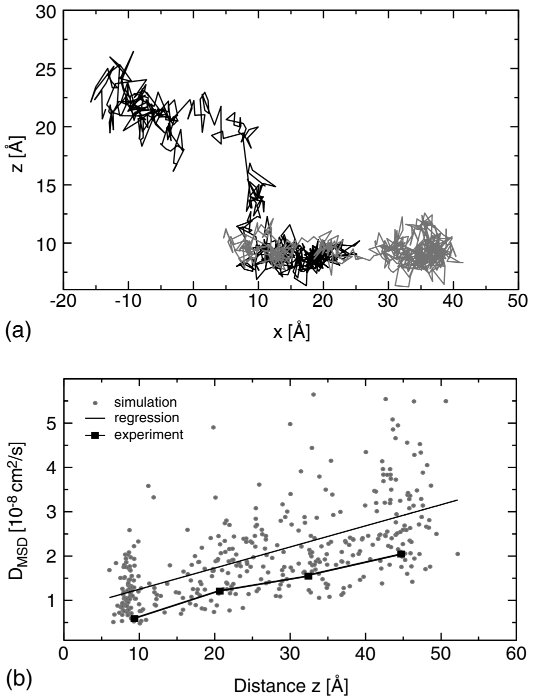

Fig. 6. Results from molecular dynamic simulations of a 4 nm thick TEHOS film on silicon: (a) two trajectories of TEHOS molecules calculated from molecular dynamics data. The *z*-axis is perpendicular to the silicon surface, the *x*-axis is parallel to the surface. (b) Diffusion constants of TEHOS molecules derived from simulations in dependence on the distance to the Si surface (grey dots). The solid line represents a linear fit to the simulation data. For comparison experimental data points (see text) are indicated by black squares.

increases significantly with temperature, as it is expected from the temperature dependence of the viscosity. Experiments with a R6G/TEHOS sample at temperatures of 237 and 243 K, reveal average diffusion constants $\langle D_{\mathrm{MSD}} \rangle = 0.13 \times 10^{-8}$ cm^2/s and $\langle D_{\mathrm{MSD}} \rangle = 0.18 \times 10^{-8}$ cm^2/s, respectively, thus showing that even at these low temperatures there is still observable diffusion which is again accompanied by a broad distribution of diffusion constants. Data obtained so far show a general trend of the temperature dependence. Further experiments are needed to evaluate a physical picture for the observed temperature dependence.

3.4. Comparison with molecular dynamics simulations

Molecular dynamics simulations (MDS) performed in our laboratory for thin TEHOS films on Si(1 1 1) surfaces show that the liquid forms layers parallel to the surface as it was found experimentally by other groups [15–17]. These MDS have been performed in an N–V–T Ensemble using 2-d periodic boundary conditions. TEHOS molecules and Si atoms were fully flexible using empirical potentials from the Universal Force Field (UFF) [23]. The simulation box of 400 TEHOS Molecules has been first equilibrated for about 20 ns with time steps of 5 fs. Data collection was done over further 20 ns with time steps of 5 fs.

The diffusion processes in such computer generated molecular layers have been analyzed by calculating MSD parallel to the surface as a function of time and were fitted it in the same way as for the experiments in order to obtain diffusion constants. Fig. 6(a) shows 2-dimensional trajectories of two TEHOS molecules in a plane perpendicular to the surface. It can be clearly seen that the diffusion process is not homogeneous but occurs preferentially within a layer and then suddenly jumps to a next layer with $\Delta z = 10$ Å being the typical layer distance which corresponds to the diameter of the TEHOS molecules. However, since the timescale of the simulation experiments (20 ns) is much shorter than the timescale of the experiment (tens of milliseconds to seconds) we cannot draw conclusions for the jump rate between the layers directly.

Nevertheless a comparison of experimental results for the distribution of *D* values strongly supports that the distribution of diffusion constants can be related to diffusion processes within the layer and discrete jumps between the layers [11]. Experimental proof for such jumps is also given in [11]. Fig. 6(b) shows a comparison of calculated diffusion constants as a function of the distance *z* above the surface. Since most of the molecules do not change the layer within the simulation time, the diffusion coefficients can directly be assigned to a certain layer (at an average distance from the surface). Also shown in Fig. 6(b) is the measured distribution of D_{MSD} for a 4 nm film, considering only trajectory lengths

$L_T > 40$ in order to reduce the experimental error when calculating D_{MSD} from the trajectories. As shown in [11], we can assign the distribution of diffusion constants in the 4 nm TEHOS films to at least four distinct values of the diffusion constants according to diffusion in four well-defined layers. Comparison of simulation and experiment shows a surprisingly good agreement both for absolute D-values and the trend with respect to z-distance dependence.

Since single molecule detection does not allow to measure the vertical position above the surface within a needed accuracy of 1 nm, we cannot conclude whether the dye molecules diffuse within a TEHOS layer or between the layers. However, comparison of simulation and experiments strongly suggest that the slowing down of diffusion and the accompanied distribution of D are preferentially due to layer formation close to the surface with well pronounced layers in the 5–10 nm regime and surface induced effects upon the diffusion up to more than 100 nm above the surface.

4. Conclusions

In this paper we have concentrated on statistical limitations of diffusion experiments in layered structures of the liquid TEHOS. Layers are induced via interaction with surfaces. In combination with extended MD simulations we safely conclude that diffusion is considerably slowed down by one to two orders of magnitude in monolayers and films of 1–17 nm thickness. The origin of slowing down of the diffusion is attributed to as compared with bulk material closer packing of molecules near to the surface and a barrier for diffusion between layers. In future investigations we attempt to proof whether activation potentials simulated for diffusion between the layers can be related to thermally activated jumping processes between layers. Obviously the diffusion is considerably reduced from a 3-dimensional process to a basically 2-dimensional process which reflects the reduced dimensionality of an interface. Finally slowing down of diffusion processes is observed to be nearly independent of the type of probe molecules.

Acknowledgements

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