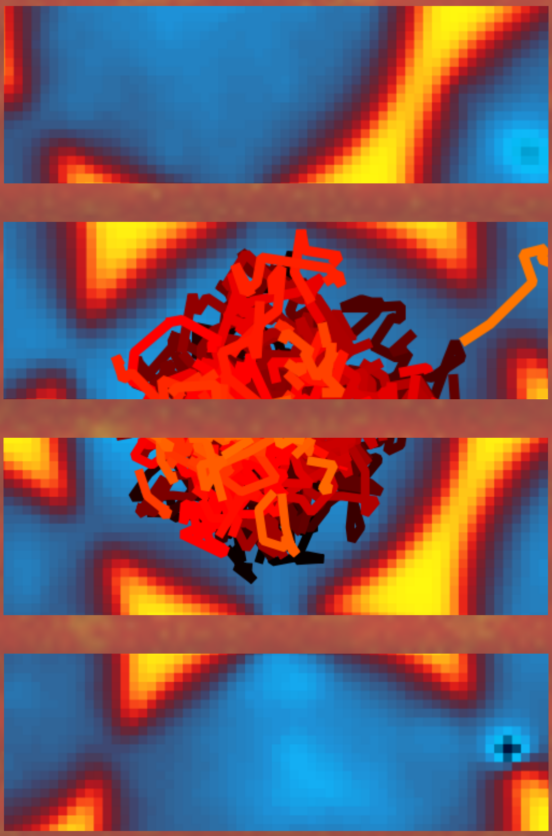
Diffusion Fundamentals V

Basic Principles of Theory,
Experiment and Application
Leipzig, Germany
August 26th–28th, 2013



BOOK OF ABSTRACTS

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Fundamentals V

Book of Abstracts

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Basic Principles of Theory, Experiment and Application

August 26th–28th, 2013

Universität Leipzig, Germany

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Frank Cichos, Klaus Kroy,
Jörg Kärger, Andrea Kramer

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Cover
Background: Diffusion of Molecular Motors along Microtubuli, Stefan Diez Lab, TU Dresden
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Surprises from single-particle imaging of passive and active diffusion

Steve Granick

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The transport of matter and energy is fundamental in nature and biology. It can occur by passive diffusion and can also be active. Predicated on fluorescence imaging at the single-particle level, this talk describes quantitative studies of how this can happen, and presents examples of how nontrivial findings emerge from observing the rare events that underly the overall ensemble-averaged distribution. For example, in living cells, we find that transportation efficiency problems bear a provocative parallel with polymer chain trajectories with their spatial extent, and with jammed matter in their time evolution. A picture emerges in which simple experiments, performed at single-particle and single-molecule resolution, can dissect macroscopic phenomena in ways that surprise.

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Hypothesis of unit rafts as organizers of the meso-scale domain structure and function in the plasma membrane

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Single-molecule imaging and tracking techniques that are applicable to living cells are revolutionizing our understanding of the plasma membrane dynamics, structure, and signal transduction functions. The plasma membrane is considered the quasi-2D NON-ideal fluid that is associated with the actin-based membrane-skeleton meshwork, and its functions are likely made possible by the mechanisms based on such a unique dynamic structure, which I call membrane mechanisms. My group is largely responsible for advancing high-speed single molecule tracking with simultaneous multicolor recording. Based on the observations made by this approach, we propose that the cooperative action of the hierarchical three-tiered mesoscale (2–300 nm) domains—actin-membrane-skeleton induced compartments (40–300 nm), raft domains (2–20 nm), and dynamic protein complex domains (3–10 nm)—is critical for membrane function and distinguishes the plasma membrane from a classical Singer-Nicolson-type model.

In this presentation, I will talk about how domains of tiers 2 and 3 are coupled, with a special attention paid to the dynamic organization of raft-associated glycosylphosphatidylinositol-anchored proteins (GPI-APs) in the plasma membrane and their stimulation-induced changes. In resting cells, virtually all of the GPI-APs are mobile and continually form transient (~200 ms) homodimers (termed homodimer rafts) through ectodomain protein interactions, stabilized by the presence of the GPI-anchoring chain and cholesterol. Heterodimers do not form, suggesting a fundamental role for the specific ectodomain protein interaction. Under higher physiological expression conditions, homodimers coalesce to form hetero- and homo-GPI-AP oligomer rafts through raft-based lipid interactions. This indicates that through evolution of GPI-anchored proteins, the physical property to form homodimers rafts have been maintained, suggesting the importance of homodimers in the function of GPI-anchored proteins.

Upon ligation, the homodimers rafts of a GPI-AP, CD59, for example, formed stable oligomer rafts containing up to four CD59 molecules, which triggered intracellular Ca^{2+} responses that were dependent on GPI anchorage and cholesterol. This result strongly suggest a key role played by transient homodimer rafts. Transient homodimer rafts are most likely one of the basic units for the organization and function of raft domains containing GPI-APs.

Surprisingly, in steady state cells, similar findings were made for glycosphingolipids.

The presence of these unit rafts emphasizes the individuality rather than generality of raft compositions, except for the ubiquitous contributions of cholesterol to the formation of the unit rafts and greater raft domains consisting of unit rafts.

How diffusion might lead to non-linear response

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Chemotaxis is a complex interplay between numerous molecular species whose coordinated interactions culminate in highly effective directed motion in concentration gradients. Many proteins that play vital, important and minor roles have been identified and biochemically characterized. Several pathways have been recognized to act in parallel each of which contributes to, but is not essential for chemotaxis. Nevertheless a definitive answer as to how cells like *Dictyostelium disciodeum* perform chemotaxis is still unknown. Qualitative descriptions of molecular interactions have proven to be insufficient when trying to understand complex cellular cascades. New techniques such as single molecule microscopy are able to add temporal, spatial and quantitative information to the network of molecular interactions. Further probing the properties of cytoskeleton meshworks and tightly controlled artificial membranes *in vitro* provides information on cellular components relevant to chemotaxis which cannot be investigated in the complex environment of the living cell. Finally simulations give insight in the effects of noise in the biological systems and lead to new ways of interpreting biochemical data. Here we will look at chemotaxis from a biophysicists' view, combining *in vivo*, *in vitro*, and *in silico* experiments with a particular emphasis on single molecule work.

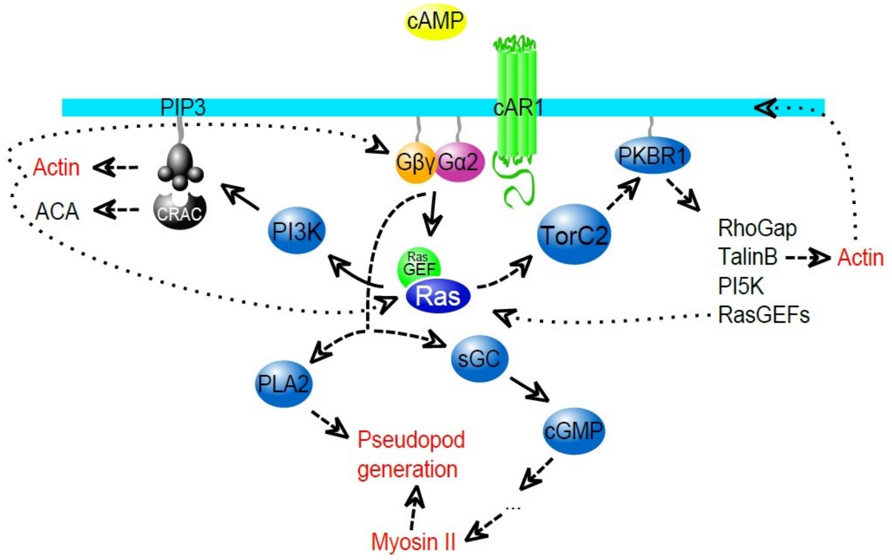

Figure 1: *D. Discoideum* chemotaxis pathway. Upon activation of cAR1 by cAMP, the Ga2β heterotrimer dissociates. Both subunits engage in signaling, Ga2 is more important in pathways that lead to pseudopod extension whereas Gβ is more important for cAMP relay involving cytosolic regulator of ACA (CRAC) and ACA. The PLA2 and soluble guanilyl cyclase (sGC) pathways are activated; these pathways play important roles in the regulation of pseudopod placement. RasGEFs activate Ras proteins. Ras proteins and other small G proteins locally activate TorC2 which via membrane localized PKBR1 subsequently activates a multitude of factors including TalinB. Talin mediates cytoskeleton membrane interactions and plays a role in cell adhesion. Ras proteins futher activate the PI3K pathway. PI3K localizes to the leading edge where it produces PI(3,4,5)P from PI(4,5)P. PI(3,4,5)P functions as a docking site for several chemotaxis-related proteins like the ACA regulator CRAC. A feedback loop involving F-actin that activates Ras proteins leads to the generation of pseudopods without G protein input facilitating random cell motility. We propose a feedback from actin acting on the Gβ subunit specifically at the leading edge. This conceivably leads to a more persistent leading edge or the stabilisation of pseudopods. More generally, actin polymers form fences in the membrane functioning as physical diffusion barriers that influence and maintain localized signaling.

Weak ergodicity breaking for anomalous diffusion

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We briefly review basic random walk approaches to anomalous diffusion: the sub-diffusive continuous time random walk, super-diffusive Lévy walks, and Lévy flights. The corresponding fractional diffusion equations are presented, and we then turn to two physical applications. For cold atoms diffusing in an optical lattice, we derive the fractional space diffusion equation from the semiclassical description of Sisyphus cooling [1]. Depending on optical lattice depth, we show that the dynamics of atoms is described by normal diffusion, Lévy flights with cutoffs, or Richardson-Obukhov dynamics, .i.e. $x^2 \sim t^3$ found in the field of turbulence. This rich phase diagram is related to the peculiar friction force induced by the laser field. Unlike Stokes friction which increases with velocity, in our system the friction decays like $1/v$ for large velocities, thus asymptotically the system is frictionless, leading to fat tailed dynamics. Comparison to experiment, indicates that open questions still remain in this field [2].

The second theme we address, is the question of ergodicity in anomalous processes. For Brownian motion the ensemble averaged mean squared displacement (MSD) $\langle x^2 \rangle$ is identical to the time averaged MSD

$$\overline{\delta^2} = \frac{\int_0^{t-\Delta} [x(t'+\Delta) - x(t')]^2 \, \mathrm{d}t'}{t-\Delta} \tag{1}$$

in the limit where the measurement time t is much longer than the lag time Δ. Recent works showed that for the above mentioned models of anomalous diffusion, and for a wide variety of anomalous diffusion processes of single molecules in the cell environment, we get $\overline{\delta^2} \neq \langle x^2 \rangle$. This being in complete contrast to normal diffusion, and it indicates that ergodicity in the MSD sense cannot be taken for granted [3]. We quantify deviations from ergodic behaviour, showing that time averaged transport coefficients, remain random with a well defined probability density [4, 5]. For the sub-diffusive continuous time random walk, the time averaged MSD exhibits ageing, namely it crucially depends on both the measurement time t and lag time Δ, in agreement with recent single molecule tracking experiments [6], on sub-diffusive Kv2.1 potassium channel in the plasma membrane.

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Diffusion driving the formation of functional nanoscale machines in cell membranes

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A great fraction of functions in cells is taken care of by membrane proteins. Their biological relevance is thereby quite exceptional, yet they do not work alone. Instead, to become functional, membrane proteins require an appropriate pool of lipids around them, and the lipids have an important function as they modulate or even govern the activation of the proteins in question through specific or membrane-mediated interactions. The key process driving the formation of functional nanoscale protein-lipid units (lipid rafts) is diffusion.

While lateral diffusion of lipids in protein-free membranes is quite well understood [1], the situation is more complicated in cases where lipids diffuse under the influence of proteins [2]. More complications arise when crowding with proteins comes into play [3]. Understanding the dynamics under crowding is highly relevant since native cell membranes are usually very crowded, typical protein:lipid molar ratios being around 1:50–1:100 [4]. What is more, membrane-spanning proteins are influenced by the transmembrane distribution of lipids around them, thus diffusion of lipids across membranes (flip-flop/translocation) is also a matter to worry about in order to understand the conditions where membrane proteins are able to fulfill their cellular commitments.

Here we discuss perspectives based on most recent atomistic and coarse-grained molecular simulations on the dynamics of lipids with proteins. We discuss, e.g., how they form functional nanoscale units, how lipids migrate into the specific lipid binding sites in membrane proteins, how lipids and proteins move in unison as collective units with long lifetimes, and how proteins control the translocation of lipids across lipid membranes.

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Modeling DNA-translocation through nanopores: Two case studies

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In the first part we reconsider the model of Lubensky and Nelson for the electrically driven translocation of polynucleotides through an alpha-hemolysin pore [1]. We show that the model correctly describes two further important properties of the experimentally observed translocation time distributions, namely their spread (width) and their exponential decay [2].

In the second part we focus on the translocation of elongated cylindrical particles (oligomers, nanorods, etc.) through a solid state nanopore. Particular emphasis is put on the interplay of electrophoresis, electroosmosis, and osmotic pressure beyond the realm of small Debye lengths. We find that the net potential energy difference across the membrane may be of opposite sign for short and long particles. Thermal noise thus leads to biased diffusion through the pore in opposite directions. The specific particle length at which this transport inversion occurs can be controlled by means of a membrane gate electrode [3].

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Driven motion of colloids in active microrheology

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In active microrheology, a strong external force is applied to a colloidal probe immersed in a complex fluid, so that among other quantities the nonlinear force-velocity relation can be measured. It provides information on the local viscoelastic properties of the complex fluid or soft solid. Generally, in dense fluids, the probe's friction coefficient decreases strongly with increasing force [1]. If the probe is pinned in a glass, the probe remains localized by the nearest-neighbor cages for small enough forces. Then the stationary probe density distribution (see Fig. 1) displays the local cage and its plastic deformation [2]. Close to the depinning threshold of a probe in glass, intermittent dynamics sets in where the probe particle undergoes a combination of highly localized motion and rare, increasingly long-ranged excursions, leading to anomalous force-induced diffusion behavior [3]. The long-time diffusion coefficients become anisotropic and strongly force dependent.

I discuss computer simulations and recent theoretical results based on the mode-coupling theory of the glass transition [1–4].

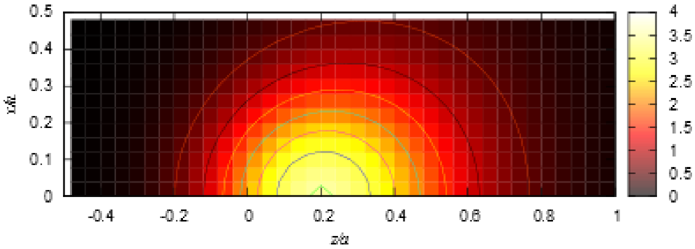

Figure 1: Probability density of a forced Brownian probe particle (radius a) pinned in a metastable amorphous solid made of equal-sized hard spheres (at packing fraction 0.52). The probe experiences a force of 10 $k_B T/a$ to the right; mode coupling theory calculation from [2]

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Diffusive transport in corrugated channels

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Diffusive transport of particles or, more generally, small objects, is an ubiquitous feature of physical and chemical reaction systems. In configurations containing confining walls or constrictions, transport is controlled by both, the fluctuation statistics of the jittering objects and the phase space available for their dynamics. Consequently, the study of transport at the macro- and nano-scales must address both Brownian motion and entropic effects.

For particles undergoing biased diffusion in static media enclosed by confining geometries, transport exhibits intriguing features [1] such as 1) a decrease in nonlinear mobility with increasing temperature or 2) a broad excess peak of the effective diffusion above the free diffusion limit. These paradoxical aspects can be understood in terms of entropic contributions resulting from the restricted dynamics in phase space. If, in addition, the suspension medium is subjected to external, time-dependent forcing, rectification or particle separation becomes possible [2].

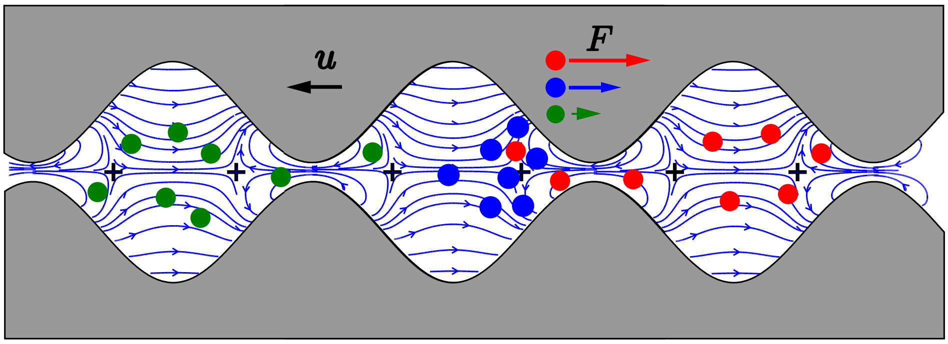

Figure 1: The competitive action of the constant force F and the pressure-driven fluid flow u in microchannels with periodically corrugated walls yields an effective entropic force field (blue lines) exhibiting characteristic stagnation points (black crosses). As the particles' properties determine the strength of the force F, separation of Brownian particles is achieved: While some particles (blues circles) are trapped, other particles are gradually sifted out to the left (green circles) and to the right (red circles).

In presence of a fluid flow across the microfluidic channel (see sketch), where a solute of Brownian particles is subjected to an external bias and a pressure-driven flow, a new phenomenon emerges [3]: namely, the identically vanishing of the average particle flow which in turn is accompanied by a colossal suppression of diffusion. This entropy-induced phenomenon, termed hydrodynamically enforced entropic trapping, offers the unique opportunity to separate particles of the same size in a tunable manner.

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The appeal of single-molecule and single-cell studies

Cees Dekker

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I will provide a number of highlights from our recent single-molecule and single-cell research:

1. Dynamics of DNA supercoils [1]

DNA in cells exhibits a supercoiled state where the double helix is additionally twisted to form extended intertwined loops known as plectonemes. Although supercoiling is vital to many cellular processes, its dynamics remain elusive. We have recently managed to directly visualize the dynamics of individual plectonemes. We observe that multiple plectonemes can be present and that their number depends on applied stretching force and ionic strength. Plectonemes are found to move along DNA by diffusion or, unexpectedly, by a fast hopping process which facilitates very rapid (< 20 ms) long-range plectoneme displacement by nucleating a new plectoneme at a distant position. The observations directly reveal the dynamics of plectonemes and identify a new mode of movement that allows long-distance reorganization of the conformation of the genome on a millisecond timescale. Follow up experiments now concentrate on the elucidating the effects of local pinning due to DNA sequence and bound proteins.

2. DNA and protein translocation through solid-state nanopores [2]

Solid-state nanopores have proven to be a surprisingly versatile probe for single-molecule analysis of DNA. I will describe some of our recent efforts to expand the capabilities of solid-state nanopores even further, in the direction of single-protein detection, graphene nanopores, plasmonic nanopores, DNA origami nanopores, and biomimetic nanopores.

3. Min oscillations in arbitrarily shaped E. coli cells [3]

I will show our ability to shape live E. coli bacteria into novel shapes such as rectangles, squares, triangles and circles. We study spatiotemporal oscillations of Min proteins – associated with cell division – in these geometries.

References

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[3] F. Wu et al, to be published

Seeing is believing: Direct visualization of fluctuations in biopolymer networks with 3D thermal noise imaging

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Intracellular biopolymer networks perform many essential functions for living cells. Most of these networks show a highly nonlinear mechanical response that originates from the properties if the individual filaments and the network architecture. While much theoretical work has been done to connect the macroscopic response to specific network properties, such as filament persistence length, cross-linking geometry and pore size, there is a lack of experimental techniques that can simultaneously determine the structure and the mechanical properties of a network in situ on the single filament level and thus basic assumptions made in theoretical and computer models are untested. Here we describe three-dimensional thermal noise imaging as a novel submicroscopic imaging technique that visualizes biopolymer networks on length scales and under conditions that are inaccessible to any other microscopic technique.

Thermal Noise Imaging is a scanning probe technique that utilizes the confined thermal motion of an optically trapped particle as a three-dimensional, noninvasive scanner for soft, biological material. It achieves nanometer precision in probe position detection at MHz bandwidth. Thermal noise imaging visualizes the excluded volume generated by the interaction of the probe particle with the filaments and allows for the quantification of their mechanical properties from their transversal fluctuations. The experiments presented here also pave the way for measuring force distributions inside biopolymer networks as well as establish thermal noise imaging as a quantitative tool for studying soft material on the nanometer scale.

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Hydrodynamic resonance in optical traps & friction of molecular machines

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Optical tweezers are high-resolution position and force transducers widely used in physics, material science and biology. Often dielectric particles of mesoscopic size are used as sensitive probes and handles for experiments. We designed and fabricated high-refractive index, anti-reflection coated titania microspheres (Fig. 1, [1]) and demonstrated nanonewton optical forces [2]. Using the coated microspheres, novel experiments are feasible. The high trap stiffness enabled us to directly measure the colored nature of noise that drives Brownian motion and how it depends on the distance to a nearby surface in quantitative agreement with theoretical predictions [3]. This hydrodynamic resonance can be increased by using larger particles and/or lower viscosity fluids. I will show our efforts in increasing the amplitude of this resonance peak.

Apart from diffusive motion of particles confined in optical traps, we are interested in diffusive motion of molecular motors and the corresponding friction when this motion is biased. We could show that the Einstein relation holds for molecular motors interacting with their tracks [4]. Our recent work indicates that kinesin-8 motors switch between their normal translocating mode and a diffusive mode in order to increase their run length [5]. Here, I will present how this diffusive interaction enables the motor to fulfill its cellular function of microtubule length regulation.

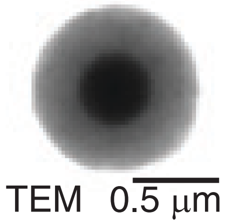

Figure 1: Transmission electron microscope (TEM) image of an anti-reflection coated, high-refractive index titania microsphere.

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First passage times: A common theme in the kinetics of macromolecular motors

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A molecular motor is made of either a single macromolecule or a macromolecular complex. Just like their macroscopic counterparts, molecular motors "transduce" input energy into mechanical work. Their diffusion is biased by the energy pumped in by the "burning fuel". In this talk I'll begin by giving an elementary introduction to the most essential and relevant features of molecular motors [1, 2] and then present three sets of examples to establish the ubiquity of first-passage times in intracellular processes. Some motors walk along filamentous proteins carrying molecular cargo. The stochastic pause-and-translocation of such a porter is characterized by the distribution of the times of its dwell at the successive positions on its track. The dwell times are essentially first-passage times and their fluctuation provides a lower bound on the number of kinetic states of the motor. For a motor that can step both forward and backward the kinetics of translocation is characterized by the distributions of four distinct conditional dwell times. DNA polymerase is a motor that can not only step forward and backward mechanically, but also step backward by catalyzing a different chemical reaction; its stepping kinetics is characterized by nine distinct conditional dwell times. As the first example of first passage times, I'll define these conditional dwell times and summarize our analytical results as well as their physical implications [1, 2]. In the nucleus DNA is stored in a hierarchical structure called chromatin. The basic unit of chromatin consists of 146 base pairs of a double stranded DNA (dsDNA) wrapped around a spool formed by proteins. The helical path of the dsDNA on a spool is also called its "footprint". We have investigated the mechanism of footprint traversal by a chromatin-remodeling enzyme (CRE), a motor that translocates along the dsDNA thereby unwrapping it from the spool. A CRE-induced biased diffusion of a small DNA loop along the footprint can lead to the sliding of the spool along the DNA. The average time needed for the traversal of the footprint, for the first time, by sliding is essentially the corresponding mean first passage time. As an example of second class of first-passage problems, I'll present our model and fuel-dependence of the mean foot-print traversal time [3]. The third type of example I'll present occurs in chromosome segregation before cell division. Each of the sister chromatids, that result from chromosome replication, is bound to a structure, called kinetochore (kt) that, in turn, is coupled to the plus ends of stiff protein filaments called microtubules (MT). The lifetime of a kt-MT attachment is also a first-passage time. I'll present our recent results that explain the experimentally observed, apparently counter-intuitive, dependence of the mean lifetime on the externally applied tension that tends to detach MT from the kinetochore [4, 5].

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Hot colloids in polymer networks: Cage formation and transient network deformation

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Laser-heated gold colloids are highly localized heat sources that allow for heat release on length scales well below the optical diffraction limit. When embedded in a binary matrix, the temperature field around the particle couples to the matrix composition via the Soret effect. In case of a polymer solution with a positive Soret coefficient, e.g. polystyrene in toluene, the polymer is depleted near the particle surface and a transient solvent-rich cage of low viscosity is formed around the colloid on the characteristic diffusion time scale of the polymer. Depending on chain length, concentration, and temperature, the polymer depletion can either be amplified by a positive or damped by a negative feedback loop. Under favorable conditions the polymer depletion is quantitative and a pure solvent bubble of approximately one micrometer in diameter is created around the particle. At high polymer concentrations the viscosity strongly depends on concentration and temperature due to the proximity of the glass transition. For semidilute solutions of high polymers, entanglements are decisive. In the latter case the deformation of the transient polymer network by the radial thermodiffusion processes can be visualized via video microscopy of 'the other' colloids that are trapped in the meshes of the network on the disentanglement time scale of the polymer.

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Drivers and impacts of the spread of alien species in Europe

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Species occurring outside their natural range due to human facilitation are called alien (synonyms: non-native, exotic). While most of these species integrate into native ecosystems without causing (major) problems, some of them can have considerable impacts on native biodiversity, ecosystems, human infrastructure and/or health, thus causing environmental or economic harm [1].

During my talk, I will specifically review the situation in Europe with a focus on plant species. Most of the plant species in Europe were introduced intentionally (e.g., as agricultural crop or forestry tree or for ornamental purposes [2] and then escaped [3]. Exchange across biogeographic barriers largely increased with human travel, transport and trade. Several environmental factors are related to spread of these species, such as rivers and canals, roads and railways. Furthermore, habitat disturbance and climate change are now known to increase invasibility [4, 5].

From an ecological point of view, this spread is most interesting and there are several methods to model spread under static and dynamic conditions. During my talk I will therefore provide an overview on the variety of model. Some of these models are based on ecological processes such as meta-population dynamics, colonization and extinction probability related to habitat characteristics, dispersal abilities related to species traits or using physical principles based on diffusion models [e.g., 6].

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Dynamics in social fluids

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Bird flocks, insect swarms and fish shoals resemble fluids made up of many individuals where the controlling interactions are social rather than physical in character [1]. Some progress has been made reverse-engineering candidates for these interactions that are local in space, either in a metric-based [2] or topological sense [3, 4]. A question that has been largely overlooked is whether the interactions should be expected to be local at all. We discuss the evidence for them having a non-local character and, furthermore, that there is a natural choice for this that is consistent with the cognitive limitations of a bird's vision. This leads us to propose a non-local *hybrid-projection* model. We study the global character of the flocks that emerge from this model and their various phenotypes. Most significantly, an emergent state arises in which the probability that a typical bird can see out (sky) in any direction divided by the probability that its view is blocked by other bird(s) is O(1). We refer to this as *marginally opaque*, see Fig. 1. We present experimental data on bird flocks that confirm this prediction. Finally, we discuss how these models may naturally be associated with evolutionary fitness, as well as being physiologically plausible.

Figure 1: The centre panel is an image of a real flock of Starlings. It is *marginally opaque*. The left and right panels show the same image artificially doctored so as to resemble states that would have a very low ($\ll$1) or a very high ($\approx$1) opacity, respectively.

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Active Brownian motion of asymmetric particles

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Self-propelled microswimmers that – similar to chemotactic bacteria and cells – autonomously steer through liquids, currently receive considerable attention from experimentalists and theoreticians because they allow detailed insights on how active matter organizes into complex dynamical structures. So far, most studies have concentrated on spherical or rod-like microswimmers and their motional behavior has been studied in great detail. In contrast, much less is known about asymmetrically shaped swimmers, whose trajectories strongly deviate from that of spherical ones because their mobility strongly depends on the orientation of the particle relative to its swimming velocity. We experimentally investigate the motion of L-shaped swimmers and observe an effective torque acting on the particles which results in a circular motion. We investigate this behavior both under bulk conditions and close to walls where the torque leads either to the reflection or a sliding along the wall. In addition, we study the self-propulsion of asymmetric particles in the presence of an external gravitational field. This leads to additional torques on the particle which leads to rather complex trajectories which may give useful insights into the gravitactical motion of microorganisms.

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Self-organization dynamics of active colloids

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Understanding transport properties of colloid under various external fields is a fundamental classical problem in soft matter physics and their fluctuating dynamics is still a central topic in non-equilibrium statistical mechanics. Recently, we studied on non-trivial dynamics and self-organization of active colloids. By fabricating Janus particles with their half hemisphere covered with gold, we realized self-propelled motion of Janus particles under AC electric field. Asymmetric surface flow around the particle caused a self-propulsive ballistic motion. We succeeded in controlling interaction between colloidal particles with changing salt condition and frequency of electric filed. Interaction between particles changed from repulsive to attractive resulting in formation of chains which swim, oscillate, and rotate under steady uniform electric fields. The mechanism of changing interactions is attributed to a dipole-quadrupole transition of Janus particle due to the response to the AC electric field. I will present the analysis and discuss the mechanism of these self-organization dynamics.

Diffusion and organization in driven particles systems

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Over the past several years we have been studying a phenomena, Random Organization, whereby apparently random interactions between particles in a driven system lead to their self-organization [1]. Particles in a viscous flow with periodic shear initially collide and undergo chaotic diffusive motion. The collisions allow the system to explore different local configurations and evolve. If the underlying physics is reversible, as at low Reynolds number, we obtain absorbing, halted, reversible states, but above a threshold strain the motion remains chaotic. In a similar phenomena for irreversible frictional interactions, simulation results show that periodically sheared *granular* matter exhibits diffusive motion that evolves into a spatially disordered *limit cycle* where each individual grain follows a different exactly retracing loop [2].

In the previous systems with external drive the organized states are spatially random but temporally periodic. In a separate system with random self-propelled colloidal swimmers we find evolution from a gas phase to clusters or even crystals due to their collisions [3]. The crystals are dynamic and form rotate, evaporate and explode. They are spatially periodic but time chaotic.

In all of these microscopically inhomogeneous systems, irreversible processes arising from collisions and dissipative interactions facilitate the exploration of local configurations. Feedback on the local force distributions and dynamics provide a mechanism for a system to evolve into absorbing (halted), time periodic or stationary states or to remain chaotic.

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Diffusion in lithium ion conductors – From fundamentals to applications

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Lithium ion conductors and concomitantly the topic of Li solid state diffusion have become enormously popular in recent years. The annual number of publications increased from 1991, the year when the Li ion battery was introduced into the market, up to this day by factors of some tens. This is mainly due to the quest for better materials and performances of Li ion batteries, the leading electrochemical energy storage system. However, fundamental research on diffusion of the lightest ion besides H^+, comprising questions about, e.g., the dimensionality of diffusion or the influence of structural disorder, has been intensified as well.

Here, exemplary results of our group are reviewed. Starting from early studies on ionic motion by ^{8}Li-beta-NMR [1], the first example of a battery cathode material, which at the same time turned out be a model system for an unambiguous proof of two-dimensional Li diffusion via frequency-dependent ^{7}Li-NMR spin-lattice relaxation time measurements, was layer-structured Li_xTiS_2 as a polycrystal [2]. This system, partly also in its nanocrystalline and amorphous forms [3], has developed into a true playground for diffusion-related NMR studies, where also the potential of ^{7}Li spin-alignment echo NMR was demonstrated [4]. Another potential cathode material is Li_3VF_6 where detailed insights into the Li diffusion process were obtained by ^{6}Li 2D exchange MAS NMR [5]. Actual or potential anode materials studied by us primarily from a fundamental point of view have been Li_xC_6 ($0 < x \leq 1$) [6], $Li_{4+x}Ti_5O_{12}$ ($0 < x < 3$) [4] and, among the silicides, $Li_{12}Si_7$ [7]. In $Li_{12}Si_7$ very fast quasi one-dimensional Li diffusion was detected. While the fast ion conductor Li_3N still plays a role as an excellent model system where the whole arsenal of NMR techniques has been applied [1, 4], $Li_7La_3Zr_2O_{12}$ is presently regarded as one of the most promising electrolytes for all-solid-state Li ion batteries and simultaneously serves for studying the influence of doping and defects on Li diffusivity [8].

Thus, diffusion in Li ion conductors is a topic *par excellence* in the tension field of fundamentals and applications with considerable cross-fertilization between the two. Methodologically, it extensively involves NMR techniques, but also impedance spectroscopy, mass spectrometry and neutron scattering are being applied.

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Ionic transport and pair formation in polymer electrolytes

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Salt-in-polymer electrolytes have interesting properties for practical use in batteries, smart windows, and electrochemical solar cells. However, a technological breakthrough is hampered by the relatively low mobility of the cations and a pronounced tendency to pair formation.

Common analysis (level 1) characterizes the degree of ion association in polymer electrolytes by the Nernst-Einstein deviation parameter Δ which quantifies the relative difference between the true ionic conductivity directly measured by electrical methods and the hypothetical maximum conductivity calculated from the individual ionic self-diffusion coefficients. Alternatively, the Haven ratio H_R may be used as key figure to specify the association degree. Despite their unambiguous definitions, Δ and H_R are global quantities with limited explanatory power. Similar is true for the cation transport number t^*_{cat} which relies on the same ionic diffusion coefficients usually measured by nuclear magnetic resonance or radiotracer methods.

In polymer electrolytes of low or moderate salt concentration neutral ion pairs dominate over higher-order aggregates. By evaluating this case in detail (level 2), more specific information can be extracted from the same body of experimental data that is used for the calculation of Δ, H_R and t^*_{cat}. This information concerns the individual contributions of pairs and free ions to the self-diffusion coefficient of cations and anions. Also the true cation transference number based on charged species only can be deduced. We present the basic theoretical framework and some pertinent examples dealing with ion pairing in systems based on poly(ethylene oxide) with inorganic salts or ionic liquids [1].

An even more extensive analysis (level 3) makes it feasible to split up each pair- and free-ion-specific contribution (or 'effective diffusivity') in a 'true diffusivity' and the relative abundance of the corresponding species. Such an extended approach requires assumptions about the basic type of temperature dependence of the true diffusivities and the reaction constant of ion pairing. This involves the introduction of parameters characterizing ionic mobility and association, such as Vogel-Tammann-Fulcher parameters as well as the enthalpy and entropy of pair formation. Within such a specific model, containing reasonable assumptions to reduce the number of free parameters, all experimental data can be simultaneously fitted using a least-squares routine [2].

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Poster Presentations

Poster Session I
Monday, August 26th, 2013, 16:20–18:45
Foyer, Faculty of Chemistry and Mineralogy

AI – Biophysics and Single Molecules I

B – Nanopores and Nanoprobes

C – Fluctuations, Optical Traps, Hot Colloids

D – Dynamics in Social and Animal Systems

Poster Session II
Tuesday, August 27th, 2013, 11:50–14:30
Foyer, Faculty of Chemistry and Mineralogy

AII – Biophysics and Single Molecules II

E – Active Brownian Motion

F – Diffusion in Material Science

Single molecule study of heterogeneous dynamics in polymers

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Polymers are very heterogeneous close to glass transition temperature (T_g) and a complex dynamics with a non-exponential relaxation is observed by bulk techniques as well as by single molecule (SM) techniques. We have performed measurements of rotational diffusion of single perylene dimide (PDI) dye molecules in poly (methyl acrylate) (PMA) and poly (vinyl acetate) (PVAc) close to their T_g. We have found that the dynamics of a single molecule is temporally heterogeneous and the heterogeneity changes with change in temperature. SM results are compared to results from dielectric measurements and to shear viscosity data. Average rotational times from single molecule measurements follow similar temperature dependences as predicted from Debye–Stokes–Einstein (DSE) law for polymer viscosity whereas dielectric spectroscopy reveals the decoupling of segmental motions from probe rotational motions.

Single dye (Alexa 488 & Cy3) labeled polymers are synthesized. Single molecule (SM) lifetime measurements of free PDI dye molecules and single dye (Alexa 488 & Cy3) labeled polymers in PMA are performed. A broad distribution of lifetimes is observed for single dye labeled polymers in PMA. This also signifies the heterogeneity in polymer systems.

This work was supported by the DFG (FOR 877).

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Characterization of diffusion processes observed with measurement noise by the distribution of diffusivities

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Diffusion is an important mechanism for the transport of particles and molecules in many physical and biological systems. In single-particle tracking (SPT) a characterization of such processes becomes possible by observing the motion of individual tracers. However, an analysis of these trajectories by conventional methods such as mean-squared displacements often conceals the effects of inhomogeneous systems. Hence, we introduced the distribution of diffusivities $p(D,\tau)$ [1], which is easily obtained from SPT experiments and can be related to ensemble-based methods such as pulsed field gradient nuclear magnetic resonance (PFG NMR) [2]. An investigation of the properties of the distribution of diffusivities and its dependence on the time lag τ between snapshots reveals details of the heterogeneities [2] or the anisotropy of the process [3]. Since in experiments the observed positions of a trajectory are always influenced by measurement noise we study such effects on the distribution of diffusivities. As depicted in Fig. 1, large noise can lead to a remarkable change in the behavior of the distribution of diffusivities for small τ but vanishes for increasing τ. This causes a non-trivial τ-dependence of the distribution of diffusivities even for simple systems. We further show how immobile tracers can be exploited to remove contributions of the measurement noise from the distribution of diffusivities, which is highly relevant for experimental data.

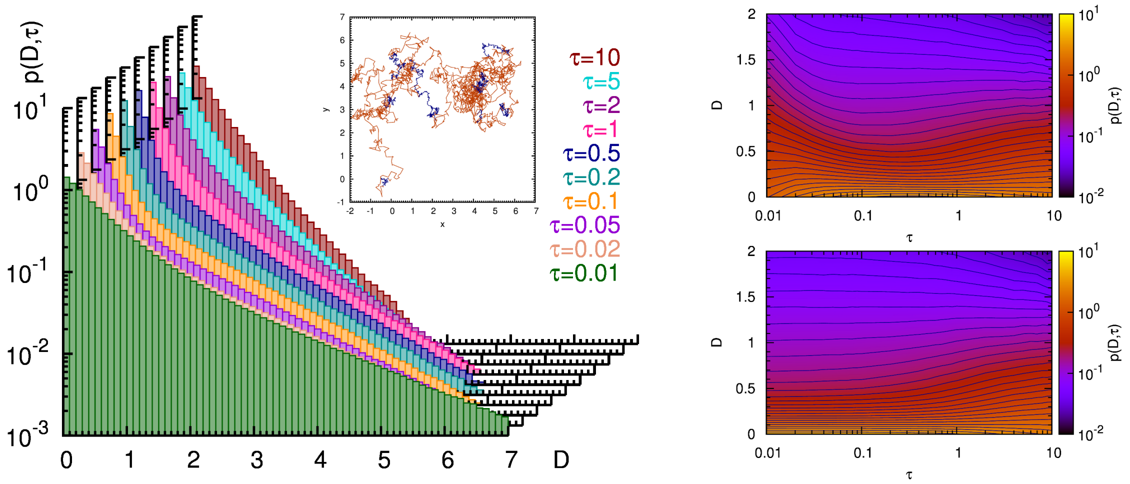

Figure 1: (left) Distributions of diffusivities (histograms) for different time lags τ of a diffusing particle simulated in a bi-layer system [2] where the observed positions are influenced by measurement noise. Both the heterogeneity of the system and the measurement noise govern the decay of the distribution and its convergence to a mono-exponential decay for large τ. The inset shows an example of such a trajectory, where, in contrast to the experiment, information about the layer is color-coded. (right) Comparison of the contour plot of the distributions of diffusivities from the left figure (top) and the same process without additional measurement noise (bottom). For small τ the measurement noise has a large impact on the behavior of the distribution of diffusivities and strongly changes the decay for small diffusivities D. For increasing τ the contribution of the measurement noise vanishes.

This work was supported by the DFG (FOR 877).

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Characterization of diffusion processes by the distribution of diffusivities

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Many transport phenomena in physical and biological systems are described by diffusion processes. The observation of individual particles such as tracer molecules offers an interesting approach to characterize the motion by single-particle tracking (SPT). The observed trajectories are typically analyzed by mean-squared displacements. However, this method conceals significant properties of the motion in inhomogeneous systems due to averaging along a trajectory or over an ensemble. Hence, instead of averaging we introduced an analysis which considers diffusivities D defined as scaled squared displacements during a time lag τ along a trajectory in the distribution of diffusivities $p(D,\tau)$ [1]. This distribution describes the diffusivity as a fluctuating quantity and allows further analysis of statistical properties. It should be noted that the first moment of the distribution corresponds to the slope of the well-known mean-squared displacements and identifies the mean diffusion coefficient of the system.

Depending on the nature of the system diffusion is governed by different mechanisms. In heterogeneous systems, such as the two-region exchange model, the diffusion coefficient changes with time. Hence, the distribution of diffusivities depends on the time-lag τ which allows a characterization of the properties of the observed system [2]. In this context we showed how this analysis is closely related to ensemble methods such as pulsed field gradient nuclear magnetic resonance (PFG NMR) providing further benefits.

The distribution of diffusivities also revealed advantages over conventional analysis when observing anisotropic processes where the diffusion coefficient depends on the direction of motion. In such systems the asymptotic decay of the distribution of diffusivities deviates from its first moment [3]. This enables a detection of the anisotropy and even allows a simple reconstruction of the diffusion tensor.

Furthermore, the distribution of diffusivities can also be obtained from an ensemble of particles which coincides with the distribution from a single trajectory for ergodic systems. This is especially interesting for anomalous diffusion, where we extended our concepts to the distribution of generalized diffusivities $p_\alpha(D,\tau)$ which takes the diffusion exponent α into account [4]. In systems showing anomalous diffusion ergodicity can be broken. The most prominent example are subdiffusive continuous time random walks which are known to show interesting phenomena such as aging and weak ergodicity breaking. As a consequence, the distributions of generalized diffusivities which are obtained from ensemble and time averages, respectively, do not coincide (see Fig. 1) and depend in a nontrivial way on the elapsed time between the beginning of the process and the beginning of the measurement. In this context our new analysis tool reveals a deeper understanding of weak ergodicity breaking.

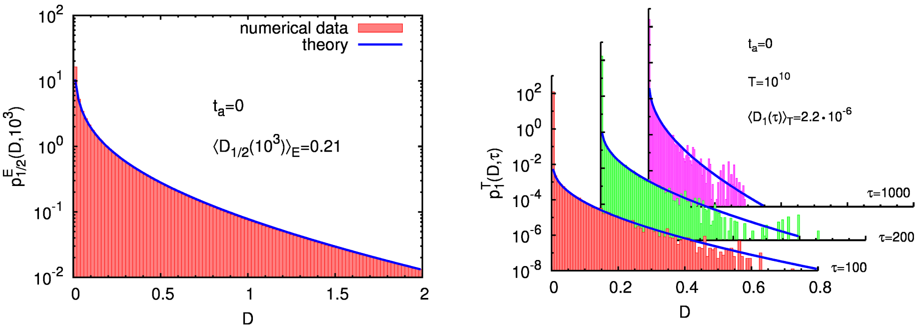

Figure 1: Distribution of generalized diffusivities obtained from an ensemble of subdiffusive continuous time random walk trajectories (left) compared to the distribution which is obtained as time average from only one realization of a subdiffusive continuous time random walk (right). The differences between both distributions, where the left one is asymptotically τ-independent for large τ and the right one shows a strong τ dependence, are obvious and caused by weak ergodicity breaking, which is known to occur in this system.

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Optical tracking of single Ag nanodots in nanostructured water films

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Monodisperse silver nanoparticles synthesized via Ag (I) carboxylate in zeolite Y cages are investigated on silicon dioxide (SiO_2) and mica surfaces with optical and atomic force techniques. Subnanometer particles escaping the Y cage show a strong and photostable fluorescence emission in the visible range (see Figure 1) and allow for optical single particle tracking revealing spatial diffusion of Ag particles on SiO_2 within a few nanometre thick and nanostructured water film. Heterogenous diffusion dynamics reflect the transition from an ice-like to a liquid-like water film as a function of film thickness. The contributions of the different diffusion coefficients strongly correlate both with the water film thickness and the chemical composition of the interface. The heterogeneity of the diffusion is caused by ad- and desorption of Ag particles to silanol groups at the SiO_2 interface which couple vibronically to the Ag particles as can be seen from single particle fluorescence spectra.

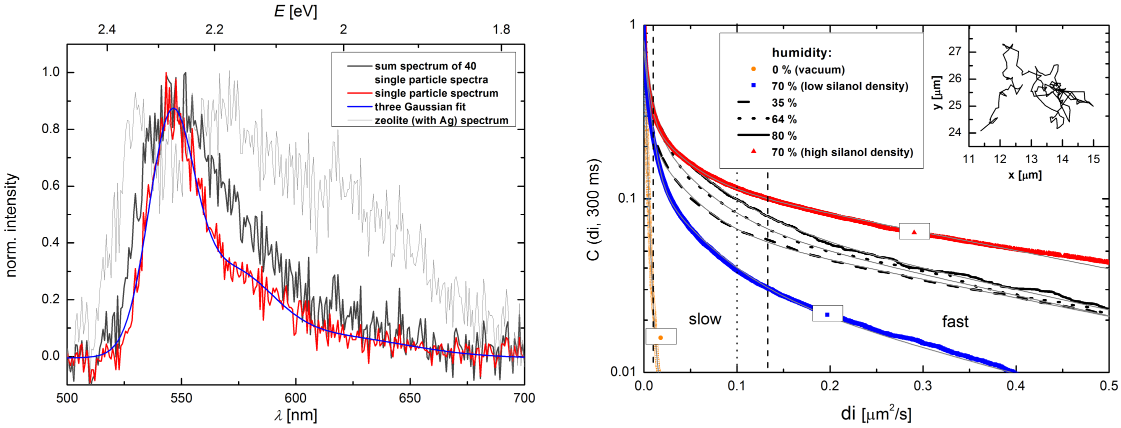

Figure 1: (left) Normalized spectrum of a single Ag nanoparticle (red data) with a three component Gaussian fit to the data (blue line) and the sum-spectrum of 40 different single particles (black line). The broad light gray line represents the spectrum taken from a zeolite particle including a variety of Ag particles with different sizes. *This spectrum is very similar to the one reported recently [1].* (right) Complementary cumulative probabilities of the diffusivities di of Ag nanoparticles on SiO_2 for four different humidities and two differently treated substrates. The curves can be roughly separated into three principle regimes as separated by the two vertical dashed lines. The first one (left) includes only very small diffusivities which in fact represent immobile particles, while the second and the third regime correspond to slow and fast diffusing particles, respectively. Each data set is fitted by three exponential functions (except the curve for 0 % relative humidity measured in vacuum). The inset shows an example trajectory.

This work was supported by the DFG (FOR 877).

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Diffusive protofilament switching of kinesin-8 investigated with optical tweezers

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The budding yeast Kinesin-8 *Kip3* is a highly processive motor protein that walks to the end of microtubules and shortens them in a collective manner [1]. Microtubules usually consist of 12 to 15 circularly-arranged tubulin polymer chains, called protofilaments. Left-handed rotations of microtubules in Kip3 gliding assays indicate sideward motion of Kip3 perpendicular to the microtubule axis [2], i.e. a switching between single protofilaments. Here, we used a high-resolution optical tweezers setup in a force feedback mode to apply sideward loads on single motor proteins. Our studies show that Kip3 steps sideward in both directions under alternating sideward loads. In control experiments with immobilized Kip3 and not protofilament switching kinesin-1, we measured no effective sideward motion. Statistical analysis and comparison with simulations propose a diffusive motion of Kip3 on the microtubule lattice with a preference to the left with respect to the direction of forward motion. This is consistent with the gliding assays. Protofilament switching has implications for the suggested mechanical signaling role of Kinesin-8 in budding yeast with respect to its ability to bypass obstacles.

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Intracellular trafficking of lipoplexes: A particle image correlation spectroscopy (PICS) study

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Particle image correlation spectroscopy (PICS) is a powerful and robust analysis technique to investigate the dynamics of molecules with nanometer and millisecond spatio-temporal resolution [1]. This tool allows one to identify and categorize populations within an ensemble of particles, without any a priori knowledge about the dynamics. PICS is here applied to investigate the intracellular trafficking of lipoplexes in CHO living cells. We measured diffusion coefficients and velocities for DOTAP–DOPC/DNA (DOTAP: 1,2-dioleoyl-3-trimethylammonium-propane; DOPC: dioleoylphosphocholine) and DC-Chol–DOPE/DNA (DC-Chol: 3β-[N-(N,N-dimethylaminoethane)-carbamoyl] cholesterol; DOPE: dioleoylphosphatidylethanolamine) lipoplexes. The results corroborate findings from previous experiments using single particle tracking and spatio-temporal image correlation spectroscopy [2, 3]. PICS allowed us to construct the displacement distributions that displayed clear non-homogeneous behavior. Detailed analyses showed for the first time a strong evidence of lipoplex transitions between active transport (mostly along microtubules) and free Brownian motion in the cytosol. For this latter finding a full theoretical description of intermittent diffusion was developed.

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High speed single molecule tracking on lipid membranes

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It is generally accepted that the cell lipid membrane is highly heterogeneous in local lipid and protein composition. This heterogeneity is believed to be induced by lipid-lipid, lipid-protein and protein-protein interactions and to be crucial for the high functionality of the membrane, e.g. for signal transduction. On the other hand, it is still a matter of debate how exactly the local organization of the membrane is mediated and on which spatial and temporal scales distinct structural features exist.

One approach to resolve this issue is to observe the motion of individual molecules in the membrane. In order to be able to draw conclusions from such measurements about the membrane molecular organization, a high spatial resolution on the order of the size of the probed molecule as well as a temporal resolution much faster that a typical membrane rearrangement time is required. We present a powerful single particle tracking approach based on interferometric scattering microscopy (iSCAT), which meets these requirements. By attaching small gold nanoparticles of ≤ 20 nm in diameter to lipid molecules and detecting their weak linear scattering signal by iSCAT, we are able to localize the position of the molecules with nanometer-accuracy at a temporal resolution of down to 10 μs.

Thus, with iSCAT it is possible to detect small-scale and short-time variations of the diffusion character of the probed molecule which opens the door to study membrane dynamics with unprecedented clarity. We present results from a systematic study on model lipid membranes and discuss possibilities of applying the method to diffusion measurements on cell membranes.

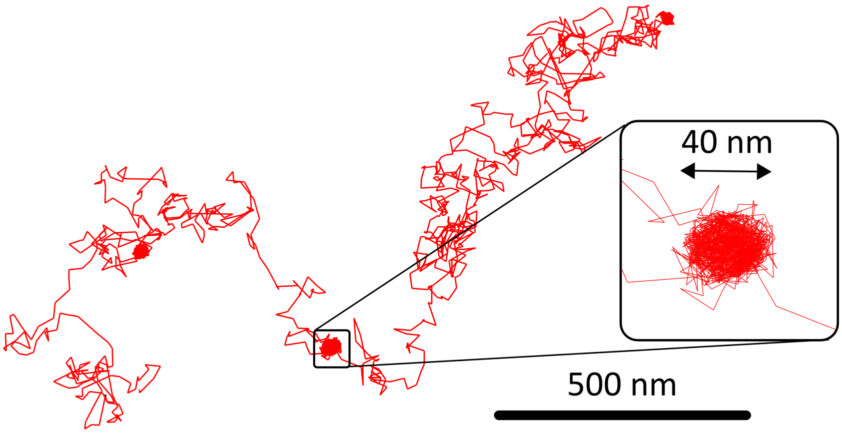

Figure 1: Trajectory of a 20 nm gold nanoparticle bound to a lipid molecule in a supported lipid bilayer. With iSCAT it is possible to detect small-scale and short-time confinements induced by the interaction of the bilayer with the glass support.

Dancing along microtubules: Molecular mechanism of one-dimensional diffusive motion of proteins along microtubules

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In a cellular environment, two kinds of motion exist: diffusion and directed transport. While diffusion (a passive process driven by thermal energy) is effective on short distances, directed motion (driven by motor proteins that convert chemical energy into directed motion) is effective over large distances. Diffusion is of interest because a number of recent studies reports examples where motor proteins and microtubule associated proteins use diffusive motion in one dimension along microtubules (MTs) for physiologically essential cell functions, such as: to search for binding sites (e.g. MCAK/ kinesin-13 [1] targeting MT ends for MT depolymerization), or to directionally slide MTs against each other (e.g. Ncd/kinesin-14 [2] and Ase1/ MAP65 [3] stabilizing the mitotic spindle during the cell division). Despite the fact that the diffusive motion along MTs is crucial for a whole variety of vital cell functions, the biophysical properties and precise molecular mechanism of such motion are remaining largely unexplored. Here, we (i) present a method for the quantitative characterization of the dynamic properties of the diffusive motion of molecules along MTs; (ii) discuss what would be an optimal way to describe the diffusive motion of molecules over MTs in single molecule experiments; and (iii) use the presented method to report on the dependence of the diffusive motion of Ase1 and Ncd on the ionic strength of the surrounding solution. It is well accepted that the diffusive motion of proteins along charged filaments occurs via two modes of motion: sliding, whereby protein remains in continuous contact with the filament, and microscopic hopping events [4]. In hopping, the protein dissociates from the filament, diffuses in solution and almost immediately reassociates in direct proximity to the dissociation point on the same filament. Here, to our knowledge for the first time, we discuss the diffusive motion of proteins along MTs in terms of hopping and sliding.

This work was supported by the DFG (FOR 877).

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The physical bounds of *in vivo* cell motility

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Migration of cells through tissues is quintessential for wound healing, neuronal plasticity, and the functioning of the immune system. In disease it is also a key determinant of cancer metastasis and nerve regeneration. Mammalian tissues are a new state of active fluid matter. A broad range of different cell types demix like non miscible fluids building natural boundaries for migrating cells. At least to some extent the cells are hold back by an effective surface tension, which is determined by cell-cell adhesion and cell contractility. Individual cells in tissues behave very much like active soft colloids. Thus, cells have a high probability to get jammed when moving through tissues and collective cell assemblies are close to be frozen by the glass transition. Cells that effectively move through tissues and are able to transgress tissue boundaries are softer and more contractile than cells that stay local in tissues. Soft and contractile avoids jamming and is optimal to overcome boundaries. Naturally, softness has to have its limits. So neuronal growth cones are too soft to carry large loads and thus excessively weak to move efficiently e.g. through scar tissue, which is required for nerve regeneration. Whereas cancer cells optimize their biomechanical and contractile properties for metastasis during tumor progression. In synopsis, the physical bounds that the functional modules of a moving cell experience in tissues may provide an overarching motif for novel approaches in diagnosis and therapy.

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Diffusion in a hard-disk fluid with immobile particles: Molecular transport in the plasma membrane

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With respect to lateral diffusion of molecules, plasma membrane of living cells can be thought as a two-dimensional fluid that is coupled to the underlying cytoskeleton. As the dynamics of cytoskeletal structures are often much slower than that of lateral diffusion, membrane proteins can become immobilized by anchoring to the cytoskeleton via direct or indirect binding. Motivated by single particle tracking observations showing that even lipid molecules are strongly affected by the membrane-cytoskeleton coupling [1], we study the effects of immobile particles on lateral diffusion. By considering a two-dimensional hard-disk fluid, which is relevant when repulsive interactions are dominant, we explicitly account for fluid dynamical interaction between particles. We perform event driven molecular dynamics and Brownian dynamics simulations of a collection of hard-disks. We focus on fluids composed of uniform disks as well as binary mixtures. In the case of uniform disks, we envisage mobile particles as lipids and immobile particles as proteins anchored to the membrane skeleton. In binary mixtures, proteins and lipids are represented by disks of different radius and mass (see Fig. 1).

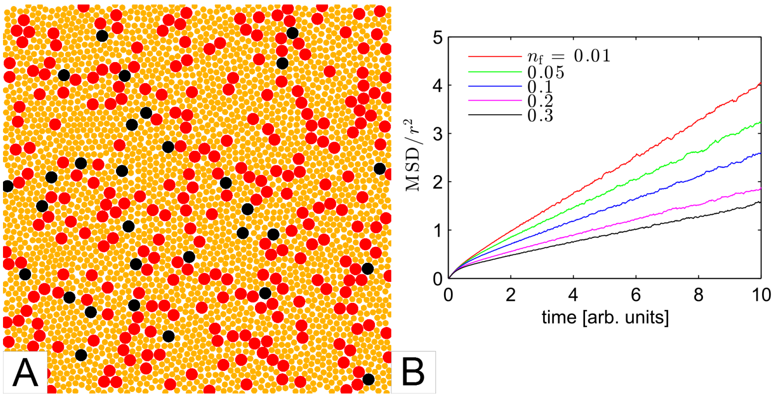

Figure 1: In A, a snapshot from the event driven molecular dynamics simulation is displayed, where red (larger) and orange (smaller) disks represent proteins and lipids, respectively, and the disks in black are immobile. The total packing fraction, that is the area covered by all disks, is equal to 0.75. In B, the mean squared displacement of larger disks (averaged over 100 particles), normalized by the square of the radius of smaller disks, r^2, is plotted as a function of time for different values of the fraction of fixed disks (denoted by n_f).

In the regime where the mixture is in the liquid state with a packing fraction of 0.5–0.75, we find that the particles are diffusive at long times, and the diffusion coefficient is very sensitive to the fraction of immobile particles. We study the effects of random and correlated distributions of immobile particles on diffusivity, as well as the effects of particles that are only temporarily immobilized. In previous studies [2, 3], it has been shown that fluid dynamical interactions can lead to a significant drop in diffusion coefficients in membranes containing immobile inclusions. However, the membrane was treated like a continuous fluid, which is only valid at length scales much larger than that of a lipid molecule. In this respect, we believe that our study fills an important gap between the molecular and macroscopic scales in describing the effects of fluid dynamical forces on lateral diffusion in the presence of immobile particles.

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Modeling Ca^{2+} diffusion in brain extracellular space

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Molecular diffusion in brain extracellular space (ECS) is primarily controlled by interactions with the geometry and the interstitial matrix. Both factors increase λ, the tortuosity, a measure of hindrance to diffusion where $\lambda^2 = D/D^*$ with D the free diffusion coefficient and D^* the effective diffusion coefficient in brain [1]. Geometry lengthens diffusion paths or creates holdup in local voids of dead-spaces in the ECS [2] and matrix interacts via specific binding reactions, some illustrated in Fig. 1a.

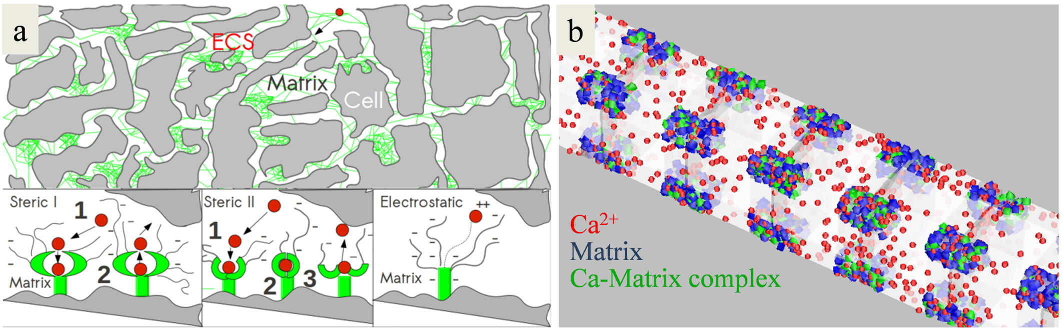

Figure 1: ECS geometry and matrix interactions, a) Schematic b) *MCell* model

Previous experiments showed a reduction in Ca^{2+} diffusion via interactions with chondroitin sulfate, a component of the matrix [3]. Here, we 1) modeled the combination of matrix and ECS geometry to determine how both factors interact to affect diffusion, and 2) studied the effect of matrix distribution.

ECS geometry was constructed from 512 impermeable cubic 'cells' aligned in a long tube and separated by a uniform ECS. To obtain a λ-value equal to that measured experimentally for ions with no matrix interactions ($\lambda \sim 1.6$), the corners of the cubes were cut off, creating a medium with voids [2]. Ca^{2+} ions were released from an instantaneous point-source and diffusion simulated with the Monte Carlo program, *MCell* (www.mcell.org) (Fig. 1b). D^* was calculated as $\langle r^2 \rangle / 6t$ where r was the distance of an ion from the source at time t. The matrix had a reduced effective concentration to take account of background cations, and interaction with Ca^{2+} was represented by a fast equilibrium binding reaction [4]. Matrix was either distributed uniformly in the ECS or localized to the voids.

Our simulations result in a $\lambda \sim 2$ (i.e. $D^* = D/4$) when geometrical hindrance and matrix interactions combine. This agrees with experimental measurements in brain slices [3], and shows that molecules that undergo interaction with matrix are more hindered than those which do not. Our model also shows that matrix localized to the voids can be as effective as when uniformly distributed, if the local concentration is elevated to maintain the average ECS concentration.

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Two-dimensional semiflexible polymers under external fields

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The non-equilibrium structural and dynamical properties of semiflexible polymers confined to two dimensions are investigated by molecular dynamics simulations. Three different scenarios are considered: The force-extension relation of tethered polymers, the relaxation of an initially stretched semiflexible polymer, and semiflexible polymers under shear flow. We find quantitative agreement with theoretical predictions for the force-extension relation and the time dependence of the entropically contracting polymer. The semiflexible polymers under shear flow exhibit significant conformational changes at large shear rates, where less stiff polymers are extended by the flow, whereas rather stiff polymers are contracted. In addition, the polymers are aligned by the flow, thereby the two-dimensional semiflexible polymers behave similarly to flexible polymers in three dimensions. The tumbling times display a power-law dependence at high shear rate rates with an exponent comparable to the one of flexible polymers in three-dimensional systems.

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Diffusible crosslinkers generate directed forces in microtubule networks

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Remodeling of cytoskeletal filament networks is essential to cell division and morphogenesis. The mechanical forces driving the restructuring processes are attributed to the activity of molecular motors and the dynamics of cytoskeletal filaments, which both consume chemical energy. Passive filament crosslinkers, on the other hand, are commonly regarded as mere friction-generating entities. Here, we report on the generation of directed forces by non-enzymatic, diffusible microtubule crosslinkers of the Ase1/PRC1/Map65 family. After experimentally confining Ase1 molecules between partially overlapping microtubules, we observed overlap expansion through directed microtubule sliding. Notably, the forces generated were sufficient to reverse the direction of motor-protein driven microtubule sliding. Force generation by Ase1 can be quantitatively explained by entropic expansion of confined Ase1 crosslinkers diffusing along microtubules in the overlap region. The thermal motion of confined filament crosslinkers is thus harnessed to generate mechanical work analogous to compressed gas propelling a piston in a cylinder. We argue that this mechanism constitutes an active, force-producing element of self-organizing filamentous networks inside cells.

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Brain microscopy point spread function in a photon diffusion limit

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In fluorescence microscopy of the brain, the image can be significantly degraded by light scattering. The individual scattering events in the brain tissue are very anisotropic, preserving to a large degree the photon direction. When the scattering coefficient is low or when the fluorophore light source is close to the tissue surface, the photons may enter the microscope without having scattered more than a few times, with only a limited detrimental effect on the point spread function (PSF). On the other hand, in highly scattering tissue or when imaging deeper sources, photons will scatter many times. Ultimately, they will lose their directional memory and enter the photon diffusion regime.

We simulated microscopy imaging of a point source located at a fixed depth of 100 μm inside a brain tissue slice 400 μm thick and varied the tissue scattering coefficient μs until the photon diffusion limit was reached. The full width at half maximum (FWHM) of the PSF was measured in each case. The simulation parameters corresponded to a typical experimental setup used in integrative optical imaging [1], with immersion objective magnification of 40, numerical aperture 0.8, and indexes of refraction 1.37 and 1.33 in the tissue and the surrounding solution, respectively. The scattering anisotropy factor g was kept constant at 0.9 and light absorption was assumed negligible [2]. The simulations employed a modified MCML program [3] to model scattering of 10,000,000 photons in each of the 22 runs.

The results are shown in Figure 1. Note that without scattering, the ballistic PSF in a typical experimental setup can be close to the pixel size of a CCD detector (in our experimental setup, less than 0.5 μm in the object space). In the other extreme, at the photon diffusion limit, no ballistic photons survive their tissue journey and the PSF is akin to a steady state diffusion pattern with a Newton boundary condition at the tissue surface. This PSF is over 100 times wider than that of the ballistic PSF, effectively destroying the image resolution. A similar effect would be observed with a constant scattering coefficient but increasing depth of the source. In conclusion, light scattering can profoundly affect the brain microscopy PSF, possibly reducing resolution by two orders of magnitude.

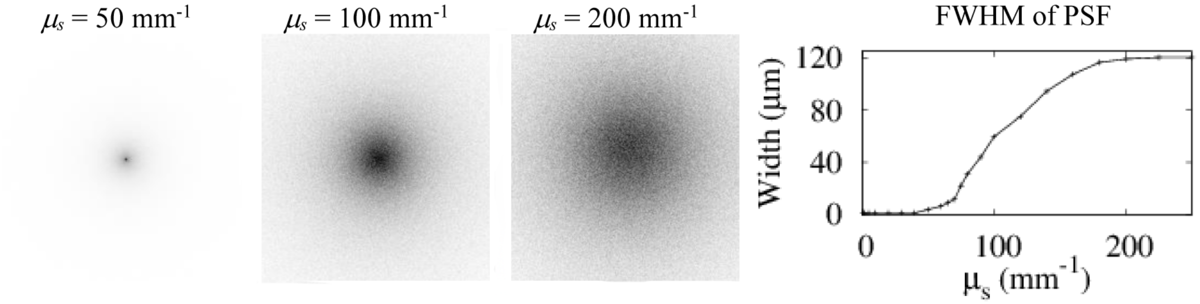

Figure 1: Simulated microscopy images of a point source for various values of μ_s (ballistic signal is omitted), and graph of the full width at half maximum of the point spread function as a function of μ_s.

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Ring polymers diffusing in a gel: Topology and dynamics

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Since the pioneering work of Edwards and de Gennes the dynamics of polymers in the melt has been understood using the tube and the reptation models. However, ring polymers continue to present a challenge to the theoretical community as the polymers lack of ends represents a severe topological constraint on the polymer configurations. This constraint is even more important when the rings are forced to diffuse through a gel. Polymers in the melt have often been compared with single chains diffusing trough a background of obstacles. However, a comprehensive description of dynamics of ring polymers moving in a gel is not yet available. We performed Molecular Dynamics simulations of a concentrated solution of un-knotted, un-linked rings in a background gel made up of a three dimensional cubic lattice of static polymer segments with lattice spacing equal to the chains Kuhn length. We observed some macroscopic similarity with the behavior of a pure melt of rings. This includes the crossover to globular state for long rings and the fact that loops have to travel many times their own size before reaching free diffusion $\langle \delta r_s^2 \rangle \sim t$. The novel aspect of this work is focused on the strategy employed to identify inter-ring penetrations. We take advantage of the ordered architecture of our gel to identify the inter-ring penetrations via linking of closed curves (Fig. (b)). Penetrations have always been conjectured to play an important role in solutions of rings, from the work of Klein in 1986 [1] to more recent studies [2], but they always proved very hard to observe and quantify. We report a method to unambiguously detect inter-ring penetrations and show that some of them have a life-time that is at least comparable to that of the longest relaxation time of the chains and argue that they may be much longer for longer chains than we ere able to simulate here. Finally, we compare the system to an evolving (directed) network of penetrating rings (Fig. (c)) and suggest that, in the limit of very long chains, a single connected component of threading rings may emerge, which would then exhibit very slow (glassy) dynamics at the scale of centre of mass motion for each chain, while retaining substantially unhindered motion at the level of individual chain segments. Having observed that the number of threading per chain grows linearly with the length of the rings, we conjecture that such topological glass is likely to emerge in the limit of very long rings.

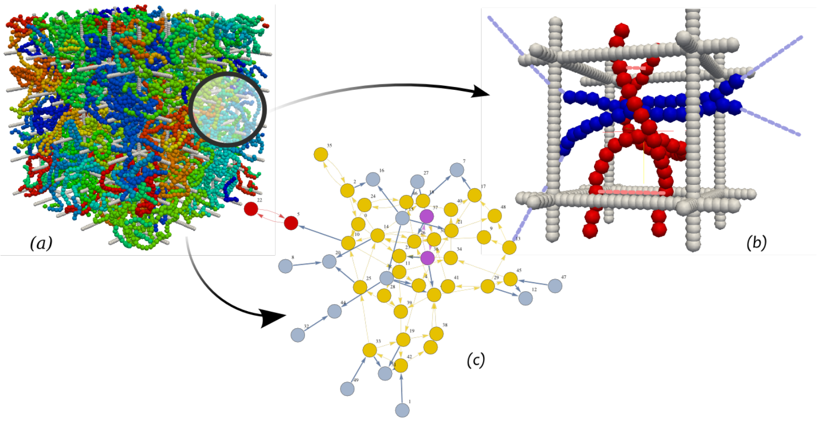

Figure 1: (a) Snapshot of our system. (b) Snapshot of a two chains configuration where the blue one is threading through the red one inside of one cubic lattice cell, bounded on the edges by gel polymer. Light red and light blue dotted lines indicate the asymptotic closure construction that we employ in order to identify threading, using a standard topological measure of contour linking. (c) Snapshot of the directed network of inter-penetrating rings. Notice the emergence of a spanning connected cluster (yellow), and smaller ones (red, purple).

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Kinesin and dynein respond differently to cytoplasmic drag

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Micron-sized cargos in living cells are actively transported in opposite directions along microtubules by the molecular motors kinesin and dynein. While these motors have been extensively studied *in vitro*, the conditions in the cell differ substantially. In particular, drag forces cease to be negligible *in vivo*. Previous experiments performed *in vitro* show that opposing loads affect the transport velocity of kinesin and dynein differently, resulting in different force-velocity curves [1, 2].

We have observed evidence for these force-velocity dependences *in vivo*. First, we quantified the cytoplasmic viscous forces experienced by motors in *Drosophila* embryos by using a combination of passive microrheology, and a novel approach to active microrheology, with endogenous lipid droplets as probes. We then treated the embryos with inhibitors or promoters of actin polymerization, thus changing the average rheological properties experienced by motor-driven cargo. This allowed us to measure the effect of cytoplasmic drag on the velocity of those same lipid droplets hauled by kinesin and dynein [3, 4]. We find that kinesin and dynein respond differently to cytoplasmic drag forces, with kinesin being load-sensitive at high opposing forces and dynein at low. Our findings agree with and – to our knowledge – constitute the first *in vivo* validation of the force-velocity curves for kinesin and dynein found *in vitro*.

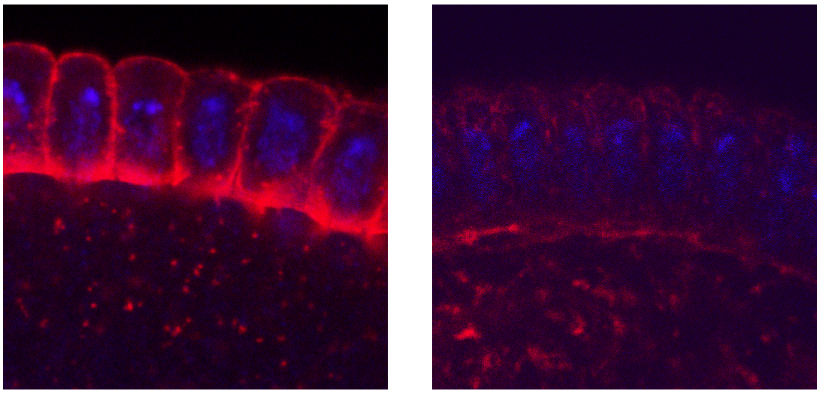

Figure 1: Motor-driven cargoes in an intact embryo (left) face more cytoplasmic drag than in embryos where actin filaments, shown in red, are depolymerized (right).

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Assessment of GABARAP self-association by its diffusion properties

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Gamma-aminobutyric acid type A-receptor-associated protein (GABARAP) belongs to a family of small ubiquitin-like adaptor proteins implicated in intracellular vesicle trafficking and autophagy. Biochemical evidence, as well as observations from X-ray crystallography, supports the view that GABARAP shows a propensity to oligomerize in solution. Here, we have used diffusion-ordered nuclear magnetic resonance spectroscopy (DOSY-NMR) to study the temperature and concentration dependence of the diffusion properties of GABARAP. Our data suggest the presence of distinct conformational states and provide support for self-association of GABARAP molecules. Assuming a monomer–dimer equilibrium, the mass fraction of the dimer could be determined for every condition. Based on a series of 1H-15N-heteronuclear single quantum coherence (HSQC) NMR spectra recorded at different temperatures, we propose residues potentially involved in GABARAP self-interaction.

Interaction of semiflexible polymers and rod-like colloidal particles with strongly charged lipid membranes

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Understanding of the mechanisms of interaction of macromolecules and colloidal particles with lipid membranes is far from complete, and the questions related to role of local perturbation of the membrane properties in these interactions are still largely unsolved. In our experiments, we use strongly charged freestanding cationic lipid membranes (mimicked by supergiant unilamellar vesicles [1]), as well as supported cationic lipid bilayers showing fluid–gel phase coexistence. Interaction of DNA molecules with strongly charged freestanding cationic lipid bilayers leads to irreversible membrane-mediated coil–globule transition of membrane-absorbed DNA [2], an unexpected phenomenon on which we provide new experimental details. For single DNA molecules on supported cationic lipid bilayers we observe the compaction–decompaction behavior related to the appearance and disappearance of micrometer-sized gel domains in the supported membrane. This effect is fully reversible, in striking contrast to the irreversible DNA coil–globule transition on freestanding fluid cationic membranes. This clearly demonstrates the extremely important role of local membrane perturbations in membrane–macromolecule interaction. To elucidate the effect of the persistence length in these phenomena, we study the behavior of much stiffer semiflexible *fd* virus particles [4] under the identical conditions of interaction with freestanding and supported cationic membranes.

This work was supported by the DFG (FOR 877).

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Cytoskeletal pinning prevents large-scale phase separation in model membranes

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During the last decades, artificial lipid bilayers have become an important tool in studies of properties of the plasma membrane of cells. One important feature of cell membranes, which has been difficult to recapitulate in the artificial bilayer systems, is the membrane-associated cytoskeleton. The cytoskeleton is believed to affect diffusion of lipid and protein molecules in the plasma membrane, and is considered to be one of the reasons for the sub-resolution size of membrane domains by preventing large-scale phase separation. Mimicking the eukaryotic actin-based cytoskeleton in vitro is inefficient and complicated, owing to the number of components involved and the nature of membrane binding of the actin-network complex. Here we describe a minimal cytoskeletal network formed by the prokaryotic tubulin homologue, FtsZ. FtsZ has been modified to interact with the membrane through a membrane targeting sequence (MTS) from MinD, another prokaryotic protein. FtsZ-MTS efficiently forms a highly interconnected network on the membrane with a concentration-dependent characteristic mesh size, much similar to the eukaryotic network underlying the plasma membrane. Using giant unilamellar vesicles formed from a quaternary lipid mixture, we demonstrate that, on the one hand, the artificial membrane-associated cytoskeleton suppresses large-scale phase separation below the phase transition temperature, and, on the other hand, preserves phase separation above transition temperature. Our experimental observations support the ideas put forward in our previous simulation study [1]: In particular, the picket-fence effect on phase separation explains why micrometer-scale membrane domains are observed in isolated, cytoskeleton-free giant plasma membrane vesicles, but not in intact cell membranes. The experimentally observed suppression of large-scale phase separation much below the transition temperatures also serves as an argument in favor of the cryoprotective role of the cytoskeleton.

This work was supported by the DFG (FOR 877).

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Translational diffusion at the surface of porous media with magnetic impurities via Fast Field Cycling NMR relaxometry

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Many natural or manufactured porous media intrinsically contain paramagnetic impurities inside their solid matrix which generate internal gradients when introduced in a magnetic field [1]. These internal gradients may lead to significant errors in the measurements of the diffusion coefficient if the classical pulse field gradient techniques are used [2]. The implementation of compensating pulse sequences based on bipolar gradients is also less effective due to the short relaxation times experienced in such samples [2]. In the present contribution exactly the shortening of the longitudinal relaxation time of protons due to their interaction with the paramagnetic centers (Fe^{3+}) located on the surface is exploited to extract information about the translational displacement of molecules on the surface. The porous samples under investigation are both porous ceramics containing increased amount of magnetic impurities and gray cement under different hydration conditions. The diffusion coefficient of water (polar) and cyclohexane (nonpolar) molecules at the interface is extracted using the Fast Field Cycling NMR relaxometry [3]. The technique relies on comparison of the experimental relaxation dispersion curves with a two phase exchange model taking into account the protons relaxation by the interaction with paramagnetic centers located on the surface of porous media [3, 4]. It is observed a stronger reduction of the diffusion coefficient by the interaction with the surface in the case of water (polar) molecules as compared with cyclohexane (nonpolar) ones. The porous ceramics under study were fabricated with a controlled amount of magnetic impurities using the conventional method of preparation from powders which are first dry pressed and then subject to thermal treatment [4]. Six samples (S0-S10) with increasing concentration of Fe_2O_3 were prepared by adding 0, 2, 4, 6, 8 or 10g of Fe_2O_3 to 100g of mixed powder. To extract the pore size distribution of the produced samples they were examined by scanning electron microscopy, the DDIF (Decay due to Diffusion in the Internal Fields) technique [1] and a new proposed technique [5] which relies on the attenuation of the echo train in the well-known CPMG technique due to diffusion in internal gradients. The magnetic characterization of the produced samples was done using a vibrating sample magnetometer indicating a linear dependence of the susceptibility constant with the Fe_2O_3 content. The cement samples under study were prepared using gray cement CEM I 52.5 R and different water to cement ratios. The diffusion coefficient on the surface of cement grains was evaluated at different hydration temperatures (5, 15, 25 and 35 °C) revealing a constant value in the investigated temperature range.

ACKNOWLEDGMENTS: This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-ID-PCE-2011-3-0238. Financial support by the Alexander von Humboldt Foundation is also gratefully acknowledged.

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Structural and transport properties of hydrogen in ZIF-22

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ZIF-22 which has a structure similar to A zeolites [1, 2] is investigated in this work because of of its high selectivity for hydrogen with respect to other gases [1]. By using Molecular Dynamics simulations with the DL_POLY package, structural and dynamical properties of hydrogen adsorbed in ZIF-22 are examined.

Moreover, the adsorption of hydrogen in ZIF-22 is simulated by Gibbs-ensemble Monte-Carlo simulation studies.

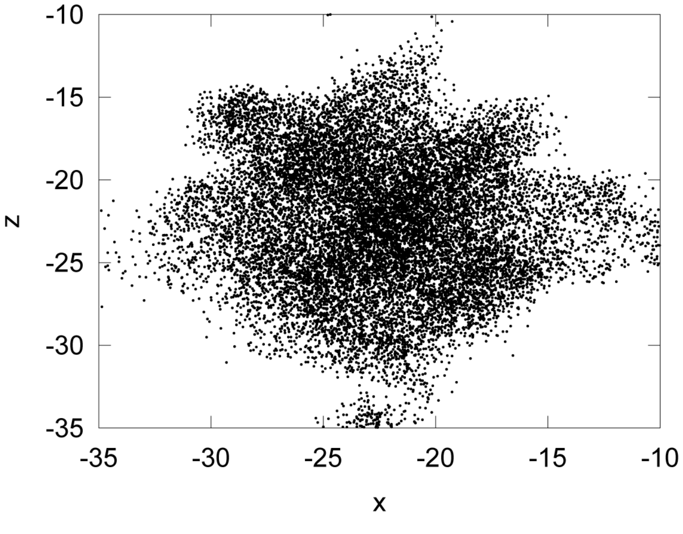

Figure 1: The density plot of hydrogen in one of the cavities of ZIF-22

The small window size turns out to be the most important reason for the high selectivity. The results are compared with experiments [1] and they are discussed by means of spatial density distributions, radial correlation functions and mean square displacements.

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NMR studies of benzene mobility in metal-organic framework UiO-67

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The self-diffusion of benzene adsorbed in the Zr(IV)-based metal-organic framework UiO-67 was studied by Pulse Gradient Stimulated Echo (PGSTE) NMR at 35 ^{o}C. The measurements where carried out on a low field instrument operating at 20 MHz proton frequency, capable of producing field gradients up to 4 T/m. Using a 13-interval pulse sequence, the effective self-diffusion was measured as a function of the square root of the diffusion time, and suggested that the confined benzene molecules interacted significantly with the internal surface of the MOF matrix during their diffusional motion.

Mass-transfer of binary mixtures in DDR single crystals

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For the first time, micro imaging by interference microscopy (IFM) is applied for studying uptake and release of guest molecules in nanoporous host material for investigating the adsorption of gas mixtures and for correlating the thus observed behavior with corresponding single-component sorption experiments. Combining the advantages of high spatial and temporal resolution in the order of 0.45 μm and 15 s, respectively, this promising approach results in time-dependent two-dimensional profiles of the intra-crystalline sorbate concentration of the single crystal under study [1, 2, 3]. However, with the lack of differentiation of different species present inside the microporous framework only certain types of experiments seems feasible, notably when the mixture consists of species with large differences in the rate of mass transport under the confinement of the channels, cages and windows of e.g. zeolite ZSM-58, which is well known from previous IFM studies [4].

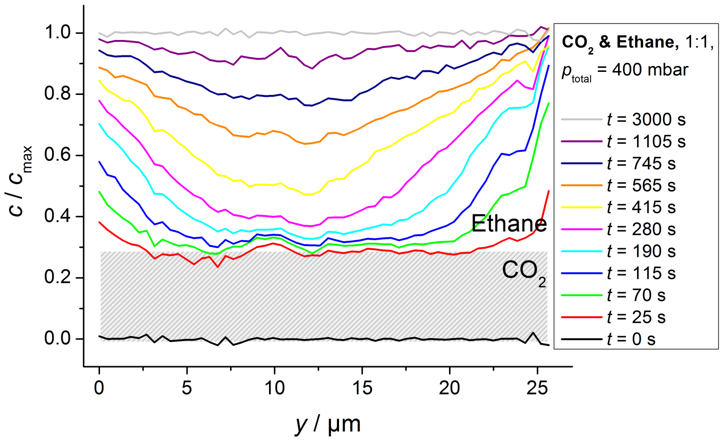

Figure 1: IFM mixture experiments are enabled by several orders of magnitude difference in the single-component diffusion rates of e.g. CO_2 and ethane leading to apparent instantaneous uptake of CO_2 and much a slower sorption process for ethane. When provided as a 1:1 gas mixture of p_{total} = 400 mbar, CO_2 reaches a quasi-equilibrium at about 30% IFM signal (shaded area) followed by additional and much slower ethane adsorption. Hence, influences of the presence of CO_2 on the diffusivity of ethane can be examined.

We report the results obtained with the host-guest-system CO_2 and ethane in ZSM-58 together with their single-component equivalent. The experiments could be carried out as true mixture adsorption IFM measurements benefitting from the huge difference of the diffusion coefficients of the two species. The almost instantaneous increase of IFM signal equally distributed throughout the whole crystal can therefore be correlated with the very fast uptake of CO_2, see shaded area in Fig. 1, with the ethane adsorption starting shortly afterwards.

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Projection of two-dimensional diffusion in a curved midline and narrow varying width channel on a curved surface

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This study focuses on the derivation of a general effective diffusion coefficient to describe the two dimensional (2D) diffusion in a narrow and smoothly asymmetric channel of varying width that lies on a curved surface, in the simple diffusional motion of noninteracting pointlike particles under no external field. To this end we extend the generalization of the Kalinay-Percus' projection method [1, 2] for the asymmetric channels introduced in [3], to project the anisotropic two dimensional diffusion equation on a smooth curved manifold, into an effective one dimensional generalized Fick-Jacobs equation that is modified due to the curvature of the surface.

The lowest order in the perturbation parameter, corresponding to the Fick-Jacobs equation contains an extra term that accounts for the curvature of the surface by the Christoffel symbols. We found explicitly the first order correction for the invariant effective concentration, which is defined as the correct marginal concentration in one variable, and we obtain the first approximation to the effective diffusion coefficient analogous to Bradley's coefficient [4] as a function of metric elements of the manifold.

Straightforwardly we study the perturbation series up to the n-th order, and we derive the full effective diffusion coefficient for the two dimensional diffusion in a narrow asymmetric channel, that have modifications due to the curved metric.

Finally, we present some examples of symmetric surfaces and we study some specific channel configurations on them.

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Enhancing diffusion selectivities by molecular traffic control in FER-type zeolites

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Detailed understanding how molecular transport in nanoporous materials is influenced by various features of the host structure can provide new insights towards further optimization of their performance in technical applications, such as catalysis, separations, molecular storage and sensing [1,2]. We present a study of the diffusivity of small alkanes and alcohols in siliceous ferrierite [3]. A surprisingly high difference in the diffusivities of methanol and ethanol has been observed ($D_{MeOH}/D_{EtOH} \approx 25{,}000$). This difference most likely results from an interplay of two phenomena, which have been recently discussed as options to manipulate mixture diffusion, viz. molecular traffic control and clustering effects. The major conclusion can be summarized in two points: (i) molecular traffic control effects can be facilitated by molecular clustering and (ii) their combination provides a new option for enhancing diffusion selectivities and, thus, for further optimizing the use of nanoporous crystalline materials in technical applications.

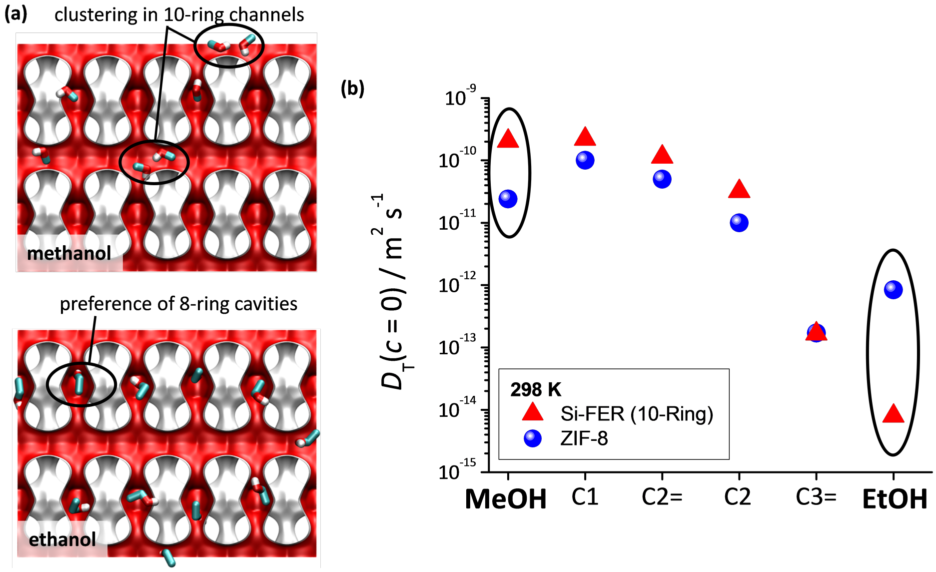

Figure 1: (a) CBMC snapshots showing the location of methanol and ethanol in Si-FER at a loading of 2 molec/uc at 298 K. (b) Comparison of the zero-loading diffusivities for various small molecules in Si-FER (triangles) and ZIF-8 (spheres).

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Diffusion and adsorption of N_2 and C_2H_6 in ZIF-8 MD and MC simulations

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Molecular Dynamics (MD) and Gibbs-Ensemble Monte-Carlo (GMC) simulations give insight into the adsorption and diffusion properties of N_2 and C_2H_6 molecules adsorbed in ZIF-8 [1]. The framework flexibility plays an important role in achieving correct transport properties [2]. Particularly, for N_2 a gate opening effect could be observed. The window sizes were determined by the orientation of the imidazolate linkers and a transition from a closed structure at low N_2 loading (approximately 0.5–18.4 N_2/cage), to an open one, at high loading (approximately 20–30 N_2/cage) was found (see Fig. 1). This is in agreement with [3]. The results of MD simulations and of experiments for N_2 and C_2H_6 are compared. The simulation results illustrate that the transition of the orientation of imidazolate linkers of the ZIF-8 framework for both, 4 and 6-membered rings were induced by N_2 guest molecules.

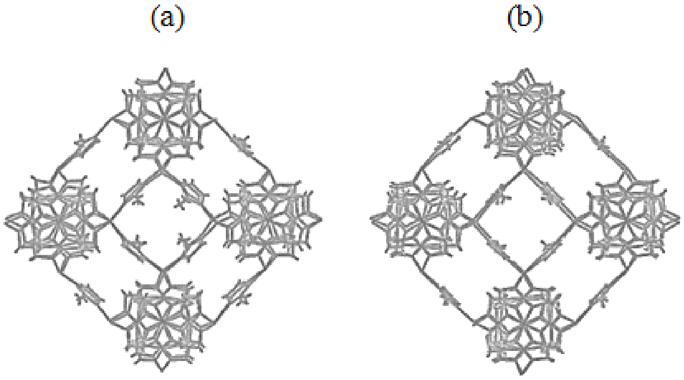

Figure 1: ZIF-8 window structures at (a) low loading and (b) high loading of N2 guest molecules.

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Simplified theory to predict mixture diffusion in zeolites: Accounting for strong correlations and examining the role of adsorption thermodynamics

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The Maxwell–Stefan (MS) equations have been extensively used to describe mixture diffusion in zeolites. Correlation effects can arise due to molecules unsuccessfully attempting to pass each other in the very narrow pores of the zeolite, e.g., at high loadings of adsorbed molecules. In an extreme situation, diffusion may even become anomalous, giving rise to a single-file phenomenon. These correlation effects are captured in the so-called "exchange terms" within the framework of the MS equations. The exchange terms are often calculated from pure component data using empirical approaches with different fits for different combinations of zeolite hosts and molecules. These computations, in turn, can be fairly tedious, especially for large multicomponent systems. It is therefore advantageous to be able to use a simplified theory to capture the effect of strong correlations. To this end, the MS equations are simplified to predict mixture diffusion behavior in the case of strong correlation effects. Intermolecular exchange coefficients are not required. No empirical relations are employed. This simplified model is used to predict the diffusion behavior in the separation of a CH_4-C_3H_8 mixture through a silicalite membrane [1].

Diffusion in zeolites is also closely coupled with adsorption due to the tightly confining pore space in the zeolite where the concept of a bulk fluid phase ceases to exist. Adsorption effects are accounted for in the MS theory through the mixture thermodynamic correction factors, which are derived using the pure component adsorption isotherms and theories such as the Ideal Adsorbed Solution Theory (IAST). The calculation of mixture thermodynamic correction factors in the MS equations can also pose a computational hurdle especially for large systems, and if theories such as the IAST have to be employed. It is expected that, if a vacant adsorption site is available, the adsorption of a species inside the zeolite pore should be dictated by the pure component adsorption isotherm alone, and that mixture adsorption thermodynamics should not play a role, or else correlation effects should be present in adsorption as well, in which case theories such as the IAST cannot be used. To this end, the MS equations are simplified to employ only the pure component thermodynamic correction factors. This simplified model was used to predict mixture diffusion for two cases of practical interest [1]: (i) the separation of a N_2-CH_4 mixture through a SAPO-34 membrane, and (ii) the alkylation of C_6H_6 with C_2H_4 over H-ZSM-5. In all cases, predictions from the simplified models are favorably compared to results from the more complex MS equations or experiments, indicating that the simplified models can serve as good starting approximations, and can also speed up mixture diffusion calculations in zeolites.

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Single-file dynamics in nanotubular materials probed by a combination of hyperpolarized tracer exchange and diffusion NMR techniques

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Diffusion of adsorbed species in one-dimensional channels can follow the mechanism of single-file diffusion (SFD) when the cross-sectional dimensions are comparable to the sorbate size. SFD preserves the relative order of particles in a channel and is characterized by a square root time dependence of the mean squared displacement (MSD), i.e. $\langle r^2 \rangle \propto t^{0.5}$. This time-scaling has been confirmed in an assortment of contrived macroscopic single-file systems, but experimental reports of SFD in molecular systems are rare [1–3] and in some cases inconsistent [3, 4].

Here we report results of experimental studies of self-diffusion and tracer exchange of xenon in dipeptide nanotubes in which distinct signatures of single-file dynamics are obtained using two different NMR techniques applied to the same single-file host-guest systems. The combination of the two techniques allowed us to investigate the MSD time-scaling over a 5 orders of magnitude variation in diffusion time. In addition, the impact of channel blockages due to defects in the crystal structures on the time-scaling of the MSD was investigated by kinetic Monte Carlo simulations.

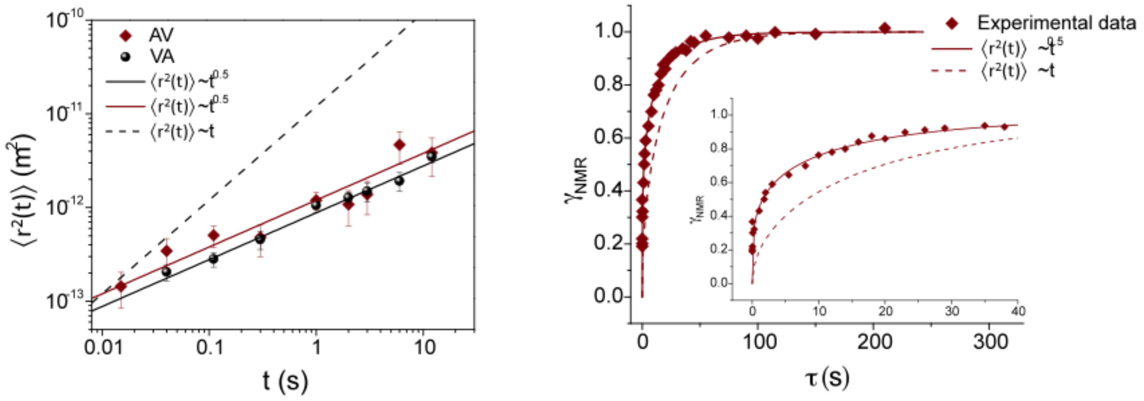

Figure 1: (Left) Time dependence of mean-squared displacements of Xe in l-alanyl-l-valine (AV) and l-valyl-l-alanine (VA) nanotubes probed by PFG NMR at 25 °C. (Right) Continuous-flow hyperpolarized tracer exchange data for Xe in AV, normalized to the steady-state. Curves represent the fully determined simple kinetic model for single-file and Fickian diffusion time-scaling, with no free parameters. Solid and dashed lines on both figures represent the $t^{0.5}$ and t time-scalings, respectively.

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Diffusion investigation for hydrogen guest molecules in an adapted force field for ZIF-11

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The large family of Metal Organic Frameworks, to which ZIF-11 belongs, demands for the possibility to predict properties regarding adsorption and diffusion behavior from their crystal structure.

Therefore, as a first step, it is important to find good parameters to describe some members of the MOF family and to try in a second step to draw conclusions to other materials from the gained experience.

In this work the structure of ZIF-11 was investigated and a force field was found that was able to reproduce experimental adsorption behavior [1]. The force field was based on the AMBER [2] parameters and was adapted to get good agreement with measured properties. Connections between adjacent cavities were identified and a way has been described to deal with uncertainties in the provided X-Ray structures [1].

Afterwards longer simulations runs have been performed to get estimates for the behavior of the diffusion coefficient.

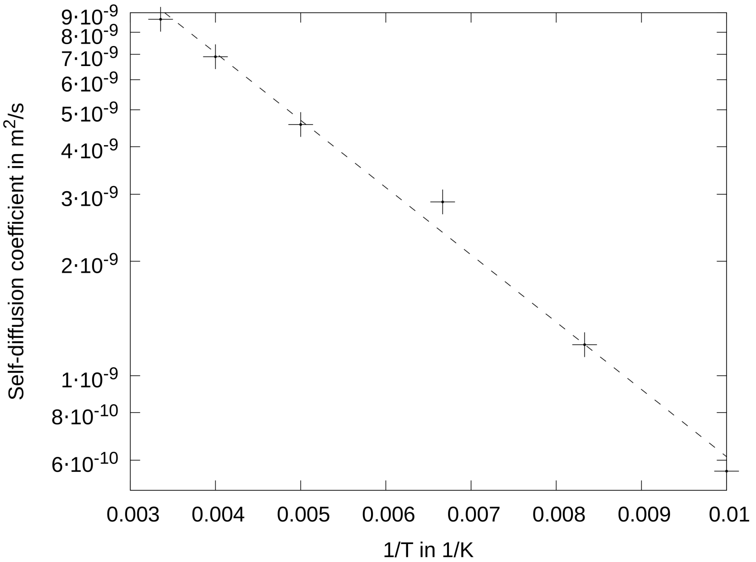

Figure 1: The temperature dependence of the diffusion coefficient for hydrogen in ZIF-11 together with a linear fit

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Surface diffusion of polymers on carbon nanotubes

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Carbon nanotubes (CNTs) are emerging materials with a wealth of applications in different areas, ranging from molecular devices and sensors to drug delivery. However, pristine CNTs tend to bundle into strongly bound aggregates due to van der Waals interactions. This is a drawback, since many applications require individually dispersed CNTs. One possibility to overcome this problem is to use non-covalent dispersants such as surfactants or polymers, which can exfoliate and stabilize CNTs in aqueous solutions. However, non-covalent dispersion is still poorly understood at molecular level [1]. In what concerns polymers as dispersants, two main qualitative models on the polymer-CNT interaction are *wrapping* where polymers coat the CNT in a tight contact and *loose adsorption* where a weaker interaction between the polymer and the CNT takes place, so that the bound polymer remains almost like in its natural state in a good solvent, i.e. a random coil [2].

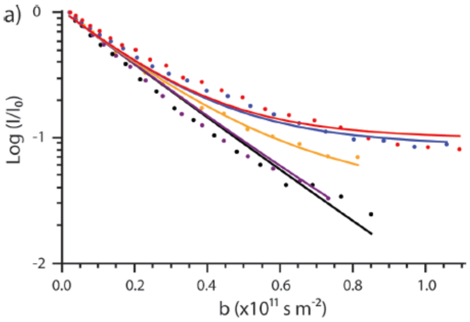

Figure 1: ^{1}H pulsed-field-gradient spin-echo decays of Pluronic® F127 recorded with different diffusion times in aqueous solutions containing single walled carbon nanotubes.

We have studied by ^{1}H NMR diffusometry the exchange and translational dynamics of triblock copolymers Pluronic® in aqueous solution containing single walled nanotubes (SWNT). The ^{1}H pulsed-field-gradient spin-echo decay (Fig. 1) was nonexponential for all investigated polymers and changed character upon changing the diffusion time Δ, which indicates a situation where there is exchange of the polymer between its free and adsorbed states and where the exchange time lies in the 100 ms range [3] set by the experimental time scale (Δ). Within the framework of the well-known Kärger model, the self-diffusion coefficient of the polymers in their CNT-adsorbed state can also be obtained. For Pluronic® F127 we found that the surface diffusion coefficient is in the order of 2.2×10^{-12} m^{2}s^{-1}, ca 30-fold smaller than that obtained for the unbound polymer in water (5.9×10^{-11} m^{2}s^{-1}). This result seems to support the “loose adsorption” model for Pluronic-CNT interaction.

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Fermi acceleration induces self-organized critical characteristics to the driven Lorentz channel

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The Lorentz gas (LG) acts in the theory of dynamical systems as a paradigm allowing us to address fundamental issues of statistical mechanics, for instance, transport processes, such as diffusion in the configuration space [1, 2]. The static periodic LG comprises a regular lattice of circular fixed scatterers and an ensemble of non-interacting particles travelling freely between collisions and scattering elastically off the circular obstacles. The transport properties of such a system are determined by the billiard's geometry, that is the specific lattice symmetry and the lattice constant. If the maximum free path length is not bounded from above, then the setup possesses a so-called infinite horizon (IH) and the diffusion in configuration space is anomalous [4, 5]. For a more compact packing of the scatterers, i.e. finite horizon (FH), arbitrarily long flights are not possible and the system exhibits normal diffusion.

Time-dependent generalizations of the original periodic Lorentz gas model have been introduced, in which the scatterers are allowed to oscillate [6, 8], rendering the study of diffusion in momentum space possible. This process is intimately linked to Fermi acceleration [3], which is considered a fundamental acceleration mechanism in many areas of physics. The mechanism consists in the indefinite increase of the mean energy of particles as a result of random collisions with moving scatterers.

In this work [9], we show the emergence of power-law (critical) cross-correlations between non-interacting particles propagating in the driven LG in a channel geometry. To reveal these cross-correlations a spatially coarse-grained description of the dynamics is employed. The dynamically infinite horizon (DIH) is introduced as a property of driven extended billiards for which ballistic corridors open up and close periodically in time, i.e. exist only for certain time intervals. The development of Fermi acceleration then enables the particles to synchronize their motion with the periodic appearance of the ballistic corridors, such that they can perform free flights of arbitrary length, which, in turn, gives rise to intermittent dynamics and the appearance of critical correlations. In this sense, it is shown that Fermi acceleration can act as an effective driving force to steer an ensemble of propagating particles towards a critical state, imparting to the system's dynamics characteristics of self-organized criticality (SOC).

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Transport into zeolite nanosheets: Diffusion equations put to test

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Ultrathin porous materials, such as zeolite nanosheets, are prominent candidates for performing catalysis, drug supply, and separation processes [1, 2] in a highly efficient manner due to exceptionally short transport paths. Predictive design of such processes requires the application of diffusion equations that were derived for macroscopic, homogeneous surroundings to nanoscale, nano-structured host systems. Because of the obvious dissonance between requirements and assumptions, we tested analytical solutions of Fick's diffusion equations for their applicability to methane transport into two different zeolite structures (Figure 1b) under instationary conditions. The two central questions were: Do the conventional diffusion equations break down at the nanoscale? And, what is the reason to the (possible) limitation of applicability?

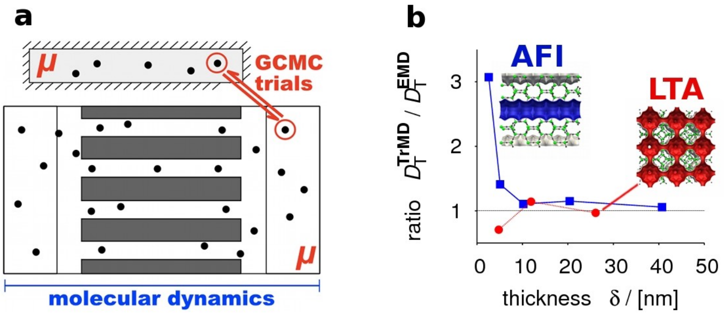

Figure 1: (a) Scheme of TrMD. (b) Deviation of TrMD transport diffusivities from EMD predictions.

Computationally demanding transient molecular dynamics (TrMD) simulations were performed, paralleling conditions of diffusion experiments with constant sorbate supply (Figure 1a). Transient concentration profiles from TrMD were fitted to standard analytical solutions of Fick's diffusion equations [3] to yield transport diffusivities, D_T, and surface permeabilities, α:

$$c(t,z)/c_\infty = 1 - \sum_i^\infty \{2L \exp[-\gamma_i^2 D_T t/(\delta/2)^2] \cos[\gamma_i z/(\delta/2)]/[(\gamma_i^2 + L^2 + L)\cos\gamma_i]\}, \quad (1)$$

where δ denotes the sheet thickness, $L = (\delta/2)\alpha/D_T$ and γ_i the positive roots of $L = \gamma_i \tan\gamma_i$. The resulting transport diffusivities relative to equilibrium molecular dynamics (EMD) predictions highlight that TrMD data can significantly exceed EMD values at small nanosheet thicknesses (Figure 1b). This represents a size limitation to the applicability of Fick's laws because transport coefficients must not vary with primary geometric parameters. We observe the effect only for smooth pores (AFI); for cage-type zeolites (LTA), the effect is absent. Therefore, we conjecture that the molecular explanation is found in a memory effect. Entering molecules cannot equilibrate in the first cage, perform a cascade of jumps across several cages ("multijumps"), and, thus, violate random walk theory on the length scale of a single zeolite cage.

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The inter and intra-molecular dynamics of polymethylphenylsiloxane under 1-D and 2-D confinement

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Broadband dielectric (BDS) and Fourier transform Infrared (FTIR) spectroscopy are employed to study molecular dynamics of polymethylphenylsiloxane (PMPS) in 1-D and 2-D geometrical constraints. PMPS under the former confinement of thin films down to thickness of 7 nm spin cast on highly conductive silicon wafers in combination with nanostructured counter electrodes are studied by BDS while in the latter case, PMPS infiltrated into porous silica membranes with unidirectional nanopores having diameters down to 4 nm are probed by both BDS and FTIR. The glass transition temperature (T_g) of thin films for all the thickness investigated remained bulk-like but the segmental relaxations of PMPS in nanopores is faster than bulk and changes from VFT to Anrhenuis-like temperature dependence for small pores (4 nm). This is attributed to the density inhomogeneity as a consequence of altered molecular packing under confinement in nanopores. Additional slower process observed in native pores is due to attractive interactions of molecules with pores walls. The vibrations of IR active moieties in PMPS follow different temperature dependencies in both the spectral position and the oscillator strength. The phenyl ring and the $\nu_{ar}(C-H)$ stretching vibrations exhibits a kink at T_g and at ca 30 K above T_g. This is attributed to coupling between intra vibrations of phenyl ring and the segmental relaxation.

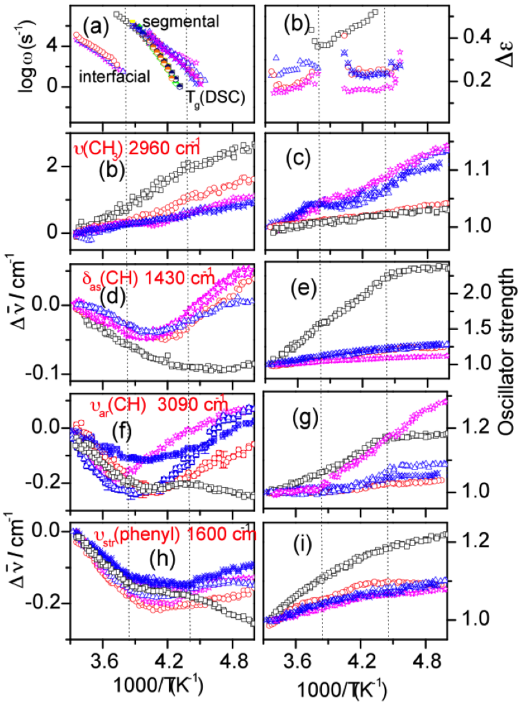

Figure 1: Comparsion of inter and intra-molecular dynamics of polyphenylmethylsiloxane in 1-and 2-D dimensional confinement: (a)inter molecular segmental dynamics from BDS; bulk (filled squares), confined in nanoporous silica of pores sizes: -8 nm (circles), 6 nm (triangles) 4 nm (stars). Crossed symbols denote silanized pores. Half filled symbols are dynamics in thin films ranging from 80–7 nm thickness. (b) the corresponding dielectric strength of bulk and confined in pores. (b–i) the temperatura dependence of bandshift of the spectral position and oscillator strength of the intra-molecular IR-vibrations in PMPS.

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On the nature of adsorption sites for CO_2 in MOF $Zn_2(bdc)_2$dabco

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$Zn_2(bdc)_2$(dabco) is a zinc-based paddle-wheel type MOF (synthesis described in [1]). The structure of this MOF can be represented as a set of parallel rectangular channels. In order to investigate dynamic behavior of absorbed CO_2 we used two different NMR techniques – spectroscopy and diffusometry complemented with simulation of molecular dynamics.

The ^{13}C NMR spectra of adsorbed CO_2 display anisotropic "powder" pattern. The linewidth decreases with increasing temperature. The rotational motion of CO_2 remains highly restricted even at room temperature. The PFG NMR diffusometry provided CO_2 translational diffusion coefficients as large as 7.4×10^{-9} m^2s^{-1}. Such a behavior cannot be explained by a simple "freezing in pores".

The MD simulation reveals that the $Zn_2(bdc)_2$(dabco) MOF structure provides several CO_2 absorption sites at the Zn-paddle wheels. CO_2 molecules jump rapidly between the available adsorption sites. Analysis of MD trajectory shows a strong orientational preference of the CO_2 molecules along the axis of the paddle wheel connected with translational diffusion anisotropy with diffusion tensor having its largest component in direction of the MOF channels.

The specific lineshapes in the ^{13}C NMR spectra are finally explained by combination of intrinsic ^{13}C chemical shift anisotropy and CO_2 orientational anisotropy due to structural anisotropy of the channel system in $Zn_2(bdc)_2$(dabco) MOF crystallites.

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Molecular dynamics investigation of the transport of hydrogen in ZIF-7

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The importance of hydrogen-based clean energy systems due to the global climate change, air pollution and energy security has lead to several studies of hydrogen production, separation and storage in industry and science [1, 2].

In the current study, we have investigated the diffusion of hydrogen within a novel Zeolitic imidazolate framework (ZIF-7, Figure 1a). ZIFs are a subfamily of porous metal-organic frameworks (MOFs) [3, 4]. For investigating diffusion behavior of hydrogen in this lattice, we have applied Molecular Dynamics (MD) simulations. At the studied temperatures in a series of MD simulations performed with a rigid lattice, no diffusion of any gas was observed in ZIF-7. The same behavior has been reported by A. Battisti et al. [5]. Applying the flexibility to the framework, the measured diffusion coefficient for hydrogen was about 2.7×10^{-9} m^2 s^{-1} while nearly no diffusion was observed for any other studied gas in ZIF-7. These results clearly elucidate the molecular sieving behavior of this material for hydrogen reported by Caro et al. and represent it as a promising membrane in this domain which is due to its very small pore structure and window size (0.3 nm) that is close to the kinetic size of the hydrogen molecule [1].

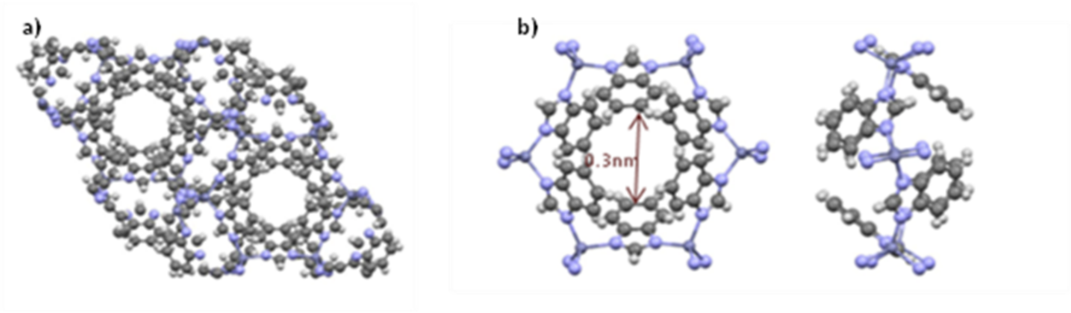

Figure 1: ZIF-7 unit cell (a). The main six-member window of ZIF-7 (b); Top view (left), side view (right).

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Polymer translocation through a nanopore: Impact of fluctuations on dynamical scaling

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We suggest a theoretical description of the force-induced translocation dynamics of a polymer chain through a nanopore. Consideration is based on the tensile blob picture of a driven chain and the notion of a propagating front of tensile force along the chain backbone, suggested by Sakaue (Phys. Rev. E 81, 041808 (2010)). The driving force is associated with a chemical potential gradient that acts on each chain segment inside the pore. Depending on its strength, different regimes of polymer motion (named after the typical chain conformation, “trumpet”, “stem-trumpet”, “stem”) occur. Assuming that the local driving and drag forces are equal (i.e., in a quasi-static approximation), we derive an equation of motion for the tensile front position. We show that the scaling law for the average translocation time versus chain length changes as the driving force f grows. As a result the corresponding scaling exponent increases with f. This and other predictions are tested by Molecular Dynamics (MD) simulation. Data from our computer experiment indicate indeed that the translocation scaling exponent increases with the pulling force f albeit the observed exponent stays systematically smaller than the theoretically predicted value [1]. In order to study the role of fluctuations (which are ignored in the quasi-static approximation), we assumed that the translocation coordinate $s(t)$ is a random process governed by the so-called velocity Langevin (V-Langevin) equation [2]. With this in mind we have derived the corresponding Fokker-Planck equation (FPE) for the translocation coordinate probability distribution function $W(s,t)$ which has a nonlinear drift term and time-dependent (running) diffusion coefficient $D(t)$. Our direct MD-simulation performed in 3D shows that the driven translocation follows a super-diffusion with a running diffusion coefficient $D(t)$. This finding being used in the numerical solution of FPE demonstrates an important conclusion: under relatively small driving forces fluctuations can facilitate the translocation dynamics [3]. Moreover, the effective translocation exponent becomes smaller. In the undriven case the translocation is slightly sub-diffusive and can be treated within the framework of fractional Brownian motion (fBm) [4]. In particular, this means that $W(s,t)$ is Gaussian but with a time-dependent variance which grows sub-diffusively. These results are supported by extensive MD-simulation.

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Exploring diffusion and reaction in nanoporous catalysts by IR micro-imaging

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Though PFG NMR has been successfully employed for the in-situ measurement of the diffusivities of the various components during chemical reactions [1] it fails to provide any information about the location of these components. Recent progress in the development of in-situ techniques for the characterization of solid catalysts [2] has overcome this limitation and provided us, with IR micro-imaging [3], with a technique offering best prospects for the recording of transient concentration profiles of the involved components during chemical reactions. The present contribution introduces into these options.

As an alternative to diffusion-reaction studies in zeolites with two-dimensional channel networks, we have cared for the option of similar investigations with three-dimensional pore networks. For this type of measurement, the catalyst is applied in the shape of small platelets, with the two large faces covered with a suitable layer which is impenetrable for the guest molecules but IR transparent at the relevant frequency. Hence, by observing perpendicular to the plane of the platelets, any diffusion in observation direction is excluded and IR micro-imaging directly yields the concentration profiles, simultaneously for each individual component!

First results of this type of measurement in a nanoporous glass [4] are shown in Figure 1. In order to show the potentials of our model-system in combination with IR micro-imaging we performed a so called counter-diffusion experiment. The sample is thereby pre-loaded with benzene and then suddenly exposed to a cyclohexane atmosphere. In Figure 1 the benzene concentration in the sample is clearly seen to decrease (a, b) while, at the same time, the concentration of cyclohexane is increasing (c, d). Concentration profiles can be recorded because the coating of the glass plates ensures that the molecules can only enter from the open side on the right and not through the surfaces on top or bottom.

We are presently performing experiments for demonstrating these potentials by recording the spatial distribution of the components involved in simple model reactions like the reduction of benzene to cyclohexane.

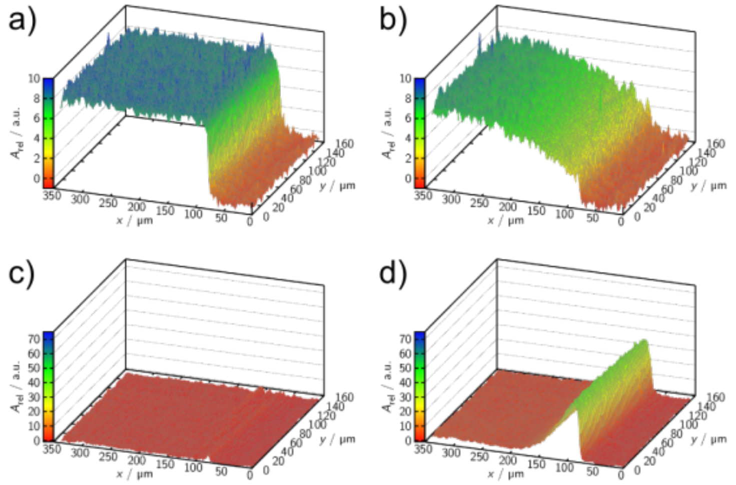

Figure 1: Concentration of benzene (a, b) and cyclohexane (c, d) before (a, c) and 20 s after (b, d) the replacement of benzene by cyclohexane in a counter-diffusion experiment

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Single-particle and ensemble diffusivities – Test of ergodicity

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Diffusion is the irregular, omnipresent motion of the elementary constituents of matter. It is prerequisite for life quite in general and key to innumerable processes in nature and technology. After one and a half centuries of diffusion measurements with large ensembles of diffusing particles [1], the option of single-particle tracking (SPT) with single molecule sensitivity [2] has recently provided us with a totally new view of diffusion. With this in mind, a central problem of matter dynamics can now be addressed by direct experimental evidence – the proof of the ergodic theorem indicating that the average value of the squared displacement $r^2(t)$ of a diffusing particle during a time interval t, if taken over many subsequent time intervals ("time average"), agrees with the average taken over many different particles ("ensemble average") during one and the same time interval t.

So far, the mutually contradicting measuring conditions have prohibited the application of ensemble and single-particle techniques to one and the same system: The trajectory of a diffusing single molecule is constructed by fitting the position of the molecule over time with SPT. Therefore the fluorescence signals of the molecules have to be clearly separated from each other, which requires very low concentrations. Additionally the measurements are limited by the signal-to-noise ratio, which is influenced by the brightness of the dye molecules as well as the integration time. Consequently there is an upper limit for the detectable diffusivity in SPT. Exactly the opposite conditions, namely high concentrations (for generating sufficiently strong signal intensities) and high diffusivities (for giving rise to observable displacements) must be fulfilled for the application of the pulsed field gradient (PFG) technique of NMR, representing the most powerful ensemble technique for diffusion studies.

By applying nanoporous glass as a host system and Atto532 as guest molecules, we found a system where the diffusivity can be controlled by adjusting the pore diameter. We were therefore able to bring the guest diffusivities into a range where both single-particle tracking and PFG NMR were applicable. The diffusivity of guest molecules in a mesoporous glass depends on their concentration. For high concentrations it is governed by guest-guest and guest-solvent interactions, whereas for low concentrations the host-guest interactions dominate. While single-molecule experiments are performed exclusively in the low-concentration regime, we managed to reduce the concentration in the PFG-NMR experiments to reach this regime.

For the first time, single-molecule and ensemble diffusion measurements are thus found to experimentally confirm the hypothesis of ergodicity, since (within the limits of accuracy) both techniques provide the same result [3]. With these experiments, the two so-far separated worlds of diffusion measurements have been brought together. As a prerequisite of this "marriage" we have considered a situation where the rules of normal diffusion are obeyed. However, single particle observations of e.g. biological systems [4] often seem to contradict ergodicity. Now, with the combined potentials of single-particle and ensemble measurements, the underlying reasons for such deviations of ergodicity can be revealed.

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Correlating phase state and transport in hierarchical mesoporous materials

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The pulsed field gradient technique of NMR (PFG NMR) is applied to explore molecular diffusion in different specimens of zeolite NaCaA, notably in samples containing hierarchical pore systems, as well in a silica material with an ordered, bimodal mesopore structure. In the hierarchical zeolithes the diffusivities in the two pore spaces are measured separately from each other by choosing ethane (capable of permeating both micro- and mesopores) and cyclohexane (unable to penetrate the micropores) as guest molecules and varying purposefully the accessibility and mobility in the mesopores by temperature variation and pore blocking. It is shown that the presence of the mesopores may give rise to dramatically enhanced intra-crystalline diffusivities while a blockage of the mesopores reduces the intra-crystalline diffusivities by an order of magnitude [1]. The well-defined pore structure of a bimodal mesoporous glass allowed for a quantitative analysis of the diffusion process in a medium with spatially-ordered distribution of the fluid density for a broad range of the gas-liquid equilibria. The measured diffusion data were interpreted in terms of effective diffusivities, which were determined within a microscopic model considering long-range molecular trajectories constructed by assembling the alternating pieces of displacement in the two constituting pore spaces. It has further been found that for the system under study, in particular, and for mesoporous materials with multiple porosities, in general, this generalized model simplifies to the conventional fast-exchange model used in the literature. Thus, not only justification of the applicability of the fast-exchange model to a diversity of mesoporous materials was provided, but also the diffusion parameters entering the fast-exchange model were exactly defined. The equation resulting in this way was found to nicely reproduce the experimentally determined diffusivities, establishing a methodology for targeted fine-tuning of transport properties of fluids in hierarchical materials with multiple porosities [2].

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Resonant optical tweezers with anti-reflection coated titania microspheres

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Brownian motion is exhibited by an optically tapped particle due to the thermally driven molecules of the surrounding medium. This motion is often considered to be a frequency-independent phenomenon which is known as a white noise process. However, fluid entrainment influences the particle in the trap and results in a frequency-dependent motion. Therefore, the power spectral density (PSD) of the noise that drives the motion is “colored”. The “colored noise” of the Brownian motion can change the behavior of an optical trap from an overdamped oscillator to a resonant one. Here, our goal was to amplify this resonance. Theoretical calculations predict that particles with a large diameter and a high trap stiffness enhance the resonance effect. Therefore, we synthesized large anti-reflection coated titania microspheres. These microspheres have a high trap stiffness in the optical trap. In comparison to our previous work [1], the results showed a roughly 4 times enhancement of the resonance in acetone. The resonant behavior could be used as a sensor in analogy to other resonant probes such as an atomic force microscope cantilever.

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Gold nanostructure assisted thermophoretic trapping of single nano-objects

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The manipulation and trapping of nano-objects that undergo Brownian motion are of great interest in soft-matter sciences. Optical tweezing is the most common technique for the trapping of individual particles in solution and is based on the optical gradient force. Hence, a sufficiently high polarizability of the particle in the solution is required. While it is thus easy to trap single dielectric particles larger than 100 nm, a trapping of smaller objects such as single molecules by means of optical tweezers can hardly be realized. Molecular trapping can be achieved by a technique called Anti-Brownian Electrokinetic trap (ABEL trap) [1], which exploits the feedback-controlled electric field of four electrodes. Hence, the latter technique requires electrical contacts, which introduce difficulties when fabricating multiple traps. Here, we present an all-optical technique which replaces the electric fields by highly localized thermal fields. The so-called thermophoretic trap exploits thermophoretic interactions of a particle and a liquid when applying a temperature gradient, which e.g. locally distorts the screening of the surface charges and by that induce a particle drift sufficient for the manipulation of small nanoparticles or molecules [2].

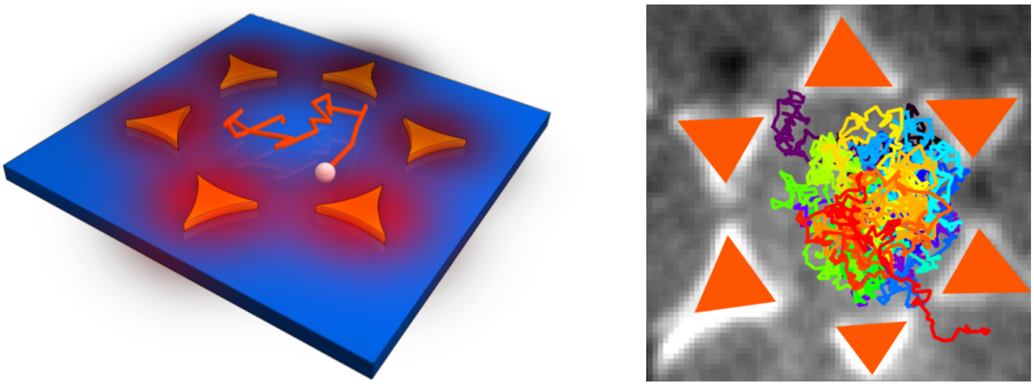

Figure 1: (left) Scheme of the thermophoretic trap consisting out of triangle-shaped Au islands (right) Trajectory of a trapped polystyrene sphere

In our approach the temperature field is generated by optically heated Au nanostructures fabricated by microsphere lithography (Fig. 1) [3]. Due to the small dimensions of the heat sources, even a small temperature increase introduces large temperature gradients causing a strong thermophoretic drift by which the motion of a diffusing particle can be manipulated.

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Effective time-dependent temperature in hot Brownian motion

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Hot Brownian motion is the diffusive dynamics of a colloidal particle maintained at constant higher temperature than the surrounding fluid [1, 2]. It is of practical relevance, e.g. for laser-heated suspended nanoparticles involved in several experimental applications ranging from particle trapping and tracking [3] to self-thermophoretic motion [4], but also of considerable theoretical interest since it can be thought as an archetypal example of systems in contact with a non-isothermal bath, thus intrinsically out-of-equilibrium. While the qualitative differences with isothermal Brownian motion, i.e. enhanced thermal fluctuations and lowered viscous friction, are easily anticipated, a complete formal description of the phenomenon was not available so far. Starting from the fluctuating hydrodynamic equations for the solvent, we obtain for the colloid's motion a generalized Langevin description that exhibits, as the most remarkable feature, a time-dependent temperature resulting from the scale separation between the dynamics of fluid and colloid. Moreover, we show that in the long-time limit different degrees of freedom, such as position and velocity, equilibrate to different effective temperatures, whose analytic expressions are verified through large-scale molecular dynamics simulations. This provides an excellent starting point for experimental tests and applications involving heated nanoparticles and paves the way for further theoretical investigations on colloidal systems in the presence of temperature inhomogeneities.

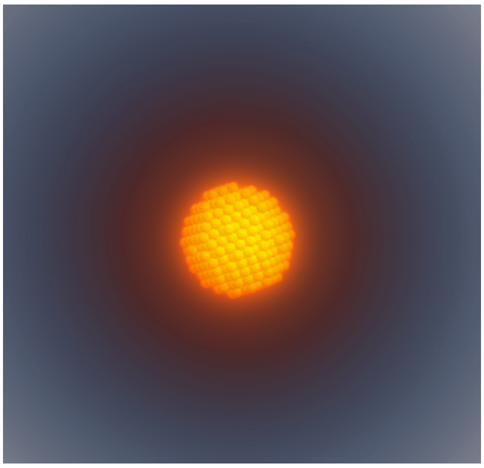

Figure 1: Artist's conception of a Brownian particle heated above the temperature of the embedding fluid.

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Two-step memory within Continuous Time Random Walk

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By means of a novel version of the Continuous-Time Random Walk (CTRW) model with memory [1], we describe, for instance, the stochastic process of a single share price on a double-auction market within the high frequency time scale. The memory present in the model is understood as dependence between successive share price jumps, while waiting times between price changes are considered as i.i.d. random variables. The range of this memory is defined herein by dependence between three successive jumps of the process. This dependence is motivated both empirically, by analysis of empirical two-point histograms, and theoretically, by analysis of the bid-ask bounce mechanism containing some delay. Our model turns out to be analytically solvable, which enables us a direct comparison of its predictions with empirical counterparts, for instance, with so significant and commonly used quantity as velocity autocorrelation function. This work extends our previous one-step memory model [2] and the capabilities of the CTRW formalism.

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Diffusion of ragweed under climate change. Cost benefit-analysis for reducing allergies.

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Ragweed (Fig.1) is rapidly spreading in Europe [1, 2, 3]. Its pollen is highly allergenic, c.5 % of Europeans being sensitized. There is an urgent need to curtail the further spread to minimize allergy costs.

In the present work we simulate the diffusion of ragweed in Austria and southern Germany (Bavaria) until 2050 with particular emphasis on the expected climate change. We analyse the potential of reducing human allergy costs, i.e. the expenses caused by allergies from ragweed pollen, by curtailing the accelerating spread of ragweed. We do so by accounting for three contrasting climate scenarios: no change, moderate and more extreme climate change, i.e. 1.5 and 2.4 degrees from 1990 to 2050.

We find that by a carefully designed management consisting of survey and eradication the spread of ragweed can be drastically reduced. Without management, mean allergy costs for the management period (2011 to 2050) amount to c. 290, 335 and 365 million euros annually under the three climate scenarios. Following an optimally allocated management strategy [4] with an annual budget of 7.5 and 30 million euros, resp. (Fig. 2) yields substantial savings, for the latter case reducing mean allergy costs down to about 10 % of the value with no management. Our analyses thus show that management of ragweed in Central Europe is profitable, therefore highly indicated from an economic point of view.

Figure 1: Ragweed in bloom (*Ambrosia artemisiifolia* L.).

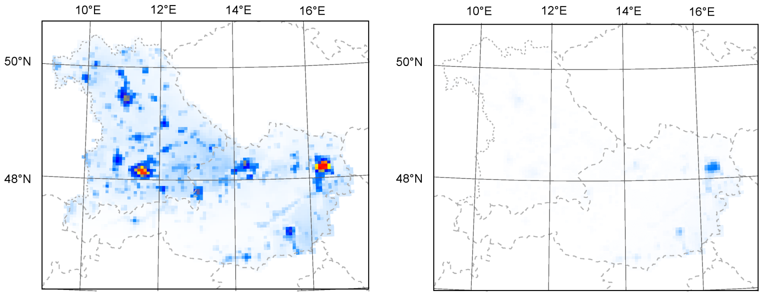

Figure 2: Density of allergy costs for Austria and Bavaria with 7.5 million euros (left) and 30 million euros (right) annual management budget. Colours indicate regions and height of allergy costs in 2050 (red highest, white lowest).

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Diffusion and freezing transition of rod-like DNA origami on freestanding lipid membranes

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During the last decade, DNA origami has become a powerful tool in research at the nanoscale. The relative ease of constructing functionalized DNA origami structures of a defined shape allows for their applications in membrane biophysics. Recently, we have constructed stiff rod-like DNA origami structures consisting of six DNA helixes, which were functionalized with hydrophobic membrane-binding anchors and fluorescently labeled at defined positions [1]. Selective fluorescent labeling allowed us to determine the translational and rotational diffusion coefficients of the DNA origami rods on lipid membranes by fluorescence correlation spectroscopy, which were found to be in a good agreement with the hydrodynamics-based theory of membrane diffusion. Further, we studied the effect of the surface density of membrane-bound origami structures on their Brownian motion. We found a strong decrease of the translational and rotational diffusion coefficients of membrane-bound nanorods with an increase in their surface density. We compare our experimental findings with results of Monte Carlo simulations of Brownian hard needles in 2D.

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Translational and rotational diffusion of semiflexible DNA polymers and rod-like *fd* virus particles on weakly charged freestanding cationic lipid membranes

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Diffusion and conformational dynamics of single semiflexible and flexible macromolecules and colloids adhereing to freestanding lipid membranes is a challenging problem both from the experimental and theoretical standpoint. Using cationic supergiant unilamellar vesicles [1] as an experimental platform for mimicking freestanding lipid membrane in combination with single-molecule fluorescence video microscopy, we have previously discovered that local interaction of single DNA molecules with moderately and strongly charged freestanding lipid membranes can lead to interesting unexpected effects [2]. In the present contribution, using the same experimental technique, we investigate the diffusion behavior of semiflexible DNA polymers and much more rigid negatively charged colloidal particles, *fd* viruses [3], upon their electrostatic binding to weakly charged freestanding cationic lipid membranes. The wide range of contour lengths of DNA macromolecules (5–48.5 kbp) and *fd* virus particles (0.88–9.7 μm), allowed us to observe the crossover from the stiff-rod to semiflexible (*fd* virus) and from semiflexible to flexible (DNA) behavior which is accompanied by a crossover in the diffusion behavior of membrane-attached particles – from the 2D membrane-controlled to 3D bulk fluid-controlled diffusion dynamics. We compare the obtained experimental results on translational and rotational diffusion of DNA and *fd* virus particles with the predictions of hydrodynamics-based theories of membrane diffusion [4–8] and determine their ranges of applicability.

This work was supported by the DFG (FOR 877).

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Simulation of diffusion in a crowded environment: The application of the Dynamic Lattice Liquid Model (DLL)

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Extensive and systematic simulation studies of two-dimensional fluid motion in a complex crowded environment were performed. In contrast to other works we focused on cooperative phenomena that occurred where the motion of particles takes place in a dense crowded system. Our main goal was to answer the question how do fluid molecules move in an environment which has a complex structure and taking into consideration the fact that motion of fluid molecules is highly correlated. The Dynamic Lattice Liquid (DLL) model, which can work at the highest fluid density, was employed. It became the basis for a parallel algorithm, which took into account coincidences of attempts of elementary molecular motion resulting in local cooperative structural transformations. Within the frame of the DLL model we considered cooperative motions of fluid particles in an environment that contained static obstacles. We studied the dynamic properties of the system, like the mean square displacement and the relaxation time of the position as a function of the concentration of obstacles. The changes of hydrodynamic interactions were also investigated by studies of the distribution of cooperative loop length. The subdiffusive motion of particles was found in the crowded system. It was also shown that the percolation threshold determined from the dynamic behavior of the mobile particles was considerably lower than that determined from the cluster analysis.

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Self-diffusion in a macroscopically aligned lyotropic hexagonal phase templated hydrogel

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Lyotropic liquid crystal (LLC) materials (e.g., LLC templated hydrogels [1]) have potential for a wide range of applications such as drug-delivery [2]. Typically the LLC phases (e.g., lamellar and hexagonal) exist as a powder distribution of director orientations, but macroscopically aligned phases can be prepared using external fields (e.g., magnetic fields) [3]. The majority of the applications of these materials are dependent on transport processes and as such characterizing this is pertinent. Self-diffusion (i.e., random translational motion) is the most fundamental form of molecular transport and provides important information regarding the size of a molecule in solution and the environment that the diffusion is occurring in (e.g., as for restricted diffusion) [4–6]. The self-diffusion in macroscopically aligned LLC phases (e.g., lamellar and hexagonal) is anisotropic due to the nanostructures present [6].

The macroscopically aligned lyotropic hexagonal phase of the non-ionic surfactant decaethylene glycol monododecyl ether ($C_{12}EO_{10}$) was used to template a polyethylene glycol diacrylate (PEG-DA) hydrogel and the self-diffusion of water was found to be independent of the diffusion time (up to 3 s) [7]. Initial diffusion tensor imaging results performed ~456 days after the sample was prepared indicated that the diffusion anisotropy was retained with storage at ~22 °C (Figure 1).

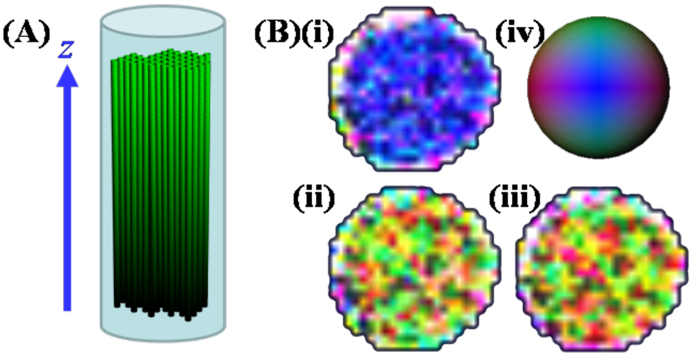

Figure 1: Diffusion tensor imaging results for the self-diffusion of water in a templated hydrogel after storage. (A) Schematic of the alignment in the hydrogel in a 5 mm Wilmad NMR tube. (B) Diffusion tensor images for an axial slice (voxel size: 0.196 mm × 0.196 mm × 0.5 mm (slice thickness), diffusion time: 70 ms). (B)(i), (ii) and (iii) show images for the first, second and third eigenvectors, and (iv) a directional representation.

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Stochastic fluctuations of vesicles – Extracting material parameters from incomplete projected information

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The mechanical properties of phospholipid membranes have been extensively studied over the past few decades [1]. Their ability to bend under very low stress is one of the main mechanical properties of such soft materials. This softness is characterized by a very small value of the bending modulus (on the order of 10 k_BT). As a result, a flaccid vesicle can attain many thermally allowed shapes at constant volume, which leads the thin-walled vesicles to fluctuate (the so-called flicker phenomenon) [1].

Measurements of these stochastic fluctuations have been used to estimate the bending modulus of red blood cells and artificial vesicles [2, 3, 4]. Here, we re-examine this methodology and discuss some of its limitations; e.g., video-microscopy gives only partial information in the sense that it provides a two-dimensional view of the three-dimensionally fluctuating vesicle. In order to overcome this technical limitation, we develop two new possible methods for inferring mechanical information about membranes from the projected intensity of fluorescent quasi-spherical vesicles.

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Wanted: Scalable tracers for diffusion

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Scalable tracers are potentially a useful tool to examine diffusion mechanisms and to predict diffusion coefficients, particularly for hindered diffusion in complex, heterogeneous, or crowded systems. Scalable tracers are defined as a homologous series of tracers varying in size but with the same shape, structure, surface chemistry, deformability, and diffusion mechanism. Both chemical homology and constant dynamics are required. Specifically, branching must not vary with size, and there must be no transition between ordinary diffusion and reptation. Ideally the tracers would be uniform, monodisperse, metabolically inert cylinders in 2D or spheres in 3D with continuously variable radius and tunable surface properties.

Scalable tracers will facilitate more rigorous diffusion measurements in which two types of measurements are clearly distinguished. Scalable tracers would be used to find the mean diffusion coefficient as a function of size, and nonscalable tracers would be used to find the variation due to differences in shape, surface properties, and the like.

Candidate scalable tracers are discussed for 2D diffusion in membranes and 3D diffusion in cytoplasm and nucleoplasm. Specific suggestions for the 3D case include the use of synthetic dendrimers or random hyperbranched polymers instead of dextran, and the use of core-shell quantum dots in which the shell thickness is used to vary the overall diameter.

Another useful tool would be a series of scalable tracers varying in deformability alone. These could be made by varying the density of crosslinking in a polymer, to make say “reinforced Ficoll” or “reinforced hyperbranched polyglycerol”. (Supported by NIH grant GM038133.)

Internal friction of a migrating Holliday junction

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Friction within biomolecules has recently gained increasing interest. Here we present a method that allows to study the friction that occurs during fast, few nm-sized refolding processes of nucleic acids. Branch migration of a homologous Holliday junction serves as an ideal system where such friction can be investigated. In this four-arm DNA junction the opposing arms possess identical sequences with respect to the junction center. In the absence of external constraints the junction is mobile such that one pair of homologous arms can expand at the expense of the other in single base pair diffusive steps. We measure the dynamics of the branch migration process by stretching a torsionally constrained Holliday junction using magnetic tweezers and measuring the length fluctuations of the arms with high-speed videomicroscopy at ~3 kHz. Since DNA has a helical structure, branch migration causes twisting of the arms with one turn per helical pitch moved. This constrains the movement of the junction within the tweezers to ~10 bp. Single base pair diffusive steps are expected to occur on a sub-millisecond time scale and to be much smaller than the overall DNA length fluctuations. Thus they can not be directly resolved. However, power-spectral-density analysis of the length fluctuations is able to clearly resolve the overall dynamics of the branch migration process. Theoretical modeling considering the elastic coupling of DNA bending fluctuations and the junction movement allows to quantitatively determine the stepping rate and thus the friction of the branch migration process. We expect that our method is widely applicable to study local-scale molecular friction in biological systems.

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Protein diffusion on DNA

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Diffusion is a major transport mechanism within living systems. Protein diffusion along elongated cellular structures (e.g. cytoskeletal filaments or DNA), often termed one-dimensional diffusion, has recently gained increasing interest. This is because confinement of the diffusion path can enhance the success rate of localizing a target on the particular structure. Here we focus on a new aspect, namely that protein diffusion along DNA can be itself a central part of an enzymatic reaction. Using magnetic tweezers and fluorescence techniques we provide single-molecule observations of the monomeric restriction enzyme BcnI which needs to turn on DNA to cut both strands of the helix. We reveal on one hand the orientation of the enzyme bound to its target site, and on the other hand the one-dimensional diffusion of the enzyme along DNA under different ionic conditions. Both observations provide evidence for a mechanism of the enzyme where indeed a monomer cuts both DNA strands in a sequential manner.

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Tracing molecular propagation in dextran solution by pulsed field gradient NMR

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Molecular self-diffusion in biological systems plays an important role by not only providing a mechanism of matter transport, but also by determining the rates and patterns of bio-chemical reactions in cells [1]. In recent years, fluorescence correlation spectroscopy (FCS) has emerged as a powerful technique for studying transport processes in biological systems on a spatial scale up to hundreds of nanometers [2]. The data obtained by this technique reveal that in most cases diffusion of tracer dye molecules under these conditions shows anomalous behavior, i.e., the mean square displacements grow not linearly with time, but as a power law with the exponent $\alpha < 1$ [3]. This finding, which is typically associated with molecular crowding effect, has far reaching consequences, among which reformulation of the concepts of bio-chemical reactions in life matter is currently under discussion. However, there are much experimental evidences of normal diffusion in highly crowded media. Therefore, experimental exploration of the origins of anomalous diffusion observed in the FCS experiments is of immediate importance for life sciences.

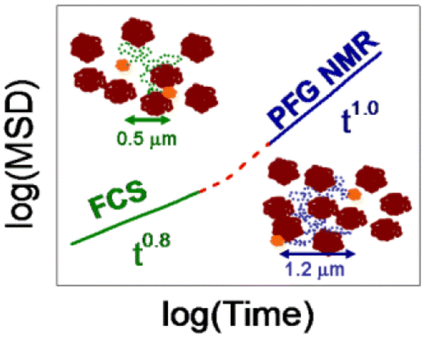

Figure 1: Schematic representation of diffusion patterns of tracer molecules obtained in model crowded media mimicking biological cells using fluorescence correlation spectroscopy and pulsed field gradient NMR.

In the present work, we have used potentials of pulsed field gradient NMR to extend the time- and space scales for the diffusion processes in the same system already probed by the FCS technique [4]. Notably, the latter technique revealed that in the aqueous solutions of dextran mixtures, mimicking crowded media in bio-cells, on the time scale up to 500 nm diffusion has shown subdiffusive behavior with the anomality exponent being a function of the solvent concentration and of the dextran molecular mass and the mixture composition [5, 6]. By choosing an optimal system with still pronounced anomality, but simultaneously providing reliable NMR signals for diffusion studies, we have traced self-diffusivities of two dextrans of 40 kDa and 640 kDa molecular mass in the mixture in deuterated water. The results obtained have provided clear evidence that for the lighter dextan, being an analogue for the probe molecule in the FCS experiments, there should be a crossover to normal diffusion on the spatial scale between 500 nm and 1200 nm. Bridging the gap between these two values in order to validate the existence of the crossover or to demonstrate that these two types of experimental approaches providing ensemble-averaged quantities (NMR) and operating with finite number of tracers (FCS) may yield differing data is among of our current activities.

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Interference reflection microscopy to visualize sub-diffraction limited objects in 3D

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The visualization of objects smaller than the diffraction limit has become a broad field, especially in life science. However, current technologies often require a fluorescent label and/or complicated optical setups. Here, we report the observation of single, non-labeled microtubules with interference reflection microscopy (IRM) using a light emitting diode for illumination. IRM can visualize sub-diffraction-limited objects, provides three-dimensional (3D) information with nanometer resolution in the axial direction, and a superior signal-to-noise ratio compared to differential interference contrast (DIC) microscopy. In comparison to other techniques such as DIC microscopy, IRM does not require any (expensive) polarizing optics, is independent of the object orientation, and can easily be implemented into conventional inverted microscopes. Also, IRM provides free access to the upper side of the sample and can be combined with other optical techniques such as fluorescence microscopy and optical tweezers.

Dynamics of single DNA molecules in spatial confinement

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The direct imaging of dynamics of biopolymers in solution with atomic force microscopy and fluorescence microscopy offers a vivid insight in the fundamentals of molecule interactions. These methods contribute to the understanding of biophysical processes in living cells and to the development of gene sequencing techniques as well as artificial functional assemblies based on DNA or proteins.

We investigate the dynamics of fluorescently labeled DNA molecules in spatial confinement. Linear polymers like DNA build entropic coils in an aqueous solution. Elongation of these coils, for example in very narrow channels, simulates a highly dense state of DNA in living cells and ensures a better insight into different spatial regions of the polymer.

The experiments are carried out in microfluidic cells made of polydimethylsiloxane (PDMS) and covered with glass. The PDMS surface is patterned with channel submicrostructures by soft lithography and direct writing via focused ion beam. The insertion of DNA molecules into channels with diameters of a few hundred nanometers is supported by electrophoretic forces. Due to fluorescence labeling and the use of transparent materials for the cell, the diffusion of single molecules can be tracked by fluorescence microscopy.

The presentation discusses the preparation of the microfluidic channel system and transport measurements of DNA molecules through these nanoscopic channels.

This work was supported by the DFG (FOR 877).

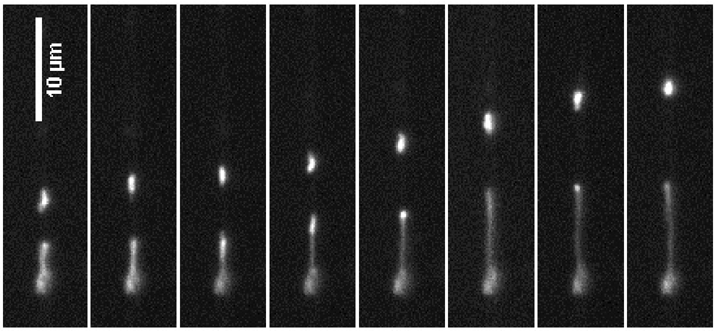

Figure 1: Micrograph series of an elongated fluorescent DNA coil during insertion into a submicrochannel.

Rapid internal contraction boosts DNA friction

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Semiflexible polymers are routinely employed as molecular handles, linkers or force transmitters in single molecule force spectroscopy assays. Their dynamic response to external forces strongly depends on the transmission and relaxation of tension within the molecular backbone, a process that has been shown to follow a diffusion-like, yet distinctly nonlinear evolution equation [1, 2]. Using bead-attached, optically trapped DNA, we show explicitly [3] that the resulting "diffusion" of backbone tension delays DNA relaxation in a manner that may appear to the outside observer as a strongly increased viscous friction, and that this apparent friction enhancement can easily dominate even the combined drag resistance of bead and polymer taken together.

This work was supported by the DFG (FOR 877).

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Integrative optical imaging of molecular diffusion in strong light scattering brain tissue

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Integrative optical imaging (IOI) is a method for measuring the effective diffusion coefficient (D^*) of fluorescent molecules in brain extracellular space (ECS) [1]. Over the last two decades the IOI method has been applied, both in brain slices and *in vivo*, to a wide variety of substances. These include epidermal growth factor, quantum dots and the synthetic drug-carrier PHPMA [2, 3]. Here we discuss further development of IOI to compensate for light scattering in brain tissue.

IOI uses epi-fluorescence microscopy combined with a CCD camera to determine D^* by fitting a theoretical expression to the image intensity of a cloud of fluorescent molecules emitted from a point source and subsequently diffusing in ECS [1, 4]. The original theoretical expression does not take into account the light scattering (LS) in tissue. Therefore in tissues that exhibit strong scattering the images may be significantly distorted and the original theoretical expression will not provide satisfactory curve fits, leading to an inaccurate determination of D^*.

In order to extend the application of the IOI method to strong light scattering tissues, we derived a new expression for image intensity. The approach is to separate the signal contributions of un-scattered and scattered photons. The un-scattered light is treated as before and therefore has an intensity profile similar to the original expression but with a reduced amplitude. The scattered photons are treated with a diffusion approximation [5] and their signal contribution is calculated by convolution of the diffusing cloud of fluorescent molecules with an approximate Green's function. As a result, the new expression involves a multiple integral that has to be calculated numerically.

The new expression has been implemented in a curve-fitting program to analyze experimental data and results obtained with 3,000 MW dextran molecules have shown that:

- In low LS media, like agarose gel, the new expression continues to fit experimental data very well, and generates essentially the same D^*-values as the original expression.
- In high LS media, the new expression fits experimental data much better and generates reduced D^*-values compared to the original expression. In more opaque brain slices, the correction to the D^*-values could be significant.

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Individually tunable micromachines driven by laser induced self propelled thermophoresis

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Trapping and guiding individual micro- or nano-objects in solution by optical means is one important task for nanotechnology. Living cells have developed strategies to transport objects with the help of molecular motors. Thus combining active motion with optical control may deliver new pathways for micro and nanomanipulation.

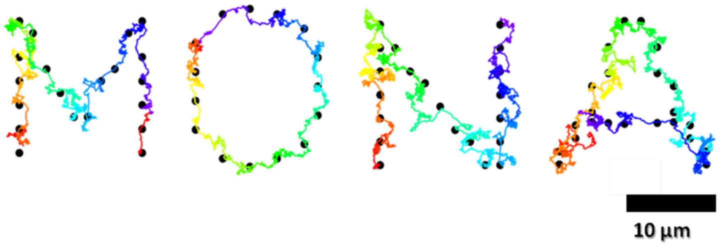

Figure 1: Sample trajectories of an individual self-propelled Janus particle along a given path.

Here we present a new concept based on self-thermophoretic action [1]. A particle which is capped by a thin metal layer is heated by an laser beam causing a temperature gradient along the particle surface. This temperature gradient leads to a directed thermophoretic propulsion of the particle. This directed motion, however, is randomized by rotational Brownian motion and just enhanced the diffusive motion on a large timescale. To overcome this randomizing a stochastic feedback mechanism can be developed, which employs the rotational Brownian motion to suppress their action. This method can be extended to the control of multiple individual particles on independent pathways (Fig. 1) or to simply localize them on individual positions (Fig. 2). This method provides numerous new perspectives for nano-manipulations in liquids.

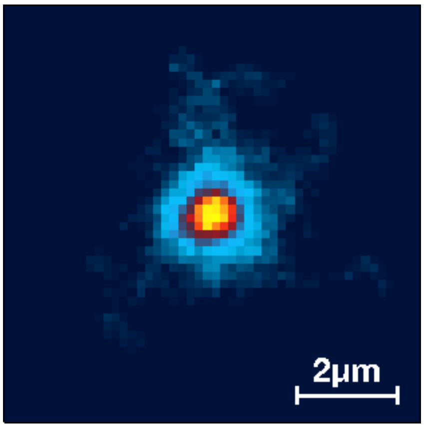

Figure 2: Localization of a 1 μm self-propelled Janus particle in the sample plane by a stochastic feedback mechanism.

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Suppressing rotational diffusion of Janus particles by surface modifications for directed thermophoretic motion

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Control over translational motion on a microscopic scale is the basis for directed transport of cargo. Besides different forms of the external driven phoretic motion, self-propelled motion gains increasing interest.

Here, the influence of various surface modifications on self-propelled motion of laser-heated gold-capped Janus particles is investigated. Wide-field laser heating of the gold hemisphere induces an asymmetric temperature profile around the particles resulting in thermophoretic self-propulsion [1]. Besides the desired directed translational motion also rotational diffusion of the Janus particles has to be regarded [2]. Therefore, we modified the Janus particles with linear DNA strands to stabilize the self-driven thermophoretic motion against the rotational diffusion. In addition, by changing the surface properties of the confining microfluidic chambers, the orientation of Janus particle was also affected. Furthermore, linking polystyrene microspheres to Janus particles via linear double-stranded DNA was investigated as a model system for transport of microcargo.

The used Janus particles consist of polystyrene microspheres with one hemisphere covered with a 50 nm thick gold layer. The water-suspended Janus particles are contained in microchambers built of cover glasses and PDMS spacers. To prevent sticking of Janus particles, the glass surfaces were passivated. Heating is achieved by laser irradiation at a wavelength of 532 nm with laser power ranging from 0 to 50 mW. From the two-dimensional trajectories of Janus particles visualized by dark-field microscopy, the mean squared displacement, rotational diffusion time, particle velocity and correlation parameters were achieved.

Linear double-stranded DNA molecules at different lengths were specifically attached to the gold side of the Janus particles via gold-thiol bonds. To this end, single-stranded λ-DNA overhangs were filled in with thiolized nucleotides in an enzymatic reaction. For flexible linking of polystyrene microspheres to Janus particles, DNA was functionalized with two different labels at both ends: thiol for binding to the gold hemisphere of the Janus particle and biotin for binding to the streptavidin-coated polystyrene microspheres. The attachement of DNA to Janus particles and polystyrene particles was verified by transmission electron microscopy.

The electrochemical properties of the passivated microchamber surfaces were characterized by zeta potential measurements and their influence on particle orientation and mobility was examined. Here, the effects of an amino-terminated and a hydrophobic silane as well as a nonionic poloxamer were studied.

This work was supported by the DFG (FOR 877).

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Correlated thermal motion of two liquid Pb inclusions on a dislocation in an Al-based alloy

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Thermal motion of a system consisting of two 14 nm and 15 nm liquid lead inclusions attached to the same fixed dislocation in Al - 0.65 at.% Pb alloy is studied in-situ at 447°C using TEM. Observation of their motion for 110 seconds was recorded on video and analyzed frame by frame. Random oscillatory motion of the inclusions in the vicinity of the dislocation line occurs as a result of their mutual repulsion and their repulsion from the fixed ends of the dislocation caused by the dislocation line tension [1–3]. The observed behavior of the inclusions is described qualitatively considering the fixed dislocation as an elastic string. The oscillations of the inclusions can be considered as their thermal motion in coupled potential wells. The effective potentials, in which the inclusions move, and the effective potential of their interaction are evaluated from the experimental data. One of the potential wells is shown in Fig. 1 (left). Also, a strong correlation in the thermal motion of the inclusions due to their interaction is found as shown in Fig. 1. The first figure shows that the cross-correlation coefficient of the positions of the inclusions on dislocation varies from about zero in the centers of the potential wells, in which the inclusions move, to close to unity near the edges of the potential wells. The second figure demonstrates a strong correlation of the separation of the inclusions along the dislocation and their separation in the direction perpendicular to the dislocation.

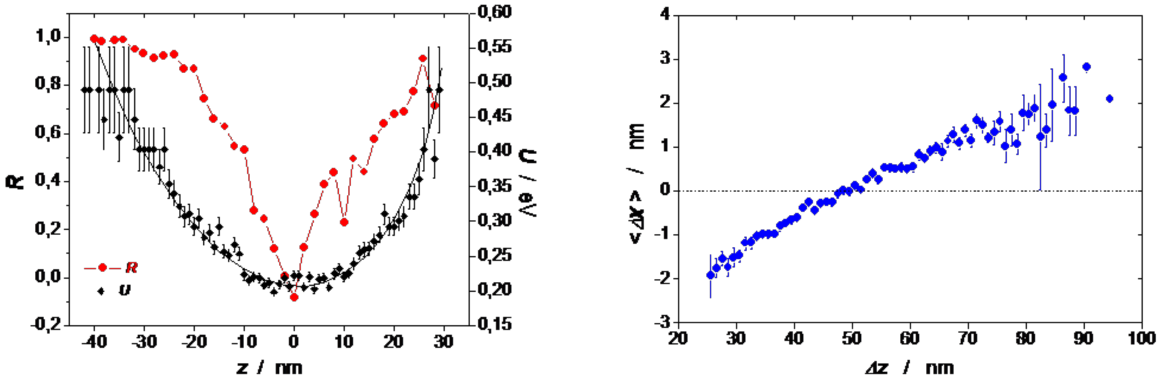

Figure 1: (left) Cross-correlation coefficient (R) of positions of the inclusions on the dislocation as a function of position of 14 nm inclusion in the potential well (U). The minimum of the potential well corresponds to $z = 0$. Solid lines are guides for eyes only. The values of R and U are obtained for 2 nm and 1 nm bins of z, respectively. (right) Averaged separation of the inclusions in the direction perpendicular to the dislocation ($\langle \Delta x \rangle$) as a function of their separation along the dislocation (Δz). The values of $\langle \Delta x \rangle$ are obtained by averaging of Δx over 1 nm bins of Δz.

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Modelling the oxygen diffusion profile in St 707 non evaporable getter material

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Non-evaporable getter (NEG) materials have become an integral part of many ultrahigh vacuum environments mainly due to their unique surface properties which are able to achieving extreme-high vacuum conditions of the order of 10^{-12} mbar and lower. NEG materials have to be “activated” after exposure to atmospheric gases. Activation is performed by heating the getter to appropriate temperature in order to remove the adsorbed gas molecules/ atoms (mainly oxygen and carbon) from the getter surface to get atomically clean metal surface of getter alloy. Main mechanism of removal of oxygen and carbon is diffusion from the surface layer into the bulk. The elements in getter alloy shall have high diffusivity and high solubility for oxygen and carbon. Diffusion of oxygen gas has been studied for pure metals, but for getter alloys there is almost no data available. At low temperature the diffusion length may be only of the order of few nm so we used surface sensitive analytical techniques such as Auger electron spectroscopy and X-ray photoelectron spectroscopy to investigate activation procedures and depth distribution of elements at various temperatures. Through this method the activation energy and diffusion coefficients are determined for two phases present in the St 707 non evaporable getter material. In the St 707 are present two phases, pure zirconium and Laves phase. Knowing the diffusion coefficients we constructed the true depth profile of Oxygen in St 707. In terms of applications, this model can helps to select appropriate conditions (temperature and time) on the occasion of their use.

Unconsolidated material characteristics obtained by PFGNMR using (two) different probe molecules

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The characteristics (surface-to-volume ratio, pore radius, diffusion, surface relaxation strength, tortuosity) of a porous system composed of a fluid confined in unconsolidated glass beads were obtained by Pulsed Gradient Stimulated Echo (PGSTE) NMR using two different probe molecules, benzene and water, respectively. The measurements were carried out on a low field NMR instrument operating at 20 MHz proton frequency. Using a 13-interval pulse sequence, the effective diffusion coefficient D of a fluid (water and benzene, respectively) confined in a porous material (unconsolidated glass beads) was measured as a function of the square-root of diffusion time t_D (Fig. 1). The limiting diffusion coefficient D_0 and the surface-to-volume S/V-ratio were determined from Eq. 1 [1] where D_0 equals the bulk diffusion. The ratio between D_0 and the limiting diffusion D_∞ at long diffusion time is termed the tortuosity factor $\Gamma(= D_0/D_\infty)$ and is an important matrix parameter

$$D(t_D) = -\frac{4}{9\sqrt{\pi}} D_0^{3/2} \frac{S}{V} \sqrt{t_D} + D_0 \tag{1}$$

Also, the interaction strength ρ between a pore confined fluid and the matrix surface is of interest and is estimated from Eq. 2. $1/T_1$ and $1/T_{1b}$ are the observed relaxation rates of pore confined- and bulk fluids, respectively. A summary of the model fit (Eqs. 1 and 2) analysis is presented in Table 1 and

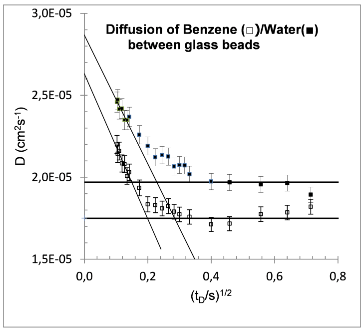

Figure 1: The diffusion coefficient of water/benzene between glass beads Vs the square root of diffusion time.

$$\frac{1}{T_1} = \frac{1}{T_{1b}} + \rho\frac{S}{V} \tag{2}$$

suggests that – within experimental error – the porous matrix characteristics (S/V and Γ) are the same, irrespective of the two fluids, and seems reasonable.

Parameter/Fluid	Benzene	Water
S/V (cm^{-1})	$1.3 \cdot 10^3$	$1.1 \cdot 10^3$
$\Gamma(= D_0/D_\infty)$	$(=2.63 \cdot 10^{-5}/1.75 \cdot 10^{-5})=1.5$	$(=2.87 \cdot 10^{-5}/1.96 \cdot 10^{-5})=1.5$
$\rho(\mathrm{cms}^{-1})$	4.9	5.4
R(μm)	23	29

Table 1: Porous matrix (glass beads) and confined fluid (benzene and water) characteristics.

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Theoretical investigation of one- two- and three-dimensional Li diffusion in solids

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Possible migration pathways for Li ions in solids are investigated theoretically at density-functional theory level. The activation energies and migration pathways for local hopping events between neighboring lattice sites are calculated with the nudged elastic band method [1] as implemented in the VASP program package [2].

The possibilities for two- and three-dimensional diffusion are investigated for h-$LiTiS_2$ by comparing the calculated activation barriers for lateral migration in the *ab* plane and along the *c* lattice vector. The concentration dependence of two competing mechanisms for *ab* migration, via octahedral edges and via tetrahedral sites, is investigated [3]. In $Li_2Ti_3O_7$ one-dimensional channels exist that may lead to one-dimensional Li diffusion. We calculated the activation barriers along these channels and in the vertical direction in order to decide if this is the case. Three-dimensional Li diffusion is studied for a number of components, e.g. $LiBO_2$ [4]

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Extreme mobility: Low-temperature NMR probes highly diffusive Li^+ ions in argyrodite-type Li_6PSe_5Cl and Li_6PS_5Br

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Lithium argyrodites represent a new class of crystalline solids exhibiting a very high Li^+ conductivity and a negligible electronic conductivity [1, 2]. This makes them ideally suited to act as electrolytes in highly stable and reliable all-solid-state lithium-ion batteries. In general, the use of a solid electrolyte inherently resolves a large majority of the safety issues associated with this technology.

The accurate characterization of Li dynamics in crystalline solids helps identify the most promising candidates so that subsequent research can focus on the improvement of their overall properties for battery applications. Here, Li diffusion parameters in a series of Li-argyrodites have been comprehensively studied by using a range of complementary time-domain NMR techniques. In particular, these include the acquisition of diffusion-induced NMR spin-lattice relaxation (SLR) rates in both the laboratory (R_1) and in the rotating ($R_{1\rho}$) frame of reference [3, 4].

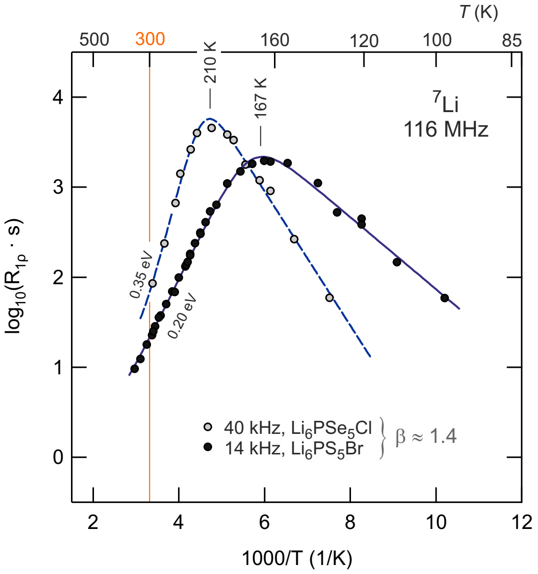

Figure 1: Arrhenius plot of the ^{7}Li SLR NMR rates recorded with the spin-lock technique in the rotating frame of reference at frequencies of 14 kHz and 40 kHz, respectively; taken from Ref. [4]. The parameter β ($1 < \beta \leq 2$) indicates the deviation from ideal BPP-type behaviour [5] which would be reflected by $\beta = 2$.

Most importantly, for the Cl- and Br-containing compounds, Li_6PSe_5Cl and Li_6PS_5Br, extremely fast Li exchange processes are found. This manifests in diffusion-induced (laboratory frame) SLR NMR rate peaks showing up at temperatures as low as 260 K while the corresponding rate peaks measured in the rotating frame of reference are shifted towards much lower temperatures (see figure and Ref. [4]). From a quantitative point of view, at ambient temperature the Li jump rate in polycrystalline Li_6PS_5Br is of the order of 10^9 s^{-1} which corresponds to an Li ion conductivity in the order of 10^{-2} S/cm, thus, indicating ultrafast translational motion of the charge carriers.

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Ion and water mobility in hydrated Li-LSX zeolite studied by ^{1}H, ^{6}Li and ^{7}Li NMR spectroscopy and diffusometry

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Crystallites of zeolite LSX with a diameter of about 10 μm are shown to allow the simultaneous investigation of intracrystalline mass transfer phenomena of water molecules and lithium ions in hydrated zeolite Li-LSX by NMR diffusometry. By MAS NMR spectroscopy with the ^{1}H and ^{6}Li nuclei, the water molecules and lithium ions are found to yield two signals, a major and a minor one, which may be attributed to locations in the sodalite cages and the supercages, respectively. By ^{1}H and ^{6}Li exchange spectroscopy the mean residence times in the sodalite cages at 373 K are found to be about 150 ms for the water molecules and about 40 ms for the lithium cations [1].

As to our knowledge, PFG NMR measurements of cation diffusion in zeolites have never been performed. Whilst, under the given experimental conditions, the water diffusivity at 373 K could be determined to be of the order of 2.5×10^{-10} m^{2}s^{-1} or even larger, the diffusivity of the lithium ions in the same sample and at the same temperature was found to be $(2.0 \pm 0.8) \times 10^{-11}$ m^{2}s^{-1}. This yields to a Haven factor of about 10 for the ion conductivity in the zeolite Li-LSX.

The new options provided by the high-intensity device for PFG NMR diffusion measurement applied in this study for the measurement of the intracrystalline diffusion of both the cations and the guest molecules in zeolite Li-LSX, in purposeful combination with the information accessible by PFG MAS NMR and two-dimensional MAS NMR spectroscopy, have all potentials for opening new routes for a deeper understanding of the dynamic processes in host-guest systems under the involvement of exchangeable cations.

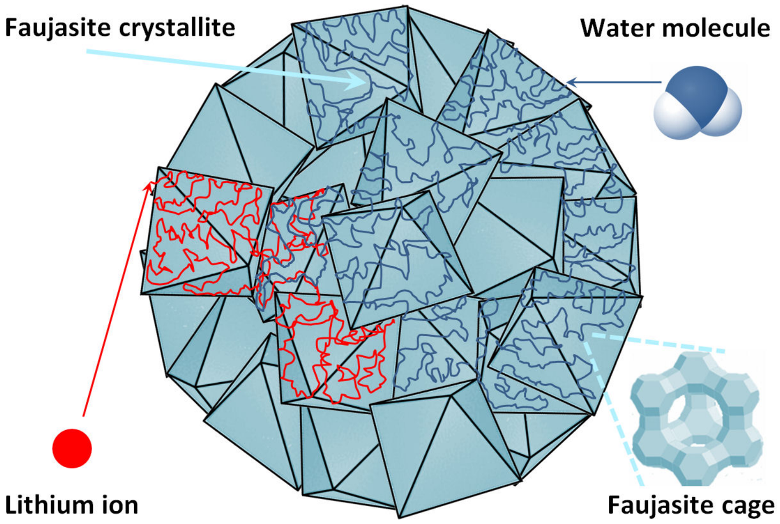

Figure 1: Water and ion diffusion in the package of zeolite crystallites.

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Diffusion and self-avoiding walks on percolation clusters

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We study random walks (RWs) and self-avoiding random walks (SAWs) on critical percolation clusters using exact enumeration. While this can be easily done for RWs, it is difficult for long SAWs due to the long-range correlations.

We employed a sophisticated algorithm that makes use of the self-similar structure of the critical clusters and allows exact enumeration of several thousand SAW steps, see [1].

For the RWs, we consider normal diffusion and the so-called maximal entropy random walk (MERW) [2] where all trajectories contribute equally to the average, as in the SAW case.

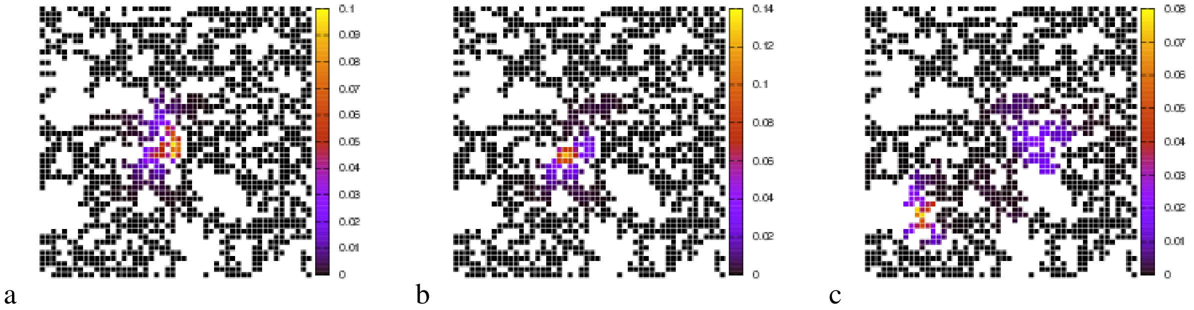

Figure 1: Probability distributions for the end-points of a random walk (a), a maximal entropy random walk (b), and a self-avoiding walk (c) of 49 to 50 steps on a critical percolation cluster. (Starting location is in the center.)

In all three cases, the asymptotic scaling behavior of the mean-square displacement is affected by the fractal nature of the critical clusters. However, while end-point distribution for the diffusive RW spreads relatively evenly from the starting point, it tends to have a sharp peak in a dense cluster region for the MERW and the SAW.

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Determining surface diffusion properties from signal fluctuations

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To describe growth kinetics of adsorbates on surfaces, knowledge of diffusion coefficients of atoms and molecules on the surface is of vital importance, especially for controlling the self-assembly of organic molecules. These usually have high mobilities and sizes large compared to the lattice constant of the substrate. In this situation, not all techniques are equally well suited for determining the diffusion coefficient. A convenient and powerful method is the recording of temporal signal fluctuations of a locally fixed probe as, for example, the current of a scanning tunneling microscope or the frequency/height modulation of an atomic force microscope. Origin of the respective fluctuations are single molecules passing the probe. This method is limited neither to sufficiently small mobilities nor to large defect-free areas.

Signal fluctuations from a fixed probe show well-defined peaks with stochastically varying widths and interpeak intervals. After transforming the signal into a rectangular one via a suitable noise-eliminating threshold value, a distribution of peak widths (Ψ_w) and interpeak distances (Ψ_d) can be obtained. In addition, the autocorrelation function (C) of the signal can be studied. We present a theory for these distributions[1], and, in extension to earlier treatments [2], for the autocorrelation function, that allows one to extract various diffusion parameters. Monte Carlo simulations of the problem are carried out for comparison with the theoretical predictions. Figure 1 shows representative examples for Ψ_w and Ψ_d, which exhibit distinct scaling behaviours in different time regimes in agreement with the theory.

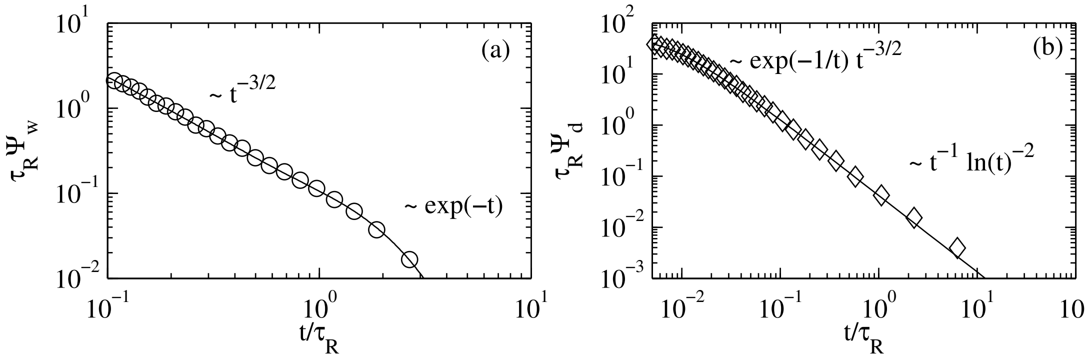

Figure 1: Analytical results (solid lines) in comparison with Monte Carlo data for (a) Ψ_w and (b) Ψ_d for a representative example. The distributions and time t are scaled with the characteristic time $\tau_R = R^2/D$, where R is the molecule radius and D the diffusion coefficient.

With respect to the applicability of the approach one has to note that Ψ_d is influenced by exchange processes of distinct particles at long times, which can only be captured approximately by the theory. The autocorrelation function is also affected by these exchange processes. Ψ_w on the other hand is governed solely by the diffusion of a single particle, but a good time resolution is necessary to resolve the peaks with high accuracy. Furthermore, Ψ_w and C can be influenced by the probe, while this influence can be neglected for Ψ_d. It is therefore advisable to use a combination of all three methods to utilize their strengths and minimize their weaknesses. This combined analysis has successfully been applied recently to the diffusion of CuPc molecules on Ag(100) [1].

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Thermal diffusivity measurements with a single nanoparticle

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Tailoring the thermal conductivity of materials is of high technological importance. Efficient thermoelectric materials are good electrical and bad thermal conductors at the same time. In recent years great efforts have been undertaken to develop nanocomposites that own these properties. We have extended photothermal single particle microscopy to characterise the thermal diffusivity of a great variety of materials on the nanoscale. In photothermal microscopy a single particle is heated optically resulting in a temperature profile around the particle. This leads to a refractive index profile which is detected by a non-absorbed probe laser beam. Usually the transmission of the probe laser is detected when the particle is heated and not heated.

We measure the modulation of the detection laser beam at several modulation frequencies where the oscillation of the heating laser is fast compared to the thermal transport. Thus the modulation of the detection laser beam decreases with frequency and the maximal signal shifts with respect to the heating laser beam (see fig. 1 (*left*)). The comparison between the experimental data and detailed numerical calculation[1] yields the thermal diffusivity (see fig. 1 (*right*)). We show that photothermal microscopy is capable to determine the thermal conductivity in a great variety of materials.

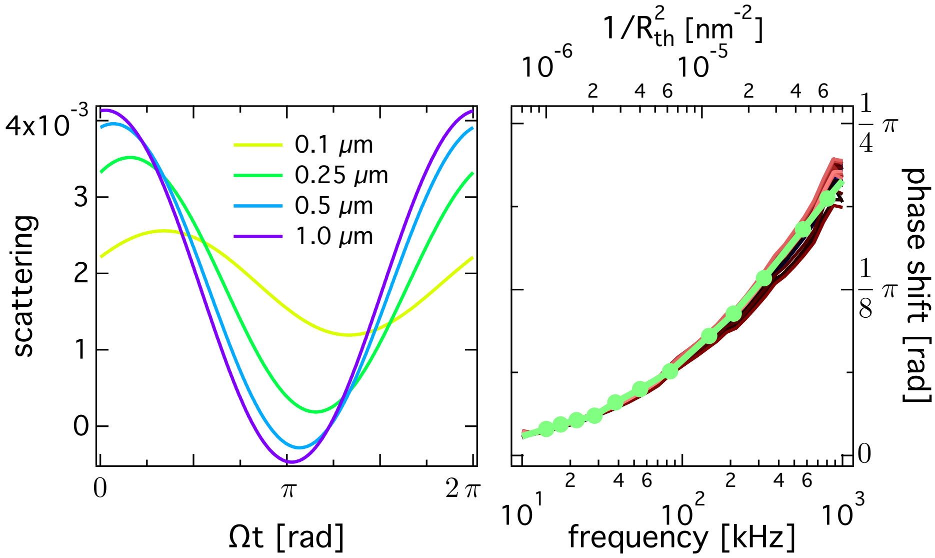

Figure 1: (*left*) The action of a modulated heat source is calculated on a laser beam at different times during the modulation cycle Ωt. The modulation amplitude and the shift of the maximum depends strongly on the thermal diffusion length R_{th}. (*right*) The calculated phase shift is plotted against $1/R_{\mathrm{th}}^2$ whereas the experimental data are plotted against the modulation frequency. The comparison between experiment and calculation gives the thermal diffusivity of $(3.8 \pm 0.6) \cdot 10^{-08}\,\mathrm{m^2\,s^{-1}}$.

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Determination of eigenvalues of the diffusion tensor in anisotropic system with spatial orientation change

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By using modern video-microscopic methods, the diffusive motion of individual particles and even molecules can be observed and followed on a sub-micrometer level. The resulting trajectories are analyzed by statistical means in order to obtain the local rheological properties of the surrounding liquid. We already introduced the distribution of diffusivities [1] as a versatile tool for such analysis and showed its utility in the analysis of heterogenous diffusion or by revealing new properties of subdiffusive continuous time random walks [2]. Another possible generalization of homogeneous diffusion processes is anisotropic diffusion. It occurs typically in systems with anisotropic media such as liquid crystals or in isotropic media when the diffusing particle or molecule has an ellipsoidal shape. It can be formally described by an extended Fokker-Planck-equation using a diffusion tensor. We show how the moments of the distribution of diffusivities [3] can be used in a simple fashion to obtain the eigenvalues of the diffusion tensor from trajectories of such anisotropic processes. For a three-dimensional anisotropic system with twist, we show how the method regains the principal diffusion coefficients. In such systems, which are mathematically equivalent to two-dimensional diffusion of an ellipsoid in isotropic media, other methods are harder to accomplish and need better data [4], or might even fail. This can be observed in the figure below, where on the left-hand side the mean squared displacement (MSD) and the angular distribution of displacements did not reveal the anisotropy, whereas on the right-hand side our distribution of diffusivities for the anisotropic system clearly deviates from the isotropic one. In addition, we show for two other systems with spatial orientation change of the diffusion tensor or likewise orientation change of the director, how this affects the distribution of diffusivities. These are a system obeying a Fréedericksz transition and a system which shows undulation of the director.

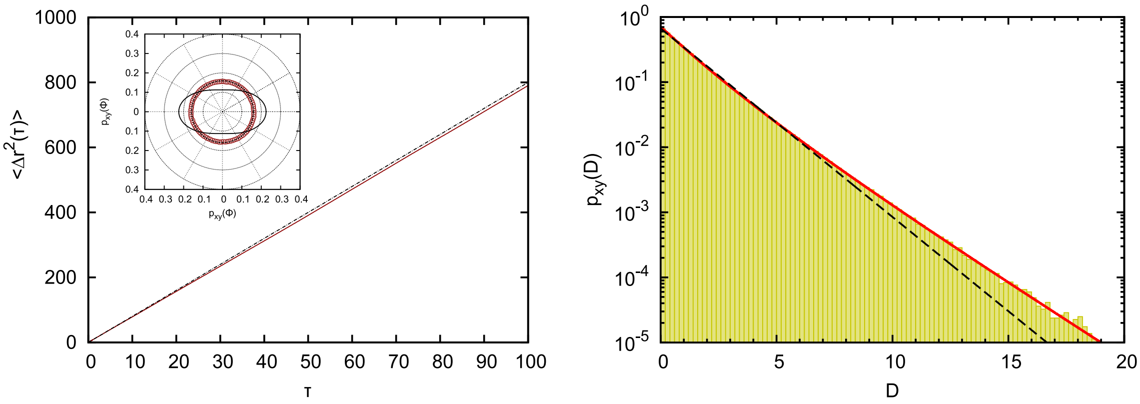

Figure 1: (left) Mean squared displacement of a diffusing ellipsoid (red) and of a diffusing sphere (black dashed) with the same average diffusion coefficient is shown in comparison. The inset shows the angular distribution of the displacements for the ellipsoid (red) and the sphere (black dashed), additionally the angular distribution is shown if the ellipsoid does not rotate (black). (right) The distribution of diffusivities is shown in a logarithmic plot, the yellow bars are the measured distribution, the black dashed line is the expected distribution of a sphere and the red line is the expected distribution of an ellipsoid.

This work was supported by the DFG (FOR 877).

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Propagation of solid-liquid interfaces under disordered confinements

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Recent progress in the synthesis of nanoporous materials with controlled structural properties made it possible to address various phenomena occurring in mesoscalic systems. Among them, different aspects of fluid phase transitions can now be related to the structural properties of the mesoporous matrices. In this work, we present the results of our experimental studies of crystal growth processes in mesoporous silicon, which was fabricated to have linear, macroscopically long pores. Notably, in an ideal cylindrical pore one expects a reduction of the freezing temperature in proportion to the pore size. In the material under study, however, freezing is found to start already before the transition temperature, determined by the average pore size, is reached. The kinetics of this process is found to be very slow and to depend on the temperature. In particular, power-law dependencies of the ice phase invasion into the pores were observed. These findings we have associated with the fact that the material under study possesses a substantial degree of disorder, namely there exist a distribution of the pore diameters along the pore axis. In light of this, the results obtained have been discussed assuming that the crystal growth processes under such strong confinements is an activated process, requiring overcoming of the pore size-dependent barriers in the free energy, rendering the overall process to occur under the occurrence of the disordered transition rates.

To justify the macroscopic model for the ice invasion kinetics, we have developed a simple lattice-fluid model [2], which is capable to model the freezing and melting processes of fluids confined to pores with arbitrary organizations of their pore spaces. We demonstrate that this microscopic lattice model reproduces quantitatively most experimental observations obtained using porous materials with very different pore geometries. As an important point, this model shows the occurrence of the confinement size- and temperature-dependent ice phase propagation rates. This finding, thus, validates the use of the macroscopic model with distribution of the free energy barriers along the pore axis, which may be considered as a coarse-grained version of the microscopic one. Different regimes of the ice phase propagation, including, in particular, the observation of Sinai-like diffusion, will be discussed [3].

This work was supported by the DFG (FOR 877).

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Water permeation across lipid bilayers studied by pulsed field gradient NMR

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The investigation of the physicochemical properties of lipid membranes is most important for understanding the structure, dynamics and function of biological membranes. One special feature of lipid membranes is the permeability for small molecules and especially for water. So far, this property has been studied for instance by isotope exchange [1], NMR relaxation [2], theoretical approaches [3] and pulsed field gradient (PFG) NMR [4, 5, 6]. The latter technique has benefited from improvements in the preparation of macroscopically oriented lipid bilayers covering glass plates, which results in samples with an anisotropic diffusion coefficient for water and lipids. This anisotropy can be characterized by application of pulsed field gradients in different directions with respect to the bilayer normal.

In this contribution we will examine the permeability of water through model bilayer systems consisting of phospholipids in the L_α phase. First, we will try to reproduce the observations of Filippov and coworkers [5, 6], who determined diffusion coefficients of water parallel to and across oriented lipid bilayers. The application of Tanner's model for diffusion through permeable parallel barriers [7] then allows the calculation of the bilayer permeability. Furthermore, we will investigate the dependency of the permeability on several experimental parameters, e.g. temperature, degree of hydration and cholesterol content.

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IR Micro-imaging of mesoporous silicon as a model system for the investigation of hysteresis phenomena

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Ensembles of molecules confined to mesopore spaces reveal features which may notably deviate from their behavior both in the bulk phase and under dominating host-guest interaction. A previous detailed investigation of molecular dynamics in Vycor porous glass with a pore diameter of 6 nm using pulsed field gradient nuclear magnetic resonance (PFG NMR) indicated that under identical external conditions (temperature, pressure), different "histories" of sample preparation may give rise to dramatic differences in their microdynamics [1–3]. One approach to rationalize the occurrence of history-dependent states in mesoporous host-guest systems is the occurrence of a geometric disorder-induced rugged landscape in the free energy. To get deeper insight into this phenomenon, novel options provided by the development of IR micro-imaging [4] have been used in the present work.

IR micro-imaging is a powerful tool for the investigation of sorption phenomena because it allows obtaining time- and space-resolved images of the concentration of guest molecules within the host material. The possibility of visualizing the variation of probe molecule arrangements at different pressures (see figure 1) is a promising experimental approach for a quantification of hysteresis phenomena and could also be the key for a more detailed insight in their correlation with underlying pore filling mechanisms.

Electrochemically etched mesoporous silicon with a spatially ordered pore system was chosen as host system for this study. The pore system has been designed in a way that 5 nm pores of 55 μm length are continued by channels of about 10 nm pore diameter with a length of 45 μm. The application of focused ion beam milling to a freshly etched porous silicon film enabled the preparation of a silicon sample with the channels open on both sides and aligned perpendicular to the incident IR beam. Before the measurements, the sample was oxidized under oxygen atmosphere to increase its optical transmissibility. Benzene was used as a guest molecule, the experiments were performed at room temperature.

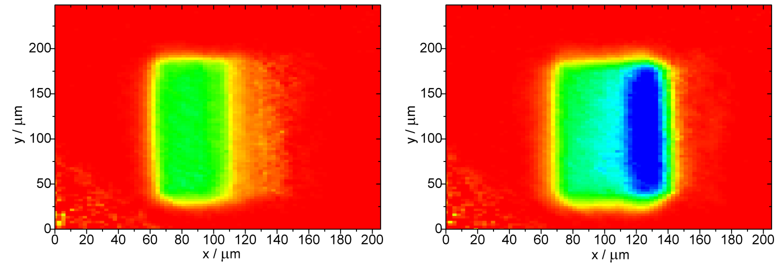

Figure 1: Selected FPA maps of benzene adsorption in a 175 μm × 100 μm × 52 μm piece of mesoporous silicon at a pressure of 75 mbar (left map) and 115 mbar (right map) with the 5 nm pores being arranged on the left half and the 10 nm pores on the right half of the sample. Light color represents low, dark color high benzene concentration.

From the maps recorded with the focal plane array (FPA) detector for pressures from 0 mbar up to saturated vapour pressure of benzene, concentration profiles were obtained (figure 2). Integration gave the respective isotherm with a well-observable hysteresis loop. The kinetics of the concentration equilibration following each pressure step were studied separately using a single element detector (right graph of figure 2). In particular, at the onset of the hysteresis the uptake kinetics were found to be slowed down.

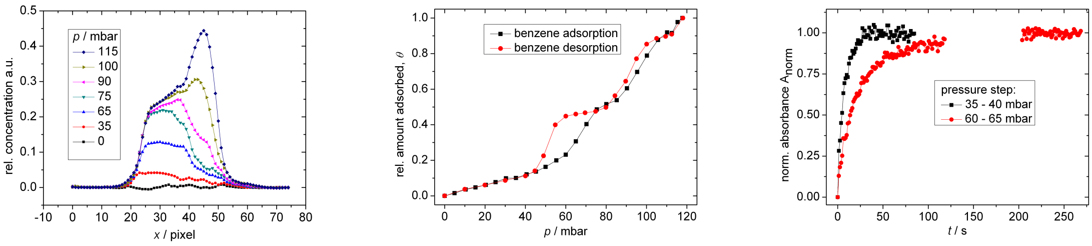

Figure 2: Concentration profiles for benzene adsorption (left graph). Sorption isotherms obtained upon integration of the concentration profiles (middle). Uptake curves showing the slowing down of the system kinetics within the hysteresis region (right graph).

By the development of suitable procedures of sample preparation and activation, we succeeded in using the full potential of IR micro-imaging for the application to mesoporous silicon. By this, the basis for further in-depth studies of a first, simply designed model system for both ad- and desorption of benzene, including FPA maps, concentration profiles, the corresponding isotherm and the uptake curves for each pressure step, was provided.

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Dependence of the relaxation time T_2 on a fluid flow velocity in a porous media

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Permeability is one of the key parameters describing the dynamic behavior of hydrocarbon-bearing reservoirs. Although proper prediction of the dynamic properties of a reservoir requires a detailed three-dimensional distribution of permeability, knowledge of this property along the well trajectory is most valuable also because the near-well bore region controls inflow performance. Permeability κ determines the flow rate caused by a pressure gradient, defined as follows [1]: $\kappa = v\eta/(dp/dx)$, where v is fluid velocity, η is fluid viscosity, and dp/dx is the pressure gradient. Consequently, permeability can only be measured by means of a (dynamic) flow experiment. This is contrary to most other petrophysical properties such as porosity, saturation and lithology, which are static properties. Direct permeability determination requires a flow measurement. The challenge is to design such a methodology of measurement that can be done under normal logging condition. We analyze a possible approach for determining flow permeability using a combined NMR logging measurement in the presence of induced fluid flow.

The NMR relaxation rates are primarily controlled by the thermal motion of the fluid molecules and the collision of the fluid molecules with the internal surface of the pores in the rock. When fluid moves relative to the formation matrix the relaxation rate is augmented by velocity dependent terms. In [2] it was shown that the relaxation rate is proportional to the v^2. However, a more rigorous analysis shows that this condition can be realized at high fluid flow velocities, and at sufficiently low flow velocity the relaxation time will be determined by the equation

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2D}} + \frac{4(\sqrt{2} - 0.5)}{35}\gamma^2 G^2 \sqrt{D} v \tau^{5/2},$$

where first term T_{2B} is the contribution from the fluid bulk relaxation mechanism, the second term $1/T_{2D} = \gamma^2 G^2 \tau^2/12$, reflects the relaxation due to the self-diffusion of a liquid in the presence of a magnetic field gradient, G, where time τ refers to the time delay between the radio frequency pulse and the refocusing RF pulse in the spin echo pulse sequence and γ is the nuclear gyromagnetic ratio. The Fig. 1 shows the show the dependence of average relaxation rate $1/\langle T_2 \rangle$ on the fluid flow velocity. As can be seen from Fig. 1, the relaxation rate in the presented range of velocities of fluid flow is proportional to the flow velocity.

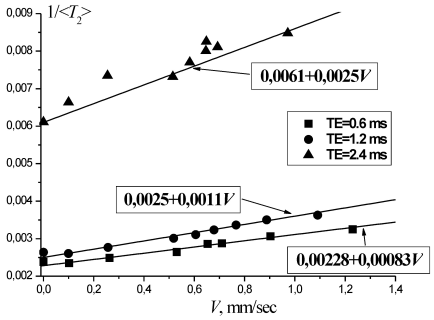

Figure 1: The dependence of the average relaxation rate $1/\langle T_2 \rangle$ on fluid flow velocity (Berea core).

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Diffusion of CO_2 in ion-exchanged zeolites Rho studied by the ZLC technique

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Here we present the use of the ZLC technique to investigate the diffusion of CO_2 in different Ion-exchanged Zeolites Rho samples. The sample were synthesized at the University of St. Andrews and tested at the University of Edinburgh using the ZLC method as part of the Innovative Gas Separations for Carbon Capture (IGSCC) project.

The ZLC technique, first introduced for diffusion measurements in zeolites, has been continuously developed proving its validity in the investigation of the kinetic and equilibrium properties in solid adsorbents. The very small size of the column offers several key advantages compared to other experimental methods: foremost, the small required sample quantity (1–2 mg for kinetic measurements to 10–15 mg for equilibrium measurements) greatly reduces the synthesis costs of the materials and allows rapid testing of prototype materials. The small size of the column reduces the complexity of the analysis methods because heat and external mass transfer resistances are negligible and axial dispersion is maximised achieving a uniform external concentration. The dynamic response of the ZLC can be interpreted easily.

In this study we have extended the use of the ZLC to very slow diffusional time constants by reducing the gas flowrates to less than 3 cc/min. When very slow kinetics are measured it is very difficult to extract the diffusivities from the traditional long time asymptotic analysis. We will show how the combination of the full saturation and partial loading experiment can provide un-ambiguous diffusional time constants. The results for the diffusivity of CO_2 in zeolite Rho samples will be shown to be strongly influenced by the framework structure as well as the nature and the position of the different cations in the framework.

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Diffusion in mesoporous zeolites

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The performance of nanoporous materials during their application in heterogeneous catalysis and mass separation is often controlled by their transport properties. This is especially true concerning microporous host systems such as zeolites. Today, the purposeful synthesis of "hierarchical" nanoporous materials, i.e. materials containing both micro- and mesoporous regions, offers the opportunity of promoting the rate of molecular transport by the presence of mesopores. At the same time, the functionality of the material is preserved owing to the contents of micropores. The incorporation of mesopores into microporous materials, however, does not automatically lead to transport-promoted nanoporous materials. Understanding of this phenomenon is, therefore, of immediate importance, but is still precluded by the lack of systematic experimental studies of transport properties in such hierarchical pore systems. In this contribution, we present the results of pulsed field gradient NMR study of diffusion process in LTA-type zeolites synthesized to include a given amount of mesopores in the range from 0 to 5 volume percents. We discuss different mechanisms determining mass transfer in these materials and make some conclusions on the design of most efficient pore systems.

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Carbon Molecular Sieves – A kinetic study

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Carbon Molecular Sieves (CMS) are unique materials which are widely used in processes based on pressure swing adsorption (PSA) for nitrogen generation by oxygen removal from air [1, 2, 3] and for the enrichment of methane from biogas or landfill gas [4]. Steadily improved CMS were launched in the last years to cover these applications. The recent materials are characterized by higher sorption capacities, compared to conventional CMS. However, in the common applications (e.g. PSA) the kinetic parameters, like kinetic selectivities etc. are the most important properties. Therefore, investigations of sorption kinetics and their temperature dependence are of great interest.

In this study, isotherms and *Uptake*-curves of CO_2, CO, O_2, N_2, H_2, Ar and CH_4 on new CMS were measured at 293 K, 313 K and 333 K. Further, Henry constants were extracted from Tòth parameters. From these constants, thermodynamic selectivities for CMS at zero coverage under equilibrium conditions were estimated and compared.

Different models, a diffusion model and a surface-resistant model were applied to describe the experimental *Uptake*-curves. In addition, kinetic selectivities were calculated from *Uptake*-curves and Henry constants and finally compared to thermodynamic selectivities. This comparison serves as a qualitative assessment for the possibility of gas separation depending on molecular size by the kinetic effect. It can be shown, that the separation performance of CMS will be much better characterized by kinetic selectivities.

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Application of a steady states transport model to condensation of water droplets on a substrate

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Condensation of water droplets on a substrate proves as a good test ground for condensation phenomena in basic stochastic transport processes. The modeled physical situation consists of a substrate at constant temperature exposed to a constant influx of microscopic water droplets from surrounding vapor.

We consider a simple one-dimensional stochastic transport process with constant particle influx. This process can be parameterized so that particles condense to droplets.

The employed transport model consists of a periodic lattice and a gas of indistinguishable particles, so that each site i is occupied by zero or m_i particles. At every time step a random site i is chosen and a particle may leave to an adjacent site with probability proportional to a hopping rate $u(m_i|m_{i-1}, m_{i+1})$. The hopping rate is chosen so that particles tend to condensate by incorporating a zero-range repulsive interaction and surface tension like short-range interaction [1]. The envelope shape of condensates can be tuned to have the same scaling of volume to droplet width as real droplets [2]. Particle influx from environmental vapor is mimicked by adding at random sites randomly with a constant influx rate.

We compare our observations with a recent study of water droplet size distributions obtained in experiment and simulation by Blaschke et al. [3]. In the experiment water vapor condenses on a glass substrate. The simulation mimics experiment by adding a new constant initial volume droplet at some point to the substrate and subsequently merging any overlapping droplets at every time step.

In contrast to the previous simulations [3] our model intrinsically includes diffusion of particles and droplet merging occurs due to movement as well as particle placement in the influx step.

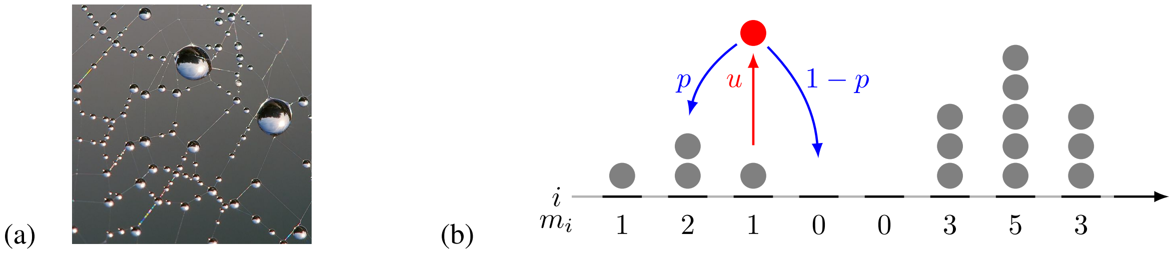

Figure 1: (a) Droplets of various sizes on a cobweb (Image credits: Luc Viatour/lucnix.be) (b) Scheme of the employed particle hopping model. Additional to normal diffusion, the asymmetry parameter p can be used to create directional flow mimicking drift of droplets.

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On the question of subaging in slow non-equilibrium dynamics

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The history of glass formation strongly affects the relaxation dynamics of glassy materials. These dynamics are found to become slower with the "age"of the system, that means with the time t_w expired since the material was brought into the glassy state. Such aging phenomena have been identified in many systems and various dynamical probes.

Relaxation or correlation functions $C(t_w + t, t_w)$ in aging experiment are measured as a function of t after the waiting time t_w has passed. For large t and t_w, they commonly follow a scaling according to $C(t_w + t, t_w) \sim F(t/\tau(t_w))$, where $\tau(t_w)$ increases with t_w as a power law, $\tau(t_w) \sim t_w^\mu$ with $\mu > 0$. In experiments best fits to measured data often yield a subaging behavior with $\mu < 1$, while most theoretical treatments suggest a normal aging with $\mu = 1$ in the asymptotic large time limit. The question hence arises, whether subaging is a transient phenomenon. Indeed, this was suggested in a recent molecular dynamics study of a binary Lennard-Jones glass [1].

Here we reinvestigate subaging in the quenched trap model [2] with respect to the question, whether it can appear as a true scaling behavior. In this model, dynamics of glassy systems are described on a coarse-grained level by thermally activated transitions between traps (inherent states) of a potential energy landscape. The probability $\Pi(t_w + t, t_w)$ of remaining in the same trap in the time interval $[t_w, t_w + t]$ was shown to exhibit a subaging behavior, see Fig. 1.

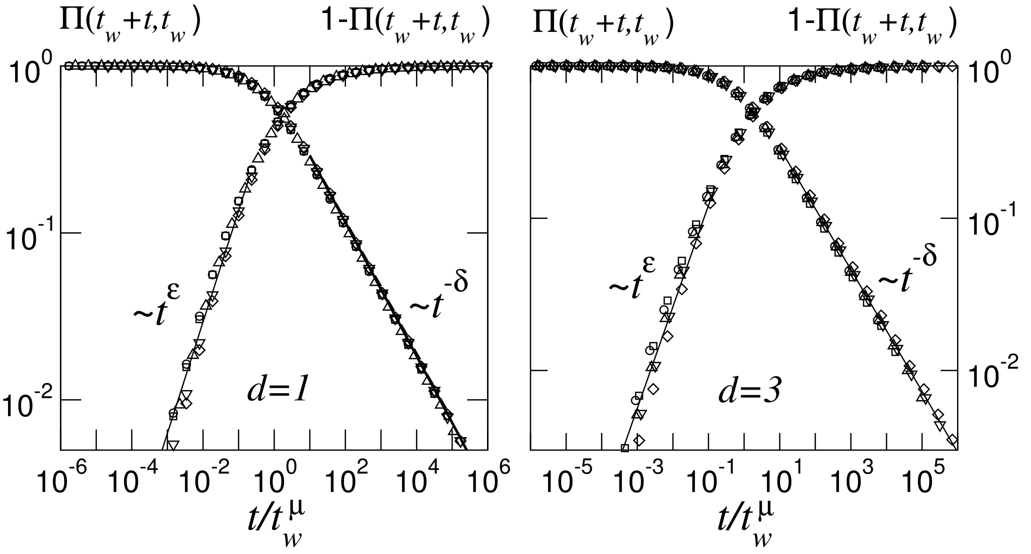

Figure 1: Double-logarithmic plots of $\Pi(t_w + t, t_w)$ and $[1 - \Pi(t_w + t, t_w)]$ as functions of $t\,/\,t_w^\mu$ in dimensions $d = 1$ and $d = 3$. For this example, $\mu = 1/2$ ($d = 1$) and $\mu = 5/8$ ($d = 3$). Different symbols correspond to various waiting times t_w in the range $10^5 - 10^{10}$. The solid lines have slope $\varepsilon = 6/5$ (small t behavior) and slope $-\delta = -2/5$ (large t behavior).

$\Pi(t_w + t, t_w)$, however, is not fully capturing the correlation dynamics. One should better consider the probability $C(t_w + t, t_w)$ that the system is at time $t_w + t$ in the same trap as reached after t_w, irrespective of whether it has left this trap in the time interval $[t_w, t_w + t]$. By performing Monte Carlo simulations we study if $\Pi(t_w + t, t_w) \sim C(t_w + t, t_w)$ for times $t \lesssim t_x$, and if t_x increases with t_w. This would imply that subaging is valid also for $C(t_w + t, t_w)$ for large t, t_w with t/t_w^μ fixed.

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Formation of α-(Ti) phase on grain boundaries in Ti-Co alloys

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One of most important processes in the heat treatment of materials is the decomposition of supersaturated solid solutions. The morphology of decomposition products strongly influences the properties of a material. The heterogeneous nucleation of a new phase in a grain boundary (GB) proceeds easier than the homogeneous one in the supersaturated matrix. In the present study a GB wetting is investigated in polycrystalline alloys of Ti with 2 wt.% and 4 wt.% Co in the temperature range from 680 to 880°C.

The alloys were prepared in the induction furnace in vacuum of approximately 10^{-5} Pa. Pure Ti and Co (both of 3N purity) were used for it. For the experiments, ∅10 mm × 5 mm slices of the alloys were annealed in a vacuum of $4{\cdot}10^{-4}$ Pa at 700°C, 730°C, 760°C and 790°C for 720, 720, 816 and 864 hours, respectively. Thereafter, the samples were quenched in water.

Composition of phases in the microstructure of obtained samples was investigated using scanning electron microscope equipped by the LINK energy-dispersive spectrometer. Morphology of the microstructures was analyzed by a light microscopy. It has been found that the solid α-(Ti) phase forms a chain of lenticels-shaped inclusions or continuous homogeneous layer in GBs of β-(Ti, Co) matrix, see Fig. 1(left). A quantitative analysis of the wetting transition in the polycrystalline samples was performed adopting the following criterion: every GB was considered to be wetted only when a solid layer had covered the whole GB. Accordingly, the percentage of wetted GBs was determined. At least 100 GBs of each sample were analyzed. The results are presented in Fig. 1 (right).

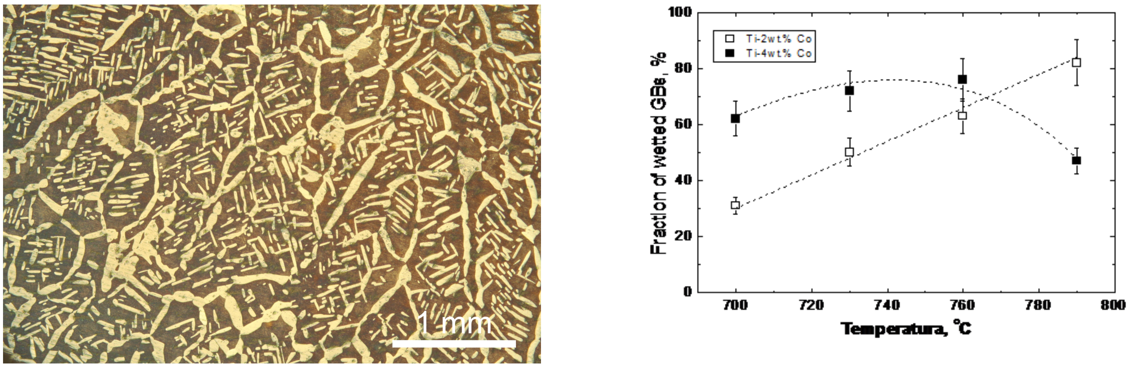

Figure 1: (left) The microstructure of Ti–4 wt.% Co alloy annealed at 760°C, 816 h. The α-Ti phase appears light, the β-(Ti, Co) phase appears dark. (right) Temperature dependence of the fraction ofr completely wetted GBs for alloys: Ti-2wt.% Co and Ti-4wt.% Co.

One can observe that the fraction of completely wetted GBs increases with an annealing temperature for Ti-2wt.% Co alloy. Whereas, this fraction for Ti-4wt.% Co alloy increases until the *solvus* line is approached, and then decreases.

Formation of the chains of single inclusions can be related to the low-energy GBs, where slower diffusion kinetics, smaller density and average size of inclusions, and, then, their slower growth velocity, are expected. In this way, formation of the continuous homogeneous GB layer is associated with high-energy GBs.

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MD simulations of $1,4$ - polybutadiene at graphite surfaces

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Polymer dynamics in confinement is both of fundamental interest concerning our understanding of the glass transition, as well as of high technological importance for the performance of composite materials. The results here presented are concerned with atomistic MD simulations of a chemically realistic model of a 1,4-polybutadiene melt (55% trans and 45% cis content) confined between two walls of graphite. The focus of our study is to investigate the effects of confinement on the chain dynamics in the melt and to reveal to what extent the walls are influencing structure and dynamics of the melt. As an example, Fig. 1 depicts the conformation that a chain adopts at an interface by forming trains, loops and tails. It is evident that the chain dynamics of an adsorbed chain may be strongly constrained in comparison to a chain which is not adsorbed at an interface.

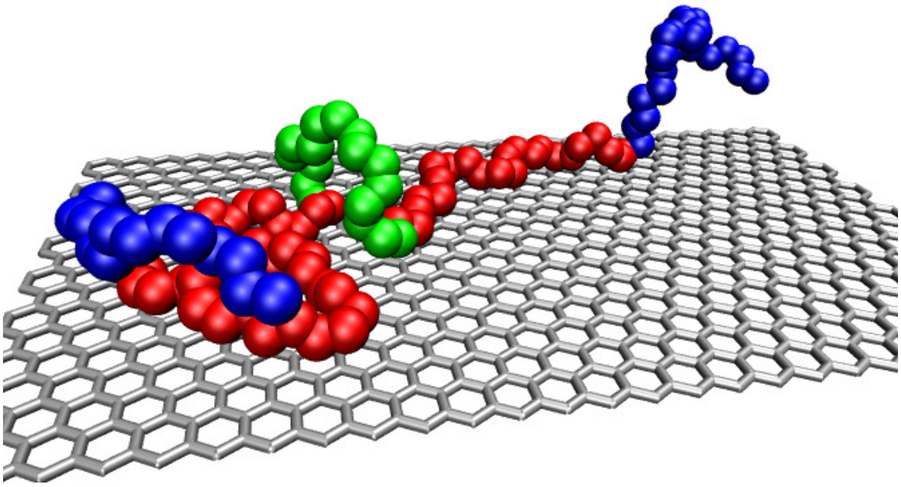

Figure 1: The conformation that a chain may adopt at an interface by forming trains (red beads), loops (green beads) and tails (blue beads). The snapshot was taken at $T = 353$ K ($\approx 2T_g$). The grey lattice represents the crystalline graphite interface

The physical properties here investigated are density profiles, the incoherent scattering function and collective dielectric relaxation. The results presented are key to a better understanding of the glass transition process in a confined polymer system.

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Studies of atomic scale diffusion by X-ray photon correlation spectroscopy

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Although Quasielastic Neutron Scattering (QNS) has proven successful in investigating diffusive dynamics at the atomic level in solid state physics, the limits for the diffusion coefficient are relatively low. Therefore QNS is in general limited to measurements in the vicinity of the melting transition. Also, because of the specific scattering cross section of neutrons, it favors selected atoms like hydrogen or lithium. The goal of our studies in the last years was to overcome these limitations by using a new method to study atomic motion at the fundamental level. This method should ideally work in a broad spectrum of solids and enlarge the accessible range of temperatures.

Our group managed to develop the relatively new technique of X-ray photon correlation to work on the atomic scale. This technique operates in the time regime rather than in the energy regime and measures chemical fluctuations instead of self diffusion. Atomic scale X-ray photon correlation spectroscopy (aXPCS) is therefore not subject to the limitations mentioned above. The time resolution towards faster dynamics is only limited by the readout time of the detector and intensity of the X-ray beam. Towards slower dynamics it is limited by the stability and the duration of the experiment. Even though at the moment a high contrast in the scattering length of the system under investigation is required due to today's technical limitations at synchrotron sources, there is practically no restriction to certain elements for this technique. aXPCS therefore allows to investigate atomic scale diffusion in the temperature range of intermetallic phases or to study dynamics of glasses well below glass transition temperatures.

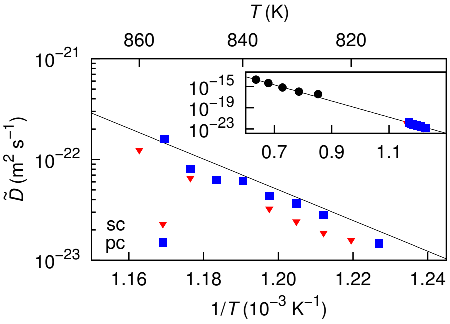

Figure 1: Diffusivities of Ni-Pt solid solution measured with aXPCS at the ESRF for single crystal (sc) and polycrystalline sample (pc) compared with tracer data (circles) [3]. (This data was published in [2].)

The first successful aXPCS experiment was carried out only a few years ago by our group [1]. This poster will give an overview of an experimental setup and show what we have been able to experimentally achieve since then. The systems presented will be a Ni-Pt solid solution with jump frequencies in the order of $\tau^{-1} \sim 10^{-3}$ s^{-1} (see Figure 1) [2] and an Fe-Al intermetallic alloy.

This work was supported by the Austrian Science Fund (FWF): P22402.

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Guest molecule diffusion and conformation influenced by local liquid crystal structure

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Optical single molecule investigations are superior to ensemble methods in revealing local structure and dynamics of thin soft matter films. Here we use tailored perylene diimide (PDI) molecules to probe the diffusion of guest molecules in 50 to 200 nm thick films of the liquid crystal 4-n-octyl-4'-cyanobiphenyl (8CB) on silicon with either thin native or 100 nm thick thermal oxide. These PDI molecules are shown to orient with the local liquid crystal director and thus follow the liquid crystal structure [1, 2].

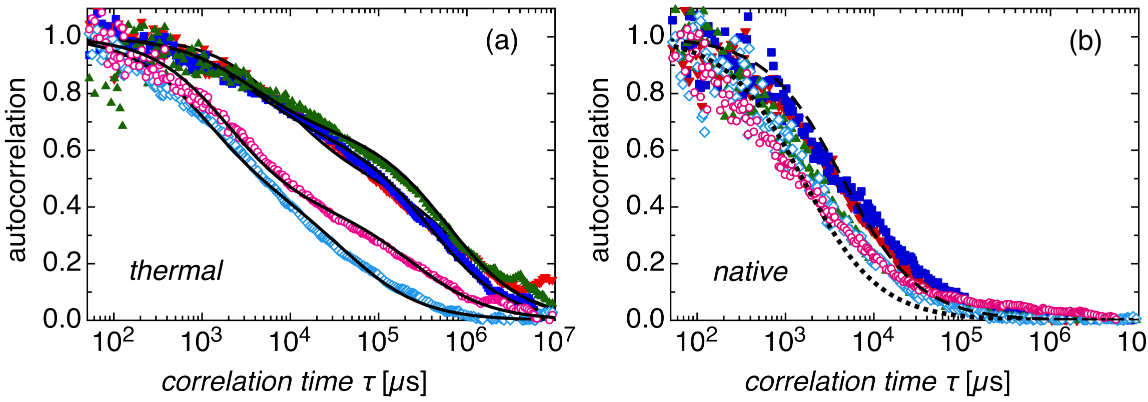

Figure 1: Normalized FCS curves of PDI in 200 nm thick 8CB films on (a) 100 nm thermal and (b) native oxide at (▲) 23°C, (■) 25°C, (▼) 28°C, (◇) 31°C, and (○) 34°C with (a, solid line) two component fits, and (b) one component fit (dashed) for 25°C and (dotted) for 34°C.

Figure 1 shows normalized FCS curves obtained from PDI in 200 nm thick 8CB films at the smectic-nematic phase transition (the bulk transition temperature T_{SN} = 33.5°C). For the film on thermal oxide (a), the correlation curves contain more than one component of diffusion. Fitting improves, when a two component function for lateral diffusion is used (solid lines). Thereby the slow component combines slowed guest molecule diffusion in the interface region with ad-/desorption events. For 31°C (◇) both components are about one order of magnitude faster in respect to the lower temperatures (filled symbols). At about bulk T_{SN}, at 34°C the obtained FCS curves vary for different positions on the sample (not shown) and tend to yield slower diffusion again (○). The latter can be ascribed to formation of LC domains with different structures [2].

The FCS curves obtained from the 200 nm 8CB film on native oxide do not show the slow component of diffusion from the interface region. In this case, fluorescence correlations spectroscopy (FCS) yields only information about the upper film region, exceeding ≈ 30 nm distance to the substrate, because of non-radiative de-excitation of PDI in proximity to the substrate. Nevertheless, also for native oxide, the FCS curves show deviations from fits with single component correlation functions for 2-dimensional diffusion (see dashed line for 25°C). The deviations increase with increasing temperature (see dotted line for 34°C). This can be ascribed to increasing vertical diffusion causing additional fluorescence fluctuations, which modulate the correlation function.

Thin 8CB films are known to show structure undulations at the nematic-isotropic phase transition [3] and so called focal conic domains in the smectic A phase when cooled from the nematic phase [2]. Figure 2a shows images in reflected light from 200 nm thick 8CB films on (top) 100 nm thermal and (bottom) 2 nm native oxide at 28°C, 31°C, and 34°C. During this approach of the smectic to nematic phase transition, the film on thermal oxide shows small sized structures already at 31°C (middle). At

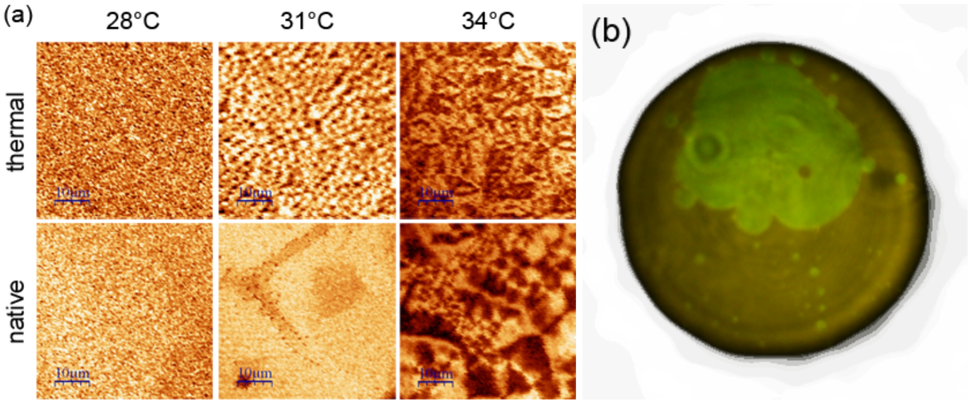

Figure 2: (a) 200 nm thick 8CB films on (top) 100 nm thermal and (bottom) native oxide at the smectic-nematic phase transition shown in reflected light. (b) Fluorescence image of MEH-PPV embedded in 8CB showing regions with different emission spectra.

this temperature, larger sized structures start to appear on native oxide. At 34°C (right) the film on native oxide still shows larger sized and less regular structures compared to the film on thermal oxide, which can be interpreted as slower phase transition dynamics on native oxide. This points to an influence of long range van der Waals interaction on self-diffusion [4]. Further information on local dynamics is expected from extended FCS studies during phase transition.

Due to their relevance for technical applications, conjugated polymers are promising materials for further guest molecule studies. Preliminary investigations show an influence of the liquid crystal structure on the emission spectra and thus the conformational order [5] of the conjugated polymer poly(2-methoxy-5-(2'-ethyl-hexoxy)-1,4-phenylene) (MEH-PPV) embedded in 8CB, see Figure 2b.

This work was supported by the DFG (FOR 877).

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Kinetic peculiarities of two-component diffusion saturation of titanium under rarefied nitrogen-oxygen-containing medium

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Previously, it was investigated the kinetics of single-component diffusion saturation of titanium by the interstitial elements (nitrogen or oxygen) [1]. It is clear that diffusion saturation of the materials by two and more components allows to change the properties of surface layers more considerably compared with single-component saturation. But it requires the theoretical knowledge about the kinetics of formation of diffusion zone, its composition and distribution of the elements. The aim of this work is to investigate analytically the peculiarities of simultaneous two-component (nitrogen and oxygen) diffusion saturation of titanium under rarefied controlled gaseous medium.

Kinetics of the compatible diffusion of nitrogen and oxygen in titanium is complicated and many-sided. The two-component (nitrogen and oxygen) diffusion saturation of titanium under rarefied controlled gaseous medium ($P_N \gg P_{O2}$) will be considered. Will be accepted that nitrogen $\mu_1^G(P_N)$ and oxygen $\mu_2^G(P_{O2})$ potentials in gaseous medium (Fig. 1) such that concentrations of nitrogen C_1^S and oxygen C_2^S on the titanium surface equilibrium with the medium do not exceed their maximum solubilities, according to the phase diagrams. For T=800 °C they are 16 at.% and 33 at.%, respectively [2].

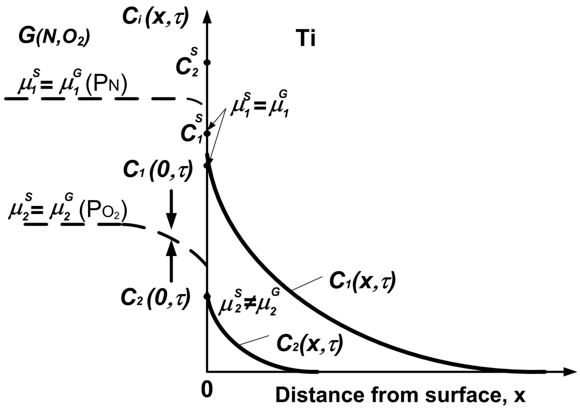

Figure 1: Scheme of mass transfer in system Ti-G(N, O_2)

It should be noted that very often in the case of two-component diffusion the influence of one component is more significant than the other component. It will be accepted that oxygen (component 2) diffuses independently, while it affects the chemical potential ($\mu_1(x,\tau) = d_{11}C_1(x,\tau) + d_{12}C_2(x,\tau)$, $\mu_2(x,\tau) = d_{22}C_2(x,\tau)$) and diffusion ability ($D_{12} = d_{12}L_{11}$, $D_{21} = 0$, L_{11} – Onsager kinetic coefficient) of nitrogen (component 1). We have a system of the differential equations for description of the diffusion of these components:

$$D_{11}\frac{\partial^2 C_1(x,\tau)}{\partial x^2} + D_{12}\frac{\partial^2 C_2(x,\tau)}{\partial x^2} = \frac{\partial C_1(x,\tau)}{\partial \tau}, \quad D_{22}\frac{\partial^2 C_2(x,\tau)}{\partial x^2} = \frac{\partial C_2(x,\tau)}{\partial \tau}. \tag{3}$$

Since the aim of diffusion treatment of titanium is strengthening of its near-surface layers, then the half-space has been chosen as the object of investigation. The following boundary ($x = 0, x = \infty$) and initial ($\tau = 0$) conditions will be set for solution of a system of the differential equations:

$$C_1(0,\tau) + \lambda_{12}C_2(0,\tau) = C_1^S = \text{const}, \quad -D_{22}\frac{\partial C_2(x,\tau)}{\partial x}\bigg|_{x=0} = H\left[C_2^S - C_2(0,\tau)\right], \tag{4}$$

$$C_1(x,0) = C_2(x,0) = 0; \quad C_1(\infty,\tau) = C_2(\infty,\tau) = 0, \quad \text{where } C_1^S = \mu_1^G/d_{11},\ C_2^S = \mu_2^G/d_{22}.$$

The condition of ideal contact ($\mu_1^G = \mu_1^S$) on the surface was be set in the boundary condition (2) for nitrogen. Surface concentration $C_2(0,\tau)$ for oxygen was proposed to consider as a function of time. It is taken into account by mass transfer coefficient H. The solution of the system of equations (1) with the boundary conditions (2) is following:

$$C_1(x,\tau) = C_1^S - C_2^S[(\lambda_{12}+\alpha_{12})f_1(x,\tau) - \alpha_{12}f_2(x,\tau)],\quad C_2(x,\tau) = C_2^S f_2(x,\tau), \tag{5}$$

here $f_1(x,\tau) = \operatorname{erfc}\left[\frac{x}{2\sqrt{D_{11}\tau}}\right] - \exp\left[\frac{H}{\sqrt{D_{11}D_{22}}}x + \frac{H^2\tau}{D_{22}}\right]\cdot\operatorname{erfc}\left[\frac{H\sqrt{\tau}}{\sqrt{D_{22}}} + \frac{x}{2\sqrt{D_{11}\tau}}\right],$

$$f_2(x,\tau) = \operatorname{erfc}\left[\frac{x}{2\sqrt{D_{22}\tau}}\right] - \exp\left[\frac{Hx}{D_{22}} + \frac{H^2\tau}{D_{22}}\right]\cdot\operatorname{erfc}\left[\frac{H\sqrt{\tau}}{\sqrt{D_{22}}} + \frac{x}{2\sqrt{D_{22}\tau}}\right],\quad \alpha_{12} = \frac{D_{12}}{D_{22}-D_{11}}.$$

In particular, the time dependences of surface concentrations of components are following:

$$C_1(0,\tau) = C_1^S - C_2^S\lambda_{12}f(0,\tau),\; C_2(0,\tau) = C_2^S f(0,\tau),\; \text{where } f(0,\tau) = 1-\exp\left[H^2\tau/D_{22}\right]\cdot\operatorname{erfc}\left[H\sqrt{\tau/D_{22}}\right]. \tag{6}$$

On the basis of obtained solutions (3), (4), the time dependences of surface concentrations of nitrogen and oxygen in titanium (Fig. 2a) and their spatial distributions in the diffusion zone (Fig. 2b) after saturation at $T = 800°C$ for 3h were calculated. The curves were plotted according to the following parameters: $D_{11} = 1.2\cdot10^{-2}\cdot\exp(-45250/RT)$ cm^2/s, $D_{12} = \lambda_{12}D_{11}$, $D_{22} = 0.8\cdot\exp(-48000/RT)$ cm^2/s, $C_1^S = 16$ *at. %*, $C_2^S = 33$ *at. %* [2], $H = 5\cdot10^{-7}$ cm/s, $\lambda_{12} = 0.5$.

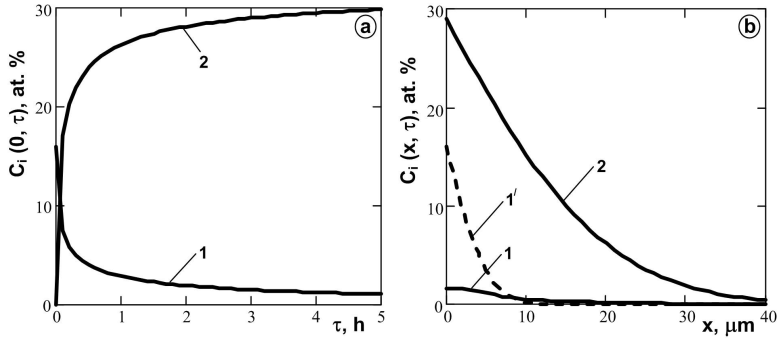

Figure 2: Time dependence of surface concentration of nitrogen and oxygen (a) and their spatial distributions in titanium after saturation at $T = 800°C$ for 3h. For nitrogen: curves 1 are for $\lambda_{12} = 0.5$, curve 1’ is for $\lambda_{12} = 0$; for oxygen: curves 2

Surface concentrations of oxygen and nitrogen depend on the saturation duration (Fig. 2a). The surface oxygen concentration (curve 2) increases gradually to equilibrium value with the medium because of slow oxygen delivery to titanium surface. The surface nitrogen concentration (curve 1), despite on the constant chemical potential on the surface, decreases with increase of exposure because of the increase of surface oxygen concentration. The diffusion zone with nonuniform distribution of oxygen and, especially nitrogen is formed in the near-surface layer of titanium as a result of gasing (Fig. 2b). The depth of the diffusion zone is determined by the distribution of oxygen concentration (curve 2), because the oxygen diffusion coefficient is two orders of magnitude larger than nitrogen diffusion coefficient. Distribution of nitrogen taking into account the influence of oxygen (curve 1) and without such consideration (curve 1’) is different substantially. Nitrogen is pushed from titanium surface into the more distant zone because of the influence of diffusion dissolved oxygen. Under the certain time and temperature parameters the nitrogen distribution (curve 1) is nonmonotonic, its maximum concentration is not fixed on the titanium surface, but in the more distant zone from surface. Such character of nitrogen distribution is agreed with the experimental data [3].

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A combined sparse sampling of time-gradient domain for NMR diffusometry and relaxometry

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Multidimensional NMR spectra can provide an information on structures of large molecules or complex chemical mixtures. However, because of time-consuming sampling of a multidimensional signal, they require days-long data collection process. This problem has been to some extent circumvented by an application of various sparse sampling techniques. Nevertheless, they were limited to time dimensions of NMR spectra. In this work, we show how to extend sparse sampling to gradient dimensions. The procedure is based on a minimum ℓ_1-norm restrained optimization using Fourier and inverted Laplace transforms. We demonstrate the performance of the algorithm on simulated and experimental data.

Diffusion in $Li_xNa_{2-x}Ti_6O_{13}$ investigated with impedance spectroscopy

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Within the system Li_2O–TiO_2, lithium hexatitanate $Li_2Ti_6O_{13}$ (*i.e.* $Li_2O \cdot 6\ TiO_2$) was already studied before by electrochemical methods with respect to its application as a potential Li-ion battery anode material [1, 2]. This compound is also attractive for fundamental cation diffusion studies, in particular due to its channel structure and the fact that Li and Na are interchangeable. The present work examines the effect of different Li : Na ratios in $Li_xNa_{2-x}Ti_6O_{13}$ on diffusion using impedance spectroscopy which measures the conductivity over a wide frequency range and thus on different length scales. This also enables the comparison with NMR results obtained by us in a separate study. Additionally, the Hebb–Wagner polarization (DC polarization) method is being used here to discriminate between the cation and a partial electronic conductivity [3].

$Li_xNa_{2-x}Ti_6O_{13}$ with $x = 0$, 0.33, 1 and 2 has been prepared via solid-state synthesis starting from $NaCO_3$ and TiO_2 to obtain phase pure $Na_2Ti_6O_{13}$. To remove sodium from the structure, an ion-exchange reaction using molten $LiNO_3$ is used [1, 2]. Depending on the reaction time, different Li : Na ratios are achieved up to the fully exchanged $Li_2Ti_6O_{13}$. Structure and phase confirmation is obtained via X-ray powder diffraction (XRPD) and inductively coupled plasma optical emission spectroscopy (ICP-OES). $Na_2Ti_6O_{13}$ (space group C2/*m*) is a channel-structured material with two Na positions per unit cell supposed to be solely located within a channel. The lattice parameters vary little during substitution of Na with Li, only leading to a change from an eight-fold (Na ion) to a four-fold (Li ion) position within a cubic cell of eight oxygen atoms [2].

The impedance data of $Li_xNa_{2-x}Ti_6O_{13}$ for the different compositions x and temperatures in the range $T = 253\ldots413$ K are analyzed in various basically equivalent representations (*e.g.* [4]). AC impedance plots $-Z''(\omega)$ vs. $Z'(\omega)$ show essentially single semicircular arc behavior. However, the complex modulus representation $M(\omega) = M' + iM''$ reveals a somewhat more involved electrical response. Depending on the Li : Na ratio, the $M''(\omega)$ spectra show a single peak for $Na_2Ti_6O_{13}$ and a continuous change to two peaks for $Li_2Ti_6O_{13}$. Plotting the real part of the conductivity σ' vs. $\omega/2\pi$ (10^{-1} to 10^7 Hz) yields in each case a plateau in the low frequency region (10^{-1} Hz to 10^2 Hz) representing the dc conductivity. It shows Arrhenius behavior with activation energies of 0.8 to 0.9 eV, roughly independent of x. It has to be noted that these results may be influenced by a contribution from electronic conductivity. This can be separated by DC polarization measurements being presently performed in our laboratory in the same temperature range as the impedance spectroscopy measurements. First results confirm that $Li_xNa_{2-x}Ti_6O_{13}$, besides being a mixed cationic, is also a mixed electronic/ionic conductor whose ionic transference number significantly depends on x.

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^{7}Li ion diffusion in isotope-diluted glassy $Li_2Si_3O_7$ — The generation of pure spin-3/2 spin-alignment NMR echoes

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Solid-state diffusion plays one of the most important roles in materials science. In particular, the precise measurement of ion dynamics in materials with structural disorder is of great interest. Spin-alignment echo (SAE) nuclear magnetic resonance (NMR), being comparable to exchange spectroscopy, turned out to be a powerful method to probe (ultra-)slow Li dynamics even in amorphous materials [1, 2]. However, ^{7}Li Jeener-Broekaert echoes can be influenced by the simultaneous generation of dipolar with quadrupolar order. In many cases, the first can be suppressed by choosing proper evolution times t_p of less than 20 μs [3].

Here, glassy $Li_2Si_3O_7$ served as a suitable model system to study the positive influence of isotope dilution on ^{7}Li SAE NMR, *i.e.*, the reduction of homonuclear dipole-dipole interactions through spatial separation of the spin-3/2 probe nuclei. Two samples, one with 100% ^{7}Li and the other one with 5% ^{7}Li (95% ^{7}Li), were investigated by ^{7}Li NMR line-shape analysis, spin-lattice relaxation NMR as well as mixing-time and preparation-time dependent ^{7}Li SAE NMR using a 32-fold phase cycle. Jeener-Broekaert echoes and their Fourier transforms show that at sufficiently short t_p the interfering dipolar interactions can be completely suppressed in that sample for which the proportion of ^{7}Li was greatly reduced by substitution with ^{6}Li. The so-obtained diffusion parameters are compared with results deduced from broadband conductivity spectroscopy.

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Condensation of a lattice gas in three dimensions

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We investigate the condensation transition of a lattice gas model [1, 2, 3]. This simplified model is restricted to nearest-neighbor interaction. For fixed density it is equivalent to the Ising model at fixed magnetization. In order to investigate the temperature dependence, we apply a novel parallel multicanonical method [4]. By this means, the diffusion properties of the particles can be adjusted in such a way that free-energy barriers can be circumvented. Keeping the density fixed, the condensation transition is studied as a function of system size. Our results may further be compared to an analytic prediction of equilibrium droplet formation [1]. To this end, we choose a fixed temperature and compare the average largest droplet to a rescaled density. Above a critical density, a single droplet is observed that includes more than half of the particle excess, consistent with theory.

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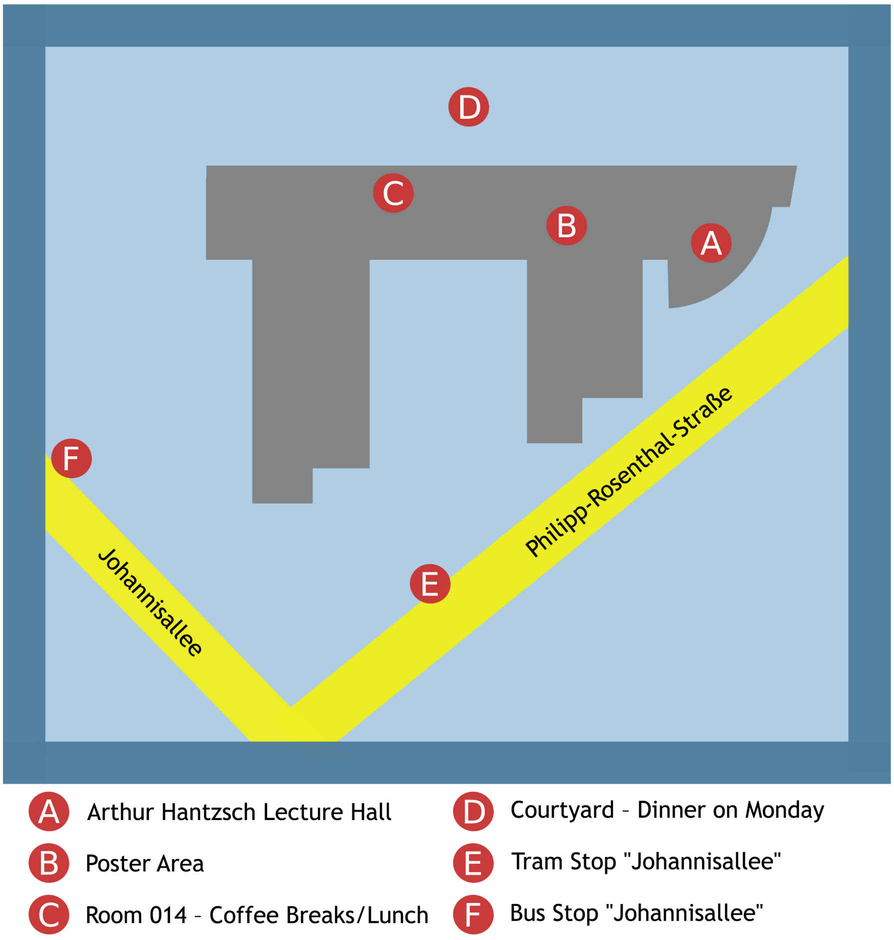
Conference Site

The conference takes place at

Universität Leipzig
Faculty of Chemistry and Mineralogy
Johannisallee 29
04103 Leipzig
Germany

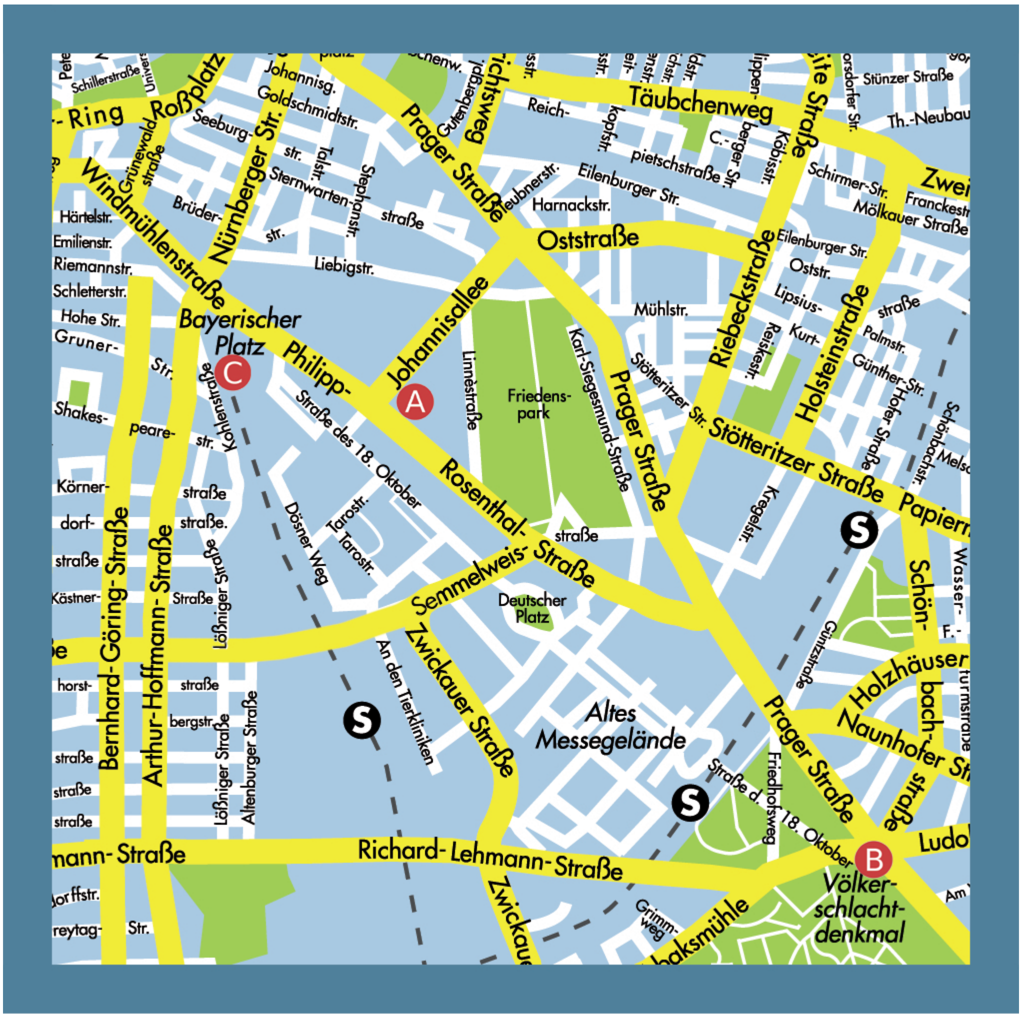
All talks take place in the Arthur Hantzsch Lecture Hall on the ground floor.
The poster sessions take place in the foyer.



All coffee breaks and lunch take place in room 014, the dinner on Monday in the courtyard of the building, and the dinner on Wednesday at the restaurant **Bayerischer Bahnhof**.

The conference is accompanied by an excursion including a trip to the **Monument to the Battle of the Nations**, a concert at the **Alte Handelsbörse** and a guided city tour. It ends with the Conference Dinner at the **Ratskeller Leipzig**.

Map of the Conference Site and Surrounding Area



Ⓐ Conference Site, Johannisallee 29

Ⓑ Monument to the Battle of the Nations

Ⓒ Bayerischer Bahnhof, Bayrischer Platz 1

Monument to the Battle of the Nations
One part of the excursion is the visit of the Monument to the Battle of the Nations, which was built to commemorate Napoleon’s defeat to the allied armies at the Battle of Nations near Leipzig in 1813. The monument is 91 meters high and has over 500 steps to the viewing platform at the top.

Bayerischer Bahnhof
The dinner on Wednesday takes place at the restaurant and brewery Bayerischer Bahnhof. Built in 1842, it is the world’s oldest and still existing head rail station and once was a central place of trade in the region.

Map of the City Center of Leipzig

Ⓐ Alte Handelsbörse, Naschmarkt 1

Ⓑ Ratskeller Leipzig, Lotterstraße 1

Alte Handelsbörse
The excursion includes a concert at the Alte Handelsbörse. It was built from 1678–1687 and is Leipzig's oldest assembly hall of the merchants and one of its oldest baroque buildings. It was burnt-out completely in 1943 and rebuilt from 1955–1962.

Ratskeller Leipzig
The Conference Dinner on Tuesday takes place at the Ratskeller Leipzig. During the dinner, the participants can climb up to the tower of the New City Hall, the highest city hall tower in Germany (114 m).

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