Lévy walks of strong adsorbates on surfaces: Computer simulation and spin-lattice relaxation

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Using a Monte Carlo method, the time dependence of the mean-squared displacements along planar and spherical liquid-solid interfaces and the displacement distribution were simulated for a random walker. In the strong-adsorption–short-displacement limit, the Cauchy propagator typical for Lévy walks was verified. It is shown that the displacements effectively taking place along surfaces follow a superdiffusive time dependence of the mean square. Surface diffusion is the crucial process of the ''reorientations mediated by translational displacements'' mechanism of spin-lattice relaxation. This is demonstrated by considering a strongly adsorbed molecule population on spherical surfaces or on planar surface patches representing a certain finite orientation correlation length. The conclusion is that Lévy walks on curved surfaces account for the experimental findings obtained with field-cycling NMR relaxometry, whereas strongly adsorbed molecules escaping to the bulk liquid play a minor role. [S1063-651X(97)00310-3]

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I. INTRODUCTION

Depending on the adsorbate-surface interactions, the adsorption of fluids may be classified as ''strong'' or ''weak.'' The strong-adsorption limit is of particular interest because in this case diffusion effectively taking place along solid surfaces was predicted to be anomalous [1–3]. In these papers, it was shown that bulk-mediated surface diffusion (BMSD) can be described in the form of Lévy walks that are characterized per definition by a Cauchy propagator [4].

The two adsorption limits may be expressed in terms of the desorption rate Q and the retention time $t_h \equiv h^2/D_0$ of the adsorbed molecules. The former depends on the interactions of the adsorbate molecules with the surface, the latter on the adsorption depth h and the bulk diffusion coefficient D_0 of the adsorbate. Strong and weak adsorption are defined by the limits $Qt_h \gg 1$ and $Qt_h \ll 1$, respectively. In the strong-adsorption limit, the displacements s occurring along planar surfaces were shown to be governed by propagators of the form

$$P(s,t) = \frac{1}{2\pi} \frac{ct}{[(ct)^2 + s^2]^{3/2}} \quad (s \ll \sqrt{D_0 t}), \quad (1)$$

$$P(s,t) \approx \left(\frac{t}{t_h}\right)^{1/2} \left(\frac{D_0 t}{s^2}\right)^2 \frac{\exp\{-s^2/(4D_0 t)\}}{D_0 t} \quad (s \gg \sqrt{D_0 t}). \quad (2)$$

Equation (1), valid for surface displacements short compared to the rms value in the bulk, is the well-known Cauchy distribution for two dimensions. In this case, the surface displacements are characterized by the speed $c = D_0/h = \sqrt{D_0/t_h}$. That is, a superdiffusive behavior of the mean surface displacement is expected.

The ''Lévy dust'' produced by the BMSD process on the surface in the short-displacement limit can be probed by field-cycling NMR relaxometry [5], as demonstrated in [6–8]. The proton or deuteron spin-lattice relaxation dispersion of polar liquids filled into porous glasses, for instance, was studied. The relaxation mechanism is reorientations mediated by translational displacements (RMTDs) [9]. Strongly adsorbed molecules tend to be oriented in a preferential direction relative to the surface. Any displacement mechanism shifting the adsorbate molecules to another surface site with a different preferential orientation direction thus reorients the molecules under investigation.

Note that the time scale of reorientation is determined not only by the propagator effective for displacements along the surface but also by the surface topology. In the strong-adsorption and short-displacement limit, the two-dimensional Cauchy propagator given in Eq. (1) is appropriate provided that the surface topology does not strongly influence the BMSD mechanism. In this approach the surface topology merely enters via a surface correlation function [7], which may be represented by a distribution of planar patches of different correlation lengths [8]. Finally, it should be mentioned that molecules that initially are adsorbed but escape to the bulk in the time interval under consideration are not subject to the Cauchy propagator and are reoriented at random as long as they are not readsorbed.

The purpose of the Monte Carlo simulation to be presented in the following first is to verify and to quantitatively characterize the surface diffusion limits mentioned above. Second, the influence of the surface topology is to be taken into account for the simple case of spherical pore surfaces instead of planar interfaces assumed by Bychuk and O'Shaughnessy [1–3]. The third point of interest is to figure out the contributions to spin-lattice relaxation of readsorbed particles and particles that have escaped to the bulk at the end of the probe time interval.

II. MONTE CARLO SIMULATION METHOD

Random walkers in the vicinity of planar or concave spherical walls with different adsorption properties were

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simulated using random numbers obtained with the aid of two independent random-number generators. One of these was used to randomly select a random number of a series generated by the second. In order to save computer time, the simulations of the mean-squared displacements and of the surface propagators were carried out only for one surface dimension, keeping in mind that diffusion on the second surface dimension is independent and leads to equivalent simulation results. By contrast, the NMR correlation function had to be simulated by taking all spatial degrees of freedom into account. For the sake of comprehension the formalism and discussion in the following refer to this latter (more general) case.

The particles performing the random walks are assumed to start at the initial position $r(x_0, y_0, z_0)$ on the surface. The displacement steps of a fixed length l occur with the cycle time τ in random directions characterized by the polar and azimuthal angles θ, ϕ relative to an external reference direction.

In each cycle time, the polar and azimuthal angles are chosen in $-1 \leq \cos\theta \leq 1$ and $0 \leq \phi \leq 2\pi$ at random [10]. Thus the position of a certain random walker after the ith step is in orthogonal Cartesian coordinates $x_i = x_{i-1} + l\cos\phi\sin\theta$, $y_i = y_{i-1} + l\sin\phi\sin\theta$, and $z_i = z_{i-1} + l\cos\theta$. An ensemble of $N = 5 \times 10^5$ independent particles was considered, permitting us to evaluate the mean-squared displacement after i displacement steps

$$\langle r^2(t_i) \rangle = \langle (x_i - x_0)^2 + (y_i - y_0)^2 + (z_i - z_0)^2 \rangle, \qquad (3)$$

where $t_i = i\tau$. In the case of unrestricted diffusion, we thus reproduce the Einstein relation $\langle r^2(t_i) \rangle = 6D_0 t_i$ with the self-diffusion coefficient $D_0 = l^2/6\tau$.

As shapes of the interfaces by which diffusion is restricted and at which adsorption takes place we have considered first an ''infinite'' plane and second the inner surface of a spherical pore of radius R. If a particle enters a surface layer of thickness b, it is assumed to be adsorbed with a probability per unit time Q_{ads} during the next cycle period. On the other hand, if the particle is already adsorbed, it is assumed to be desorbed with the probability per time unit Q during the next cycle period.

Desorption means that the distance of the particle from the interface is increased to $b + \epsilon$, where $\epsilon \ll l$. From this position the particle can jump with equal probabilities back to the surface layer or to the free space. In the simulations the step length l and the surface layer thickness b were equated for simplicity, i.e., $l = b$.

The simulation concerns particles that are initially adsorbed or are within the surface layer of thickness b. The effective mean-squared displacement along the surface $\langle s^2(t) \rangle$ was evaluated as a function of time. That is, the ensemble average merely takes into account particles that are still or again on the surface after the time t.

III. RESULTS

Without absorption, that is, $Q_{ads} = 0$, $Q = \tau^{-1}$, surface diffusion obeys the law for ordinary two-dimensional displacements $\langle s^2 \rangle = 4D_0 t$. This behavior is still approached for rates $Q_{ads} = 0.1\tau^{-1}$, $Q = 0.9\tau^{-1}$ (see Fig. 1). In this case, the
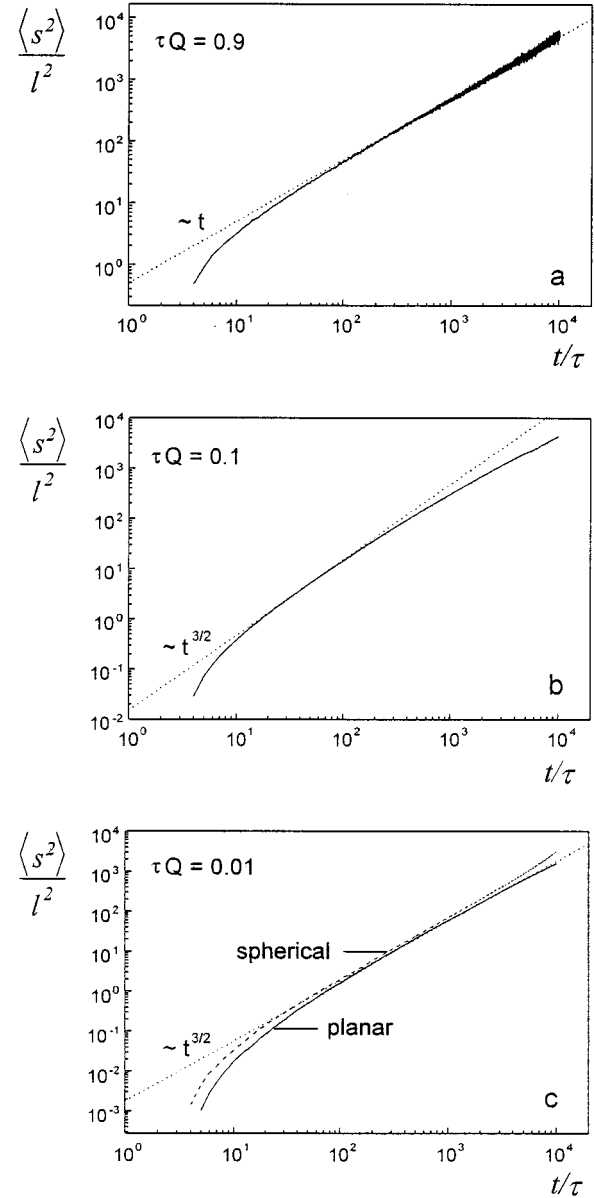

FIG. 1. Simulated time dependences of the mean-squared surface displacement of a random walker in the vicinity of a planar liquid-solid interface for different adsorption strengths. (a) Weak adsorption $Q = 0.9\tau^{-1}$, $Q_{ads} = 0.1\tau^{-1}$, and $Qt_h = 0.011$. The function for ordinary diffusion $\langle s^2 \rangle = 2D_0 t$ is also plotted for comparison (dotted line). (b) Intermediate adsorption $Q = 0.1\tau^{-1}$, $Q_{ads} = 0.9\tau^{-1}$, and $Qt_h = 8.1$. The function $\langle s^2 \rangle = Kt^{3/2}$ is plotted for $K = c\sqrt{D_0} = 0.0275l^2\tau^{-3/2}$ (dotted line). (c) Strong adsorption $Q = 0.01\tau^{-1}$, $Q_{ads} = 0.9\tau^{-1}$, and $Qt_h = 81$. The relation $\langle s^2 \rangle = Kt^{3/2}$ is plotted for $K = c\sqrt{D_0} = 0.00275l^2\tau^{-3/2}$ (dotted line). Furthermore, the mean-squared surface displacement for a spherical liquid-solid interface with radius $R = 100l$ is shown for the same parameters (dashed line).

adsorption depth and the retention time are $h = bQ_{ads}/2Q = 0.055l$ and $t_h = h^2/D_0 = 0.012\tau$, respectively, so that the criterion for weak adsorption $Qt_h = 0.011 \ll 1$ is fulfilled.

Larger deviations from ordinary displacement behavior were found in the cases $Q_{ads} = 0.9\tau^{-1}$, $Q = 0.1\tau^{-1}$, that is, $Qt_h = 8.1 > 1$, and $Q_{ads} = 0.9\tau^{-1}$, $Q = 0.01\tau^{-1}$, i.e., $Qt_h = 91 \gg 1$ (see Fig. 1). In a certain time region the mean-
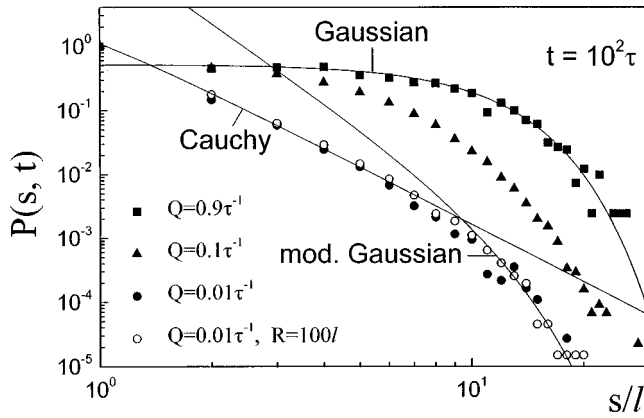
FIG. 2. Normalized distribution of displacements along surfaces after a time $t=100\tau$ simulated for different adsorption strengths at planar and concave spherical liquid-solid interfaces. The adsorption rate was assumed to be $Q_{ads}=0.9\tau^{-1}$. The modified Gaussian [Eq. (2)] and the Cauchy [Eq. (1)] propagators are also plotted for comparison.

squared surface displacement curves approach the superdiffusive law

$$\langle s^2(t)\rangle = D_0 t\left(\frac{t}{t_h}\right)^{1/2} \propto t^{3/2}, \qquad (4)$$

as predicted in [1–3]. The time dependence of the mean-squared surface displacement in spherical pores in the strong-adsorption limit is similar to that for planar surfaces at short times, but approaches a power law proportional to t^κ at long times even with $\kappa>3/2$. This is considered to be due to the finite size of the pore, contrary to adsorption on plane surfaces terminating an infinite bulk volume.

Figures 2–4 show the normalized displacement distribution function for surface diffusion after different diffusion times. For weak adsorption (simulation for $Q=0.9\tau^{-1}$) and short times, the distribution may be approached by a Gauss-
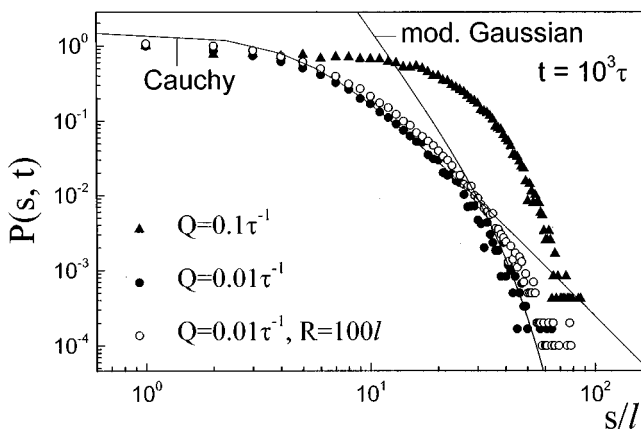

FIG. 3. Normalized distribution of displacements along surfaces after a time $t=1000\tau$ simulated for different adsorption strengths at planar and concave spherical liquid-solid interfaces. The adsorption rate was assumed to be $Q_{ads}=0.9\tau^{-1}$. The modified Gaussian [Eq. (2)] and the Cauchy [Eq. (1)] propagators are also plotted for comparison.
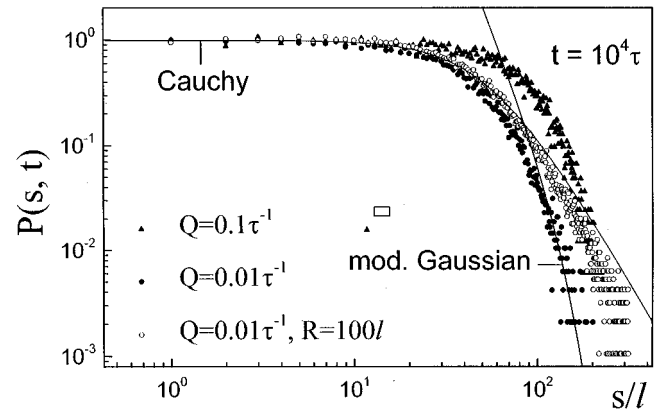

FIG. 4. Normalized distribution of displacements along surfaces after a time $t=10\,000\tau$ simulated for different adsorption strengths at planar and concave spherical liquid-solid interfaces. The adsorption rate was assumed to be $Q_{ads}=0.9\tau^{-1}$. The modified Gaussian [Eq. (2)] and the Cauchy [Eq. (1)] propagators are also plotted for comparison.

ian propagator (see Fig. 2). With decreasing Q, that is, the stronger the adsorption becomes, the distribution function adopts a shape that can be described by a Cauchy distribution [Eq. (1)] at short displacements and by a modified Gaussian [Eq. (2)] in the long-displacement limit. Note that in the strong-adsorption case surface diffusion in spherical pores can be described particularly well by the Cauchy distribution.

IV. NMR CORRELATION FUNCTION

From the experimental point of view, the frequency dispersion of spin-lattice relaxation is of particular interest [5]. For the dipolar interaction the relevant correlation functions refer to the spherical harmonics of second order

$$G_m(t) = \langle Y_{2,m}(0) Y_{2,-m}(t) \rangle \quad (m=1,2), \qquad (5)$$

which are functions of the polar and azimuthal angles ϑ, φ of the interdipole vector relative to the external magnetic field $\mathbf{B}_0$. The intensity function is then defined as $\mathcal{I}(\omega) = \int_{-\infty}^{\infty} G(t)e^{-i\omega t}dt$. The spin-lattice relaxation rate is given by $1/T_1 \propto [\mathcal{I}(\omega)+4\mathcal{I}(2\omega)]$. In the following we restrict ourselves to the simulation and discussion of the correlation function $G_1(t)$, which, in principle, contains all information needed for the prediction of surface effects on spin-lattice relaxation.

Without loss of generality, the intramolecular internuclear vector of adsorbed molecules is arbitrarily assumed to be directed perpendicularly to the liquid-solid interface. The direction of the external magnetic field relative to the surface is irrelevant for the qualitative results of the simulation. In the bulk, adsorbate molecules are assumed to tumble so fast that the orientation correlation can be regarded to be lost instantaneously.

The simulation of the correlation function $G_1(t)$ refers to an ensemble of molecules initially adsorbed on the surface. Adsorption is assumed to be strong ($Q=0.01\tau^{-1}$). If the surface is planar and has an infinite surface orientation correlation length r_c, the correlation to the initial orientation
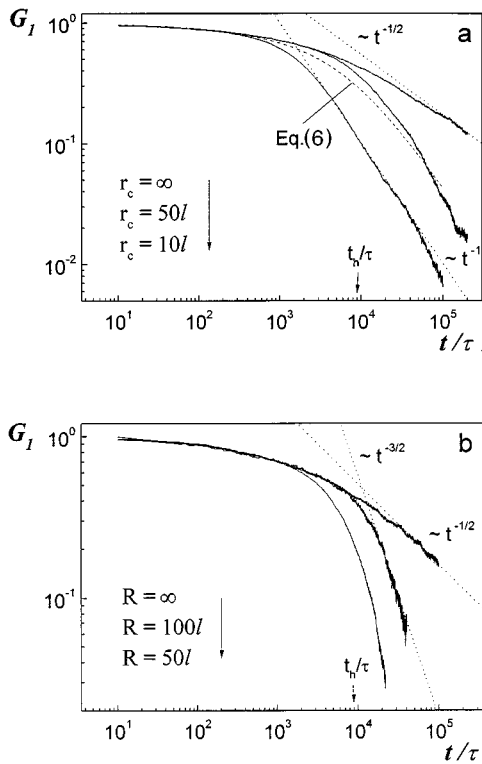
FIG. 5. Normalized NMR correlation function $G_1(t)$ for strong adsorbate molecules on (a) planar and (b) concave spherical surfaces. The desorption rate was assumed to be $Q = 0.01\tau^{-1}$. The quantity R is the curvature radius of the surface and r_c is the orientation correlation length of the surface. Power laws approaching the decays at long times are represented by straight dotted lines. For comparison relation (6) is also plotted (dashed line).

can only decay by desorption and diffusion into the bulk. A molecule that is initially on the surface and finally in the bulk has no orientation correlated with the initial one. On the other hand, an adsorbate molecule that is initially in the bulk and at time t adsorbed on the surface has no correlated initial and final orientations either. The correlation functions (5) for an infinite planar surface therefore reflect the fraction of adsorbate molecules sitting initially as well as finally on the surface irrespective of any bulk excursions in between.

For an analytical description we assume that all particles diffusing along the surface a distance longer than the root-mean-squared displacement in the bulk, i.e., $s > \sqrt{D_0 t}$, have escaped from the surface. That is, the NMR correlation functions based on Eq. (1) become for infinite planar surfaces

$$G_m(t) = \int_0^{\sqrt{D_0 t}} P(s,t) 2\pi s \, ds = \int_0^{\sqrt{D_0 t}} \frac{ct}{[(ct)^2 + s^2]^{3/2}} s \, ds$$

$$= 1 - \frac{1}{\sqrt{1 + t_h/t}}. \tag{6}$$

Note that for $t \ll t_h$ this function coincides with the fraction of particles $1 - (t/t_h)^{1/2}$ that have not yet left the surface in the time t [1]. Equation (6) approaches the simulated data represented in Fig. 5 for this case.

In a further simulation, planar patches with a finite surface orientation correlation length r_c were considered. That is,

adsorbate molecules, which are initially on the surface, lose their orientation not only by escaping from the surface to the bulk but also by leaving the surface patch in which they were adsorbed initially [8]. The consequence is that the correlation function decays faster than for infinite correlation lengths. The simulation results for two planar patches of different correlation lengths are shown in Fig. 5(a).

Finally, the correlation function in spherical pores was simulated. In this case the motions of the adsorbate molecules were treated in all three dimensions assuming pore radii of $R = 50l$ and $R = 100l$. The resulting correlation function $G_1(t)$ is plotted in Fig. 5(b). The decay found in this case is the steepest one. The reason is that the correlation to the initial adsorbate orientation is lost not only by molecules lost to the bulk but also by (bulk-mediated) diffusion to surface positions with orientations of reduced correlation to the initial orientation.

The conclusion is that on a time scale $t \ll t_h$ the NMR correlation function is dominated by the surface geometry probed by Lévy walks along the surface. The propagator effective in this case is the Cauchy distribution for two dimensions. On longer time scales the adsorbate molecules escaping to the bulk contribute in addition.

V. DISCUSSION

The mean-squared (curvilinear) displacement of adsorbate molecules being initially and finally adsorbed on solid surfaces has been simulated with the aid of a Monte Carlo method. The predictions expected in the weak- and strong-adsorption limits for infinite plane surfaces [1] could be well reproduced. In particular, the Lévy walk character of surface displacements in the short-time limit of the strong-adsorption case could be demonstrated in full agreement with the BMSD model [1]. Concave spherical surfaces show some deviations that are considered to be mainly due first to the finite bulk volume in the sphere.

The NMR correlation function for dipolar interaction was evaluated on the same basis. The decay due to escape to the bulk becomes relevant only in the long-time limit relative to the retention time. At short times, correlation losses are mainly due to the surface geometry in the sense of the RMTD mechanism. In the strong-adsorption case when the Cauchy propagator applies, characteristic decays were found for finite plane patches and for concave spherical surfaces.

Typical pore diameters of porous glasses studied in adsorption NMR experiments are in the range 1–100 nm. This length scale tends to be much shorter than $h = \sqrt{D_0 t_h}$. The frequency dependence of the spin-lattice relaxation time T_1 of strong adsorbates is therefore determined by Lévy walk surface diffusion in combination with the surface topological properties. This reorientation mediated by translational displacements mechanism of spin-lattice relaxation is a specific indication of strong adsorption [7,8].

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