Proton and Deuteron Field-Cycling NMR Relaxometry of Liquids in Porous Glasses: Evidence for Lévy-Walk Statistics

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^{1}H and ^{2}H field-cycling NMR relaxometry of polar and nonpolar liquids in porous glasses (4 and 30 nm pores) shows pronounced differences of the spin-lattice relaxation dispersion for "weak" (nonpolar) and "strong" (polar) adsorption. In the latter case bulk-mediated surface diffusion was predicted so that Lévy walks with a Cauchy propagator follow [Bychuk *et al.*, Phys. Rev. Lett. **74**, 1795 (1995)]. The data can be perfectly interpreted by this mechanism in combination with reorientations mediated by translational displacements. The evaluated surface correlation functions are characterized by correlation lengths in the same order as the pore diameters.

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Field-cycling NMR relaxometry [1] of liquids in porous media indicates fluctuations of the spin interactions with correlation times ranging up to 8 orders of magnitude above those of the bulk liquid [2–4]. On the other hand, self-diffusion of liquids in such materials is comparatively fast. The diffusivities measured with the aid of the NMR field-gradient technique [3,4] are within 1 order of magnitude of the bulk values even when the pores are entirely filled so that the vapor-phase enhancement of diffusion [2,5,6] is not operative.

As a NMR relaxation mechanism explaining the extraordinarily long correlation times we have suggested "reorientations mediated by translational displacements" (RMTD) [2–4,7]. That is, adsorbate molecules adopt preferential orientations relative to the local pore surface. Displacements along crooked surfaces therefore give rise to reorientations of the adsorbate molecules. Note that the translational diffusion mechanism, which is responsible for displacements on the surfaces, need not be surface diffusion in the proper sense. Desorption and readsorption at more or less remote sites may contribute as well [3].

From the theoretical point of view, such a "bulk-mediated surface diffusion" (BMSD) mechanism becomes effective if adsorption is strong [8,9]. In this case the displacements on the surface underlie Lévy-walk statistics [10–12] so that a Cauchy distribution [13] is expected to apply.

The purpose of the present study is to give experimental evidence that Lévy walks are effective for displacements along surfaces. As a technique probing a particularly wide frequency range, we have employed field-cycling NMR relaxometry for proton as well as deuteron spin-lattice relaxation.

The field-cycling measurements were carried out with home-built instruments. The detection magnetic-flux density was up to 1.5 T. In the deuteron experiments, typical field switching times were about 1 ms so that the relaxation times could be measured reliably even at the lowest frequencies. Spin-lattice relaxation times

at frequencies beyond the field-cycling range were recorded with conventional spectrometers operating at 2.1 and 7 T. The total frequency ranges were $3 \times 10^3 - 3 \times 10^8$ Hz for ^{1}H, and $3 \times 10^2 - 4 \times 10^7$ Hz for ^{2}H. Within the experimental error, all relaxation curves were found to decay monoexponentially over at least one decade. Transverse relaxation curves could be shown to be monoexponential even over three decades, so that there is no doubt that the fast-exchange limit is valid irrespective of the occurrence of any diversity of the liquid phases. This finding is confirmed by the monoexponential spin-lattice relaxation behavior observed in the rotating frame with Cab-O-Sil fine particles having equivalent surface properties [3].

Bioran B30 porous glass was purchased from Schott Glaswerke, Mainz, Germany. The mean pore diameter is specified by the manufacturer as 30 nm with a narrow pore size distribution (90% within $\pm 5\%$). The porosity is in the range $0.67 - 0.69$. Vycor Porous Glass (VPG, No. 7930, 96% SiO$_2$) was provided by Corning Inc., Corning, NY 14831. The mean pore diameter is 4 nm (96% of the pores have diameters within 4 ± 0.6 nm). The porosity is 28%, the specific surface 250 mm^2/g.

The samples were filled with diverse fluids using the bulk-to-bulk method after extended evacuation. The glass particles were carefully dried to avoid any artifacts by excess liquid outside of the pore space. The measurements were performed immediately thereafter. The data were reproduced several months later using the same samples, so that aging effects in this period can be excluded. Replacement of surface OH groups by propyl groups led only to minor changes of the spin-lattice relaxation time T_1 [3].

Figure 1 shows the dispersion of the proton and deuteron spin-lattice relaxation times of Bioran B30 filled with water. In order to eliminate all isotope-specific constants, the quotient with the relaxation times measured in the bulk liquid is plotted. The frequency dependence of spin-lattice relaxation is extended down to the kHz regime corresponding to correlation times on the order of 10^{-4} s.
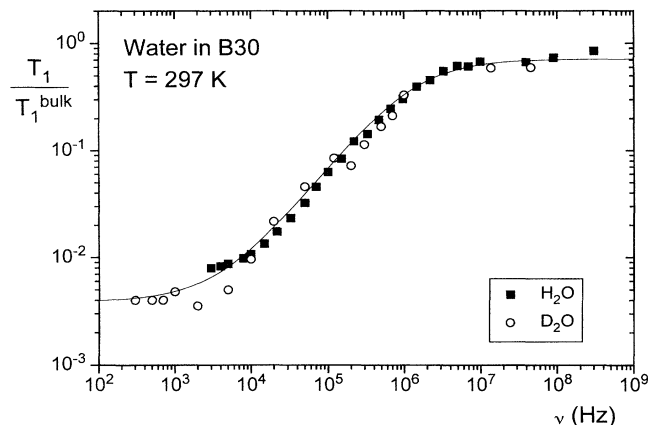
FIG. 1. Frequency dependence of the proton and deuteron spin-lattice relaxation times of water in Bioran B30 porous glass at 297 K. The data are given relative to the values measured in the bulk liquid. For further evaluation, the dispersion is represented by the solid line obtained with the aid of a formal correlation time distribution analysis.

For comparison, the rotational correlation time in bulk water is on the order of 10^{-12} s at room temperature.

The proton and deuteron dispersion curves practically coincide. This is an important finding because it clarifies the spin interactions which are relevant for spin-lattice relaxation in this context. Proton relaxation is governed by dipole-dipole couplings. Therefore intramolecular as well as intermolecular interactions must be considered. In principle, the latter can refer to protons on different water molecules or to hydrogen nuclei located in surface groups of the matrix material. Intramolecular interactions fluctuate due to molecular reorientations, whereas intermolecular interactions are modulated as well by the distance variation of the interacting particles, i.e., directly by translational diffusion [14]. If translational effects of this sort contribute, the interpretation can be rendered ambiguous.

Fortunately, the two contributions can be readily distinguished by comparing the deuteron and proton relaxation data. Deuteron relaxation is governed by quadrupole coupling to electric-field gradients within the molecules, whereas dipole-dipole interaction is negligible. In contrast to protons, the data measured with deuterons, therefore, solely indicate molecular reorientations irrespective of any variation of internuclear distances. Furthermore, the strong coupling constant of quadrupole interaction makes this nuclear species practically insensitive to the influence of paramagnetic impurities. The conclusions from the coincidence of the proton and deuteron dispersion thus are first, that molecular reorientations dominate in the relaxation mechanism, and, second, that paramagnetic impurities do not contribute.

The shape of the spin-lattice relaxation dispersion indicates two processes. The high-frequency plateau is attributed to the β process, i.e., a reorientational component which is fast relative to our frequency scale, but is restricted [3]. On the other hand, the main dispersion region which extends down to the kHz regime reflects the α process, a mechanism by which the orientational correlation of the adsorbate molecules eventually decays to zero.

Figure 2 shows proton spin-lattice relaxation dispersions of different organic liquids in Bioran B30. Equivalent results were obtained with Vycor. The liquids examined in this study may be classified into "polar" (acetone, hexanol, ethanol) and "nonpolar" (tetradecane, hexane, cyclohexane). Corrected for different dipolar coupling constants by division by the bulk-relaxation times, the dispersion curves of the three polar liquids practically coincide, and those of the three nonpolar liquids do so as well.

The spin-lattice relaxation dispersion of the nonpolar species is minor, that is, the influence of the pore surfaces on the reorientation dynamics of the adsorbate molecules is weak, whereas polar liquids show a rather steep slope. The different relaxation dispersion behavior of nonpolar and polar adsorbates may be taken as the criterion for "weak" and "strong" adsorption, respectively [8]. Weak adsorption leads to flat and strong adsorption to steep spin-lattice relaxation dispersions.

The phenomena observed in the strong-adsorption case are extraordinarily striking: A pronounced relaxation dispersion is extended down to the kHz regime and beyond, whereas self-diffusion of the adsorbate molecules is relatively weakly slowed down by the porous matrix.
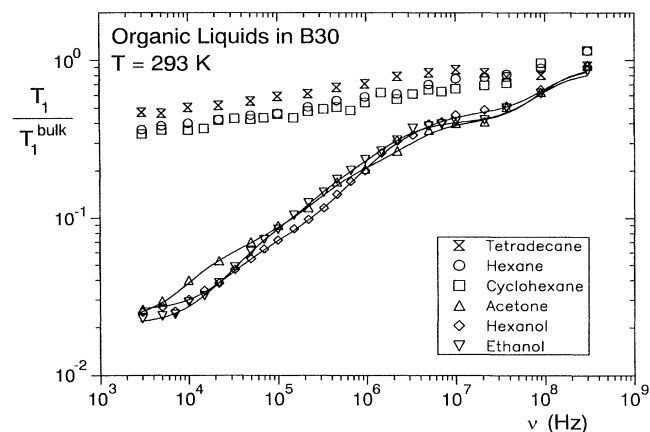

FIG. 2. Frequency dependence of the proton spin-lattice relaxation times of diverse organic liquids in Bioran B30 porous glass at 293 K. The data are given relative to the values measured in the bulk liquids. Depending on the polarity of the solvent molecules, the limits of "strong" and "weak" adsorption can be discriminated as strong and weak dispersions, respectively. The solid lines are based on a formal correlation time distribution analysis, and merely serve the analytical representation of the data.

The transverse relaxation curves are monoexponential over three decades.

These findings unambiguously indicate that the mean exchange time of adsorbate molecules between locations on the pore surfaces and in the bulk are fast in the time scale of the (transverse and longitudinal) relaxation times, but slow relative to the longest correlation times, that is, $10^{-4} < \tau_e < 10^{-3}$ s in the case of water.

A monoexponential autocorrelation function of the spin interactions is out of the question for a description of the experimental data. On the other hand, one might think of a "heterogeneous" distribution of correlation times as an explanation of the extension of the T_1 dispersion and its peculiar slope. However, this interpretation is ruled out for several reasons. There is no obvious rationale for a corresponding chemical heterogeneity of the surface. Different porous glasses and silica fine-particle agglomerates virtually show the same main-dispersion slope and range with different polar adsorbates and for different surface treatments. Even water adsorbed on protein surfaces falls into this category of T_1 dispersions [7,15].

A universal molecular fluctuation process must exist which requires polar surfaces and adsorbate molecules, but no specific chemical binding sites on the surfaces. In our previous reports we have suggested "reorientations by translational displacements" [2,3] as an efficient mechanism prolonging the orientation correlation times while maintaining the translational mobility.

In the following a model proposed by Bychuk and O'Shaughnessy [8,9] is considered which predicts surface diffusion of adsorbate molecules enhanced by Lévy walks. In this context, a Lévy-walk step of an adsorbate molecule consists of desorption, fast diffusion within the bulk liquid, and readsorption at a more or less remote site on the surface.

Strong adsorption means that the mean time t_h a particle remains on the surface is much longer than the desorption time t_d. The adsorbed molecules therefore return frequently to the surface before they escape to the more remote parts of the bulk medium. This is in contrast to weak adsorption, where the adsorbate molecules tend to leave the vicinity of the surface after a single desorption process. It is clear that merely the strong adsorption case provides the basis for an efficient RMTD mechanism, and, hence, for a pronounced low-frequency relaxation dispersion. The different dispersion behavior of polar and nonpolar adsorbates thus directly confirms the existence of the two limits.

Strong adsorption shows peculiar features as concerns transport on the surfaces. Theoretically, the displacement behavior was predicted to be superdiffusive; i.e., the propagator should be strongly non-Gaussian. The effective displacements measured in the—on short length scales—topologically two-dimensional surface layer of adsorbate molecules are described by a Cauchy distribution [8,9]:

$$p(r,t) = \frac{1}{2\pi} \frac{ct}{[(ct)^2 + r^2]^{3/2}} \qquad [r \ll (Dt)^{1/2}], \quad (1)$$

where the two-dimensional displacement on the surface is denoted by r and the bulk diffusion coefficient by D. The quantity $c = D/h$ has the dimension of a velocity. The length h is called the "adsorption depth."

The adsorption layer is assumed to form an isotropic, topologically two-dimensional space. The probability that a particle is displaced a distance in the range r to $r + dr$ in a time t is then given by $p(r,t)2\pi r\, dr$. The spatial orientation correlation function of sites on the surface separated by a distance r is designated by $\tilde{g}(r)$.

More specifically, the orientational properties of spin interactions are described by spherical harmonics of second order. $\tilde{g}(r)$ therefore stands for the correlation function of the second-order spherical harmonics describing the orientation of the interaction tensors [3,14]. The NMR time correlation function is then

$$G(t) = \int_0^\infty \tilde{g}(r)p(r,t)2\pi r\, dr$$

$$= ct \int_0^\infty \frac{r\,\tilde{g}(r)}{[(ct)^2 + r^2]^{3/2}}\, dr$$

$$= t \int_0^\infty \left(\frac{r}{c}\right) \frac{g(r/c)}{[t^2 + (r/c)^2]^{3/2}}\, d\left(\frac{r}{c}\right). \quad (2)$$

For comparisons between theory and experiment, a special numerical procedure was developed. The strategy is first to represent the T_1 dispersion data analytically by a suitably chosen correlation function and then to analyze this correlation function in terms of the Lévy-walk expression (2). As a result, a spatial correlation function of the surface orientations eventually comes out, which can be discussed with the given characteristic lengths of the systems.

The correlation function is formally assumed to consist of a discrete distribution of exponential functions,

$$G_{\exp}(t) \approx \sum_i a_i e^{-t/\tau_i}. \quad (3)$$

The coefficients a_i and the time constants τ_i are determined in such a way that the experimental data are represented by [14]

$$\frac{1}{T_1} = K[I_{\exp}(\omega) + 4I_{\exp}(2\omega)], \quad (4)$$

where K is a constant and $I_{\exp}(\omega)$ is the empirical intensity function given as the Fourier transform of $G_{\exp}(t)$, that is, a discrete distribution of Lorentzian functions [3]. Numerically, this analysis was carried out employing the so-called NNLS method [16].

The discrete distributions obtained in this way are of an entirely formal nature, of course, and must not be taken as a distribution of real dynamic processes. They merely serve as the analytical representation of the experimental T_1 dispersion. The quality of this analysis may be judged
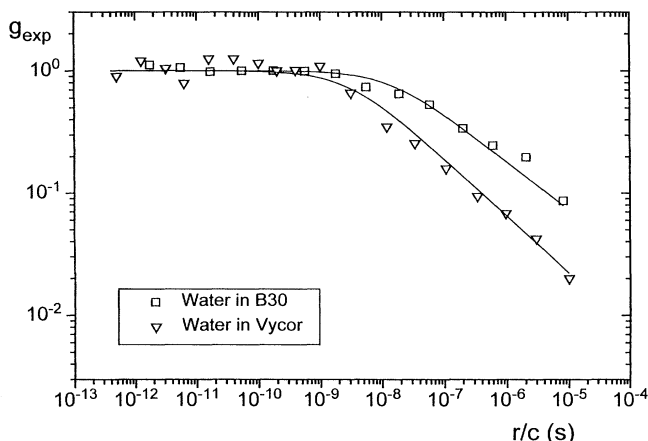
FIG. 3.   Surface correlation functions evaluated from the T_1 dispersions of water in B30 and Vycor porous glasses. The evaluations are based on the Lévy walk formalism of surface diffusion. The data points are connected with guidelines for the convenience of the reader.

In conclusion, deuteron and proton field-cycling NMR relaxometry reveals pronounced effects concerning molecular dynamics of adsorbate molecules in porous glass. The findings correspond to the behavior anticipated by the bulk mediated surface diffusion formalism [8]. The predicted limits of strong and weak adsorption reveal themselves as dramatic changes in the spin-lattice relaxation dispersion in the sense of strong and weak dispersions, respectively. The Cauchy distribution associated with Lévy-walk displacements forms the basis of a process circumscribed as reorientation mediated by translational displacements, which is in agreement with the observed relaxation dispersion behavior. The surface correlation function decays with a correlation length in the same order as the mean pore diameter which quantifies the length scale of the pore confinement. It should be noted that to the best of our knowledge there is no other experimental study probing Lévy-walk statistics.

from the solid lines shown in Figs. 1 and 2, which were recalculated from the empirical intensity function.

In a second step, the time correlation function $G_{exp}(t)$ is compared with Eq. (2). Employing the same numerical NNLS procedure again, but now with respect to the Cauchy distribution function in Eq. (2), leads to the empirical surface correlation function $g_{exp}(\frac{r}{c})$. The starting equation of this analysis is the approximate representation of Eq. (2):

$$G_{exp}(t) \approx t \sum_j \left(\frac{r_j}{c}\right) \frac{g_{exp}(r_j/c)}{[t^2 + (r_j/c)^2]^{3/2}} \left(\frac{\Delta r}{c}\right), \quad (5)$$

where Δr is the "resolution" of the analysis. The NNLS evaluation yields a series of discrete function values $g_{exp}(r_j/c)$. The results for water in B30 and Vycor are shown in Fig. 3. Vice versa, the experimental T_1 dispersion can be reproduced by the function $g_{exp}(r_j/c)$ and Eq. (2) without further parameters.

The water diffusivity at 20 °C is 1.9×10^{-9} m^2/s. The adsorption depth is assumed to be two water molecule diameters thick, that is, $h \approx 7 \times 10^{-10}$ m. Thus $c = D/h \approx 2.7$ m/s. This value permits us to estimate the surface correlation lengths r_c beyond which the spatial correlation functions begin to decay.

The experimental data for B30 and Vycor (Fig. 3) suggest $r_c/c \approx 1.0 \times 10^{-8}$ s and $r_c/c \approx 1.5 \times 10^{-9}$ s, respectively. The correlation lengths are then estimated to be $r_c \approx 27$ and 4.1 nm, respectively. The order of magnitude of these data is in good accordance with what one expects from the RMTD/BMSD viewpoint: It coincides with the length scale by which the porous glasses are specified, i.e., the mean pore dimensions of 30 and 4 nm, respectively.

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