PHYSICAL REVIEW B VOLUME 47, NUMBER 18 1 MAY 1993-II

NMR relaxation and the orientational structure factor

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(Received 28 April 1992; revised manuscript received 4 December 1992)

A class of NMR relaxation mechanisms is considered which is characterized by molecular reorientations mediated by translational displacements. This particularly refers to systems in which molecules are confined to disordered structures determining the local preferential orientations of the incorporated molecules and providing translational degrees of freedom with a certain reduced dimensionality. Examples are solvent molecules adsorbed on surfaces of macromolecules, particle aggregates, or porous media. The orientation correlation function of molecules diffusing along such confining structures therefore does not only reflect the molecular dynamics but also the structural properties of the system. An orientational structure factor is introduced analogous to the structure factor of scattering theory. A number of typical model situations is treated. Experimental relaxation data of the hydration shells of lipid bilayers, proteins, and silica fine-particle aggregates are considered for comparison. The main measuring technique was field-cycling NMR relaxation spectroscopy permitting the record of frequency dependences over many decades. The data for hydrated proteins can perfectly be described by an equipartition of surface wave numbers in a certain range defined by the dimensions of the protein and, on the other hand, of the water molecules.

I. INTRODUCTION

The purpose of this work is to investigate effects of structural confinements to molecular reorientations and the consequences for nuclear magnetic relaxation. Solvent molecules adsorbed and diffusing on surfaces are of particular interest. Typical examples are water molecules in hydration layers of proteins[1,2] or silica fine particles.[3,4] For a review of some chemical problems related to disordered surfaces of catalysts, macromolecules, and colloidal aggregates see Ref. 5.

Using the NMR field-gradient method,[6] water diffusion coefficients in an order of magnitude characteristic for liquids were measured in the above-mentioned systems even when the water concentration was less than the saturation value of the hydration shells or when the so-called free water was frozen, i.e., when the hydration water was the only liquid phase.[2,4,7] A correspondingly high translational mobility therefore must be attributed to molecules in the hydration shells. (Note that systems without free space are considered so that no vapor phase enhancement of translational diffusion[8-10] could contribute.)

On the other hand, orientational correlation times longer than those in bulk water by at least 6 orders of magnitude have been concluded from deuteron as well as proton relaxation experiments.[1,2,11-13] The measuring technique was predominantly field-cycling NMR relaxation spectroscopy.[14] The interpretation[1,2] of these results was that the orientation correlation of water molecules decays partly as a consequence of translational displacements along the rugged and/or curved surface relative to which the adsorbed molecules have a certain preferential orientation.

Fast but anisotropic rotational fluctuations about the local orientation axis are certainly not excluded in such systems. However, such motions are expected to leave a finite residual orientation correlation in the long-time limit. It is this residual correlation which is of interest here. It decays further down to zero by much slower "reorientations mediated by translational displacements" (RMTD).

This translational diffusion process is not to be confused with relaxation by internuclear distance variation often referred to as "translational diffusion mechanism" of NMR relaxation.[15,16] Here we are dealing with the intramolecular part of the interactions of deuterons or protons which is relevant for quadrupolar coupling generally and for dipolar coupling in the low-frequency limit when the molecules are already displaced translationally.

Relaxation by RMTD is the combined consequence of the proper dynamics of molecular motion and the structure of the confining medium. The information of the latter will be represented in the form of an "orientational structure factor" in analogy to the structure factor of scattering theory.

II. ORIENTATION CORRELATION FUNCTION FOR THE RMTD MECHANISM

Nuclear magnetic relaxation is determined by the autocorrelation function of quantities $F^{(m)}(\theta,\phi)\equiv F^{(m)}(\Omega)$ characterizing the dependence of the relevant spin interactions on the orientation Ω expressed in spherical coordinates θ and ϕ with respect to the external magnetic field. For dipolar as well as for quadrupolar couplings these functions are proportional to spherical harmonics of order 2:[16]

$$F^{(m)}(\Omega)=fY_2^{(m)}(\Omega)\ , \tag{1}$$

where $m=0,1,2$ and $F^{(m)*}=F^{(-m)}$. The factor f characterizes the type and the strength of the coupling.

In the case of dipolar interaction it is a function of the distance of the interacting spins. As we are dealing with intramolecular interactions depending solely on the orientation, f is taken as a constant for dipolar and quadrupolar couplings as well.

The displacement is $\mathbf{r}(t)$, where $r(0)=0$. The orientations at these positions are $\Omega(t)$ and $\Omega(0)$, respectively. The reduced autocorrelation function $G(t)$ decaying from the initial value $G(0)=1$ to $G(\infty)$ is defined as

$$G(t)=\frac{\langle F^{(m)}\{\Omega(0)\}F^{(-m)}\{\Omega(t)\}\rangle}{\langle |F^{(m)}|^2\rangle} , \tag{2}$$

where the brackets indicate ensemble averages. The residual correlation in the long-time limit is then

$$G(\infty)=\frac{|\langle F^{(m)}\rangle|^2}{\langle |F^{(m)}|^2\rangle} . \tag{3}$$

With Eq. (1) we have

$$G(t)=\frac{\langle Y_2^{(m)}\{\Omega(0)\}Y_2^{(-m)}\{\Omega(t)\}\rangle}{\langle |Y_2^{(m)}|^2\rangle} . \tag{4}$$

The numerator on the right-hand side can be rewritten as

$$\begin{aligned}\langle Y_2^{(m)}\{\Omega_i\}Y_2^{(-m)}\{\Omega_J\}\rangle &= \left\langle \frac{1}{4\pi}\int P(\Omega_i,\Omega_f,t)Y_2^{(m)}(\Omega_i)Y_2^{(-m)}(\Omega_f)d\Omega_J \right\rangle_{\Omega_i}\\ &= \frac{1}{4\pi}\int \langle P(\Omega_i,\Omega_f,t)Y_2^{(m)}(\Omega_i)\rangle_{\Omega_i}Y_2^{(-m)}(\Omega_f)d\Omega_f ,\end{aligned} \tag{5}$$

where $P(\Omega_i,\Omega_f,t)$ is the conditional probability density that the final orientation is $\Omega_f=\Omega(t)$ after a time t if the initial orientation was $\Omega_i=\Omega(0)$.

This probability can be analyzed in terms of the RMTD process:

$$P(\Omega_i,\Omega_f,t)=\int \Phi(\Omega_i,\Omega_f,\mathbf{r})\Psi(\mathbf{r},t)d^zr , \tag{6}$$

where the integration is carried out over the whole topologically z dimensional $\mathbf{r}$ space ($z=1$, 2, or 3). $\Psi(\mathbf{r},t)$ is the diffusion profile, i.e., the probability density that a particle is displaced by a distance $\mathbf{r}$ in the topological space in a time interval t. $\Phi(\Omega_i,\Omega_f,\mathbf{r})$ represents the probability density that the orientation changes from Ω_i to Ω_f in a distance $\mathbf{r}$.

Note that the formal prerequisite of Eq. (6) is the stochastic independence of the orientation at a position $\mathbf{r}$ and the displacement to this position. $\Psi(\mathbf{r},t)$ is independent of the orientations of the molecule, at the initial as well as at the final position. The orientations at different positions are a matter of the surface structure alone and are linked by the function $\Phi(\Omega_i,\Omega_f,\mathbf{r})$.

Using the expansion in terms of spherical harmonics

$$\Phi(\Omega_i,\Omega_f,\mathbf{r})=\sum_{l',m'}\Gamma_{l',m'}(\mathbf{r})Y_{l'}^{(m')}(\Omega_f) \tag{7}$$

with the initial condition

$$\begin{aligned}\Phi(\Omega_i,\Omega_f,0)&=\delta(\Omega_i-\Omega_f)\\ &=\sum_{l',m'}Y_{l'}^{(-m')}(\Omega_i)Y_{l'}^{(m')}(\Omega_f) ,\end{aligned} \tag{8}$$

we find

$$\Gamma_{l',m'}(0)=Y_{l'}^{(-m')}(\Omega_i) . \tag{9}$$

The coefficients of the above expansion thus can be expressed as

$$\Gamma_{l',m'}(\mathbf{r})=Y_{l'}^{(-m')}(\Omega_i)g_{l',m'}(\mathbf{r}) , \tag{10}$$

where $g_{l',m'}(0)$. Inserting Eq. (10) in Eq. (7) gives

$$\Phi(\Omega_i,\Omega_f,\mathbf{r})=\sum_{l',m'}Y_{l'}^{(-m')}(\Omega_i)Y_{l'}^{(m')}(\Omega_f)g_{l',m'}(\mathbf{r}) . \tag{11}$$

With Eqs. (4), (5), (6), and (11) we immediately obtain the orientation correlation function

$$G(t)=\frac{1}{\langle |Y_2^{(m)}|^2\rangle}\int g_{2,m}(\mathbf{r})\Psi(\mathbf{r},t)d^z\mathbf{r} . \tag{12}$$

This concept refers specifically to the low-frequency part of the fluctuations, i.e., typically to frequencies $\nu \ll 10^{10}$ Hz. There are other degrees of rotational freedom expected to be relevant at fluctuation rates typical for low-molecular liquids ($>10^{10}$ s^{-1}). What can be studied by the field-cycling technique and what refers to the surface structure is the decay of the residual correlation left over by such fast, but restricted reorientations at high frequencies. The consequence is that the low-frequency part of the reorientations of the diffusing molecules is slaved to their displacements.

III. THE ORIENTATIONAL STRUCTURE FACTOR

The diffusion profile $\Psi(\mathbf{r},t)$ depends, in principle, on the dimensionality z and on the validity of the Einstein relation for normal diffusion

$$\langle r^2\rangle=2zDt , \tag{13}$$

where D is the diffusion coefficient. In this case the solution of the diffusion equation is given by the Gaussian probability density

$$\Psi(\mathbf{r},t)=\frac{1}{(4\pi Dt)^{z/2}}e^{-\mathbf{r}^2/4Dt} \tag{14}$$

where the integral over the whole space is $\int \Psi(\mathbf{r},t)d^zr=1$.

The Gaussian function can be represented by the spatial Fourier transform

$$e^{-r^2/4Dt}=\frac{(\pi Dt)^{z/2}}{\pi}\int e^{-Dtk^2}e^{i\mathbf{k}\cdot\mathbf{r}}d^zk \tag{15}$$

where **k** is the wave vector. The integral covers the whole z-dimensional **k** space. The orientation correlation function for normal diffusion can then be written as

$$G(t)=\int \tilde{S}(\mathbf{k})e^{-Dtk^2}d^zk \tag{16}$$

with the orientational structure factor

$$\tilde{S}(\mathbf{k})=\frac{1}{2^z\pi\langle |Y_2^{(m)}|^2\rangle}\int g_{2,m}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d^zr \ . \tag{17}$$

The integral covers the whole topologically z-dimensional **r** space in which the translational diffusion takes place.

Let us now define the radial orientation structure factor

$$S(k)=\langle \tilde{S}(\mathbf{k})\rangle\beta(k) \tag{18}$$

with $\beta(k)=1$, $2\pi k$, and $4\pi k^2$ for the topologically one-, two-, and three-dimensional space, respectively, in which the diffusion process takes place. The average refers to all directions of the wave vector. The orientation correlation function thus can be expressed as

$$G(t)=\int_0^\infty S(k)e^{-Dtk^2}dk \ . \tag{19}$$

The corresponding spectral density is given by

$$\begin{aligned}\mathcal{J}(\omega)&=2\int_0^\infty G(t)\cos(\omega t)dt\\&=\int_0^\infty S(k)\frac{2\tau_k}{1+\omega^2\tau_k^2}dk \ ,\end{aligned} \tag{20}$$

where

$$\tau_k=\frac{1}{Dk^2} \ . \tag{21}$$

The spin-lattice relaxation rates $1/T_1$ and $1/T_{1\rho}$ in the laboratory and rotating frames of reference, respectively, are given by[16,17]

$$\frac{1}{T_1}\approx\left[\frac{\mu_0}{4\pi}\right]^2\frac{3}{2}\gamma^2\hbar^2I(I+1)\langle |F^{(1)}|^2\rangle[\mathcal{J}(\omega_0)+4\mathcal{J}(2\omega_0)] \ , \tag{22}$$

$$\begin{aligned}\frac{1}{T_{1\rho}}\approx\left[\frac{\mu_0}{4\pi}\right]^2\frac{3}{4}\gamma^4\hbar^2I(I+1)\langle |F^{(1)}|^2\rangle\\\times[3\mathcal{J}(2\omega_1)+5\mathcal{J}(\omega_0)+2\mathcal{J}(2\omega_0)] \ ,\end{aligned} \tag{23}$$

where we have assumed dipolar interaction, i.e., $F^{(1)}=a^{-3}\sin\theta\cos\theta\exp(i\phi)$ with a,θ,ϕ the spherical coordinates of the effective internuclear vector. γ is the gyromagnetic ratio, $\hbar$ is Planck's constant divided by 2π, μ_0 is the magnetic-field constant. $\omega_0=\gamma B_0$ and $\omega_1=\gamma B_1$ are the circular Larmor frequencies in the external field B_0 and the rotating radio-frequency field B_1, respectively.

$\mathcal{J}(\omega)$ [Eq. (20)] has the form of a convolution integral so that the orientational structure factor can be deduced from field-cycling data of the spin-lattice relaxation rate. The orientational structure factor can, in principle, be obtained by numerical deconvolution of the experimental T_1 dispersion.

A. Delta structure factor: Application to the "ripple phase" of lipid bilayers

Assume a topologically two-dimensional surface undulated in one direction according to a wave vector $\mathbf{k}_0$. Molecules confined to this space will be reoriented by displacements along $\mathbf{k}_0$. The orientational structure factor is then

$$\tilde{S}(\mathbf{k})=a_1\delta(\mathbf{k}-\mathbf{k}_0)+a_2\delta(\mathbf{k}) \tag{24}$$

with $a_1+a_2=1$. The orientation correlation function for this structure factor and for normal diffusion decays exponentially according to

$$G(t)=a_1e^{-Dtk_0^2}+a_2 \ . \tag{25}$$

A practical situation where a δ structure factor is expected to be relevant is water adsorbed on lipid bilayers

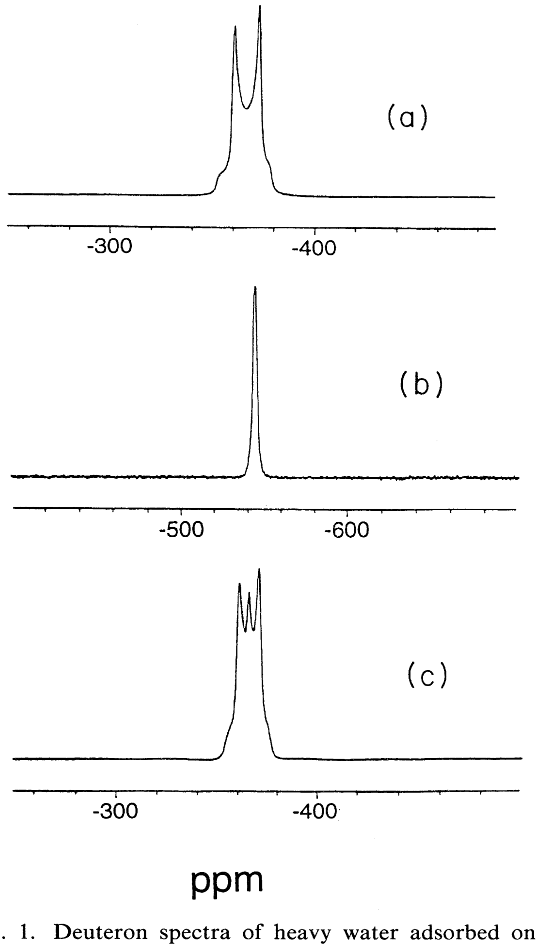

FIG. 1. Deuteron spectra of heavy water adsorbed on dipalmitoyllecithin bilayers in (a) the liquid crystalline (L_α) phase, (b) the ripple ($P_{\beta'}$) phase, and (c) the gel ($L_{\beta'}$) phase. The water content was 24% D_2O b.w. The quadrupole splitting of the spectra (a) and (c) are explained by the preferential orientation of the water molecules on the bilayer surfaces. These are more or less plane in these phases so that translational displacements are not connected with reorientations in the first instance. This is in contrast to the ripple phase (b) where, as a consequence, the quadrupole splitting collapses.

in the so-called ripple phase.[18] In this phase the topologically two-dimensional surfaces of the bilayers are undulating with a definite wavelength of about 140 Å while the gel and the liquid crystalline phases appearing below 34.5 °C and above 42 °C, respectively, show smooth surfaces. The undulating orientations of D_2O molecules are demonstrated by the deuteron quadrupole splitting averaged out by the translational diffusion process along the ripple surfaces in contrast to the other two phases (Fig. 1). Preliminary deuteron relaxation dispersion studies confirm this interpretation.

B. Gaussian structure factor

Instead of a single wave vector characterizing the surface structure we assume now a Gaussian distribution of the magnitude about a certain average value k_0. The radial orientation structure factor is then given by

$$S(k)=\sqrt{2/(\pi\sigma^2)}\,e^{-(k_0-k)^2/(2\sigma^2)} . \tag{26}$$

The corresponding orientation correlation function is

$$G(t)=\int_0^\infty S(k)e^{-Dtk^2}dk$$
$$=\frac{1}{(1+2\sigma^2Dt)^{1/2}}e^{-k_0^2Dt/(1+2\sigma^2Dt)} . \tag{27}$$

This function is characterized by two correlation times:

$$\tau_0=(k_0^2D)^{-1} , \tag{28}$$

$$\tau_\sigma=(2\sigma^2D)^{-1} . \tag{29}$$

The decay becomes exponential in the limit $t \ll \tau_\sigma$,

$$G(t)\approx e^{-t/\tau_0} \tag{30}$$

and

$$G(t)\approx e^{-k_0^2/(2\sigma^2)}(\tau_\sigma/t)^{1/2} \tag{31}$$

in the opposite limit. The corresponding frequency dependences are determined by the intensity function ob-

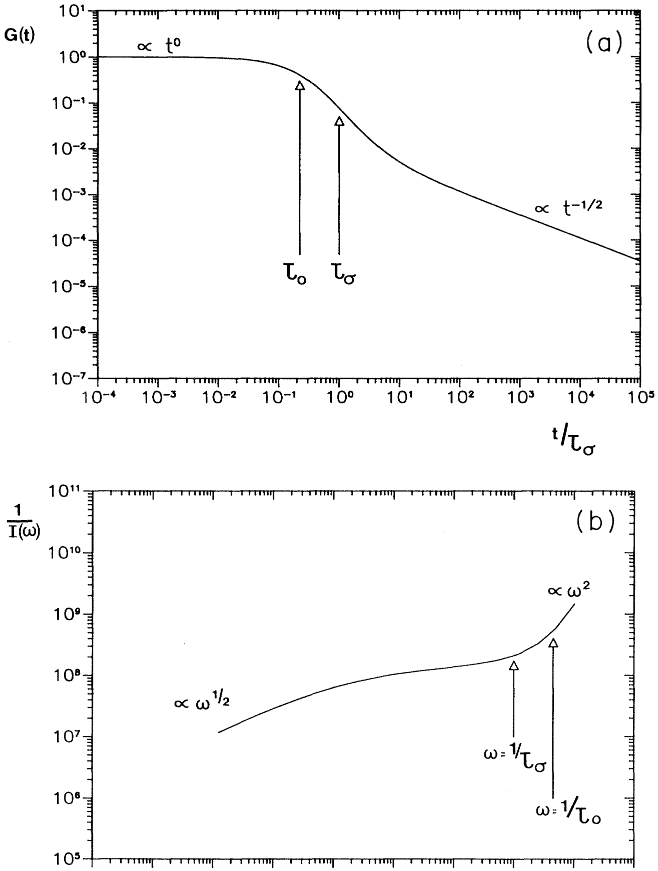

FIG. 2. (a) Orientation correlation function and (b) reciprocal intensity function for a Gaussian structure factor. The curves have been calculated on the basis of Eq. (27) and its numerical Fourier transform. The indicated limits correspond to Eqs. (30)–(33). The reciprocal intensity function essentially reflects the expected T_1 dispersion.

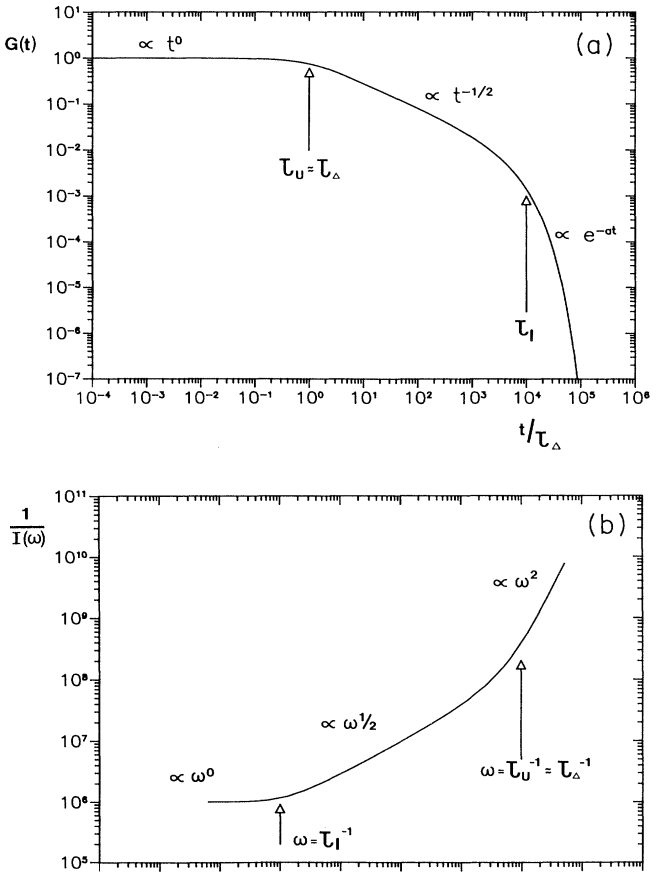

FIG. 3. (a) Orientation correlation function and (b) reciprocal intensity function for an equipartition of wave numbers. The curves have been calculated on the basis of Eq. (35) and its numerical Fourier transform. The reciprocal intensity function essentially predicts the expected T_1 dispersion.

tained as the Fourier transform of $G(t)$,

$$\mathcal{J}(\omega)\approx\frac{2\tau_k}{1+\omega^2\tau_k^2}\quad\text{if } \omega\tau_\sigma \ll 1 \tag{32}$$

and

$$\mathcal{J}(\omega)\approx e^{-k_0^2/(2\sigma^2)}(2\pi\tau_\sigma/\omega)^{1/2}\quad\text{if } \omega\tau_\sigma \gg 1\ . \tag{33}$$

Figures 2(a) and 2(b) show the numerically evaluated functions $G(t)$ and $1/\mathcal{J}(\omega)$, respectively.

C. Equipartition of wave numbers: Comparison with protein hydration water data

The case of equipartition of wave numbers corresponds to a purely stochastic distribution of orientations in a certain wave-number range. The upper and lower cutoff magnitude values are designated by k_u and k_l, respectively. Assuming molecules diffusing on a topologically two-dimensional surface and a "white" distribution of wave numbers independent of the direction suggests a radial orientation structure factor

$$S(k)=\begin{cases}\dfrac{1}{\Delta k} & \text{if } k_l \le k \le k_u\ ,\\ 0 & \text{otherwise}\ ,\end{cases} \tag{34}$$

where $\Delta k = k_u - k_l$. The orientation correlation function is then

$$G(t)=\int_0^\infty S(k)e^{-Dtk^2}dk$$
$$=\frac{1}{2\Delta k}\sqrt{\pi/(Dt)}[\operatorname{erf}(\sqrt{Dt}\,k_u)-\operatorname{erf}(\sqrt{Dt}\,k_l)]\ , \tag{35}$$

where $\operatorname{erf}(x)=(2/\sqrt{\pi})\int_0^x e^{-x'^2}dx'$ is the error function. The decay of the orientation correlation function is characterized by three correlation times given by

$$\tau_u=(k_u^2D)^{-1}\ , \tag{36}$$

$$\tau_l=(k_l^2D)^{-1}\ , \tag{37}$$

$$\tau_\Delta=[(\Delta k)^2D]^{-1}\ . \tag{38}$$

Figures 3(a) and 3(b) show the numerically evaluated functions $G(t)$ and $1/\mathcal{J}(\omega)$. The proportionality $1/\mathcal{J}(\omega)\propto\omega^{1/2}$ in the intermediate-frequency range is characteristic for this type of orientational structure factor. It corresponds particularly close to the T_1 dispersion observed with water deuterons adsorbed on protein surfaces. Figure 4 shows a representative data set.[1]

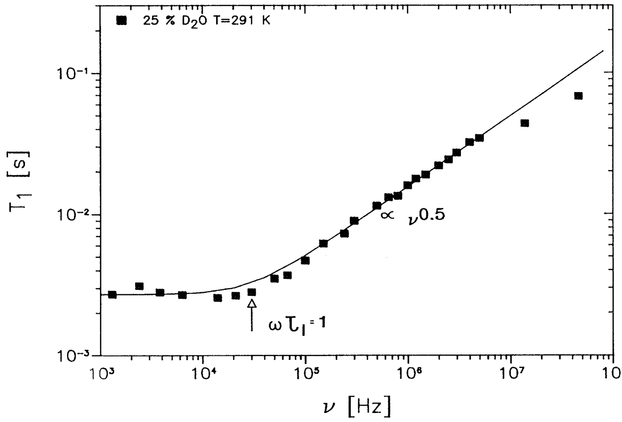

FIG. 4. Representative frequency dependence of the deuteron spin-lattice relaxation time, T_1, of heavy water adsorbed on bovine serum albumin (BSA) at 291 K. (Data are from Ref. 1.) The water content (25% b.w.) is somewhat below the saturation concentration of the hydration shells, but safely above the percolation threshold (Ref. 4) of 15% b.w. The solid line represents the reciprocal intensity function (times an arbitrary proportionality factor) which was calculated by numerically Fourier transforming Eq. (35) for an equipartition of wave numbers [compare Fig. 3(b)]. The crossover from the low-frequency plateau for $\omega\tau_l \ll 1$ to the square-root slope at intermediate frequencies, $\tau_l^{-1} \ll \omega \ll \tau_u^{-1}$, corresponds to the experimental finding. From the fitted value $\tau_l = 1.6\times10^{-5}$ s and the translational water diffusion coefficient measured to be (Ref. 4) $D=2\times10^{-11}$ m^2/s, one estimates a lower cutoff wavelength of 110 Å which corresponds well to half of the mean circumference of a BSA molecule. At high frequencies the influence of local but restricted rotational diffusion of the water molecules becomes visible (Ref. 1) (Only the residual orientation correlation left over by this process was considered in this treatment of the low-frequency T_1 dispersion.)

IV. DISCUSSION

A nuclear magnetic relaxation process has been considered owing to molecular reorientations mediated by translational displacements. In other words, reorientations are slaved to translations. An orientational structure factor has been introduced permitting the separation of the structural information of the confining system from the dynamics of the molecules diffusing on it. This is a formalism generally suitable for this class of relaxation mechanisms.

A number of different orientational structure factors has been suggested. The features specific to the diverse systems considered here deserve a more detailed analysis of the data then was appropriate in the frame of the present work. This will be the objective of a forthcoming paper.[19] The aim was rather to demonstrate that the RMTD mechanism is of general importance for the relaxation of molecules confined in systems with a disordered surface structure.

Diffusion along surfaces is a phenomenon reducing the dimensionality of the transport process.[20] This may explain the amazing efficiency in biological systems where reactions are known to be extremely fast in spite of the limitation by diffusion. The study of surface guided transport therefore is of particular interest. The RMTD mechanism of NMR relaxation spectroscopy is a concept providing the basis for corresponding interpretations.

The hydration layers discussed above form topologically two-dimensional spaces. An example for a topologically one-dimensional space is considered in context with "reptation," i.e., a polymer diffusing along its own contour.[21] Experimental evidence thereof is also provided by field-cycling NMR relaxation spectroscopy.[22,23] Finally, the three-dimensional case can be imagined with liquid crystals, where the diffusion connects positions with different director orientations.

In the above cases a normal diffusion behavior within the topological space was assumed so that Eq. (13) is valid. In other words, the topological space is considered to be homogeneous. The displacement **r** is measured in the (curvilinear) coordinates of the topological space, and the displacement probability density $\Psi(\mathbf{r},t)$ has a Gaussian character.

On the other hand, a deviation from Gaussian probability densities is expected if the topological connectivity of the surface is incomplete so that a kind of percolation cluster is approached. This situation may arise if the coverage of surfaces by the diffusing molecules is incomplete,[4] for instance. Diffusion tends then to be anomalous in length scales within the correlation length of the clusters.[24–26] For fractal percolation clusters in particular, i.e., self-similar structures, the time dependence of the mean-square displacement is given by a power law

$$\langle r^2 \rangle = \alpha t^{2/(2+\Theta)} \quad (\Theta \geq 0) \,, \tag{39}$$

where $2+\Theta$ is the anomalous diffusion exponent (sometimes denoted as d_w) and α is a constant (being equal to $2zD$ if $\Theta=0$).

If the displacements along the surface are measured in the Euclidean rather than in the topological space, and if the surface forms a three-dimensional object which cannot be approached by a plane, the probability density $\Psi(\mathbf{r},t)$ also implies the principal accessibility of the position **r**, i.e., to the geometry of the object. By contrast, the solutions of the normal diffusion equation are valid under the assumption that any position can be reached without structural restriction.

Diffusion on a fractal object requires a generalization of the diffusion equation leading to a modified probability density for displacements r in a time t. Approaches of that kind were reported in Refs. 27 and 28, for instance. The consequence is the appearance of "stretched Gaussian" probability densities, where the fractal dimension plays a crucial role. In a pore fractal, for instance, the displacement of molecules in the pores are expected to be characterized by a non-Gaussian probability density $\Psi(\mathbf{r},t)$ which is determined by the fractal structure of the pores. Deviations from normal diffusion behavior have also been found in gelatin networks using dynamic light scattering.[29]

In such cases, **r** refers to the Euclidean space. The function $g_{2,m}(\mathbf{r})$ given in Eq. (12) can be defined with the same probabilistic meaning as with normal diffusion. An orientation structure factor suitable for anomalous diffusion thus can be introduced analogously to Eq. (17). The problem is, however, to analyze the non-Gaussian function $\Psi(\mathbf{r},t)$ similarly to Eq. (15). A corresponding treatment is, in principle, possible but would be beyond the scope of the present paper.

The process considered in this study has a time-scale aspect: The prerequisite for the introduction of the orientational structure factor is the restriction of local reorientations, that is, the interaction of the medium with the molecules prevents complete reorientation by fast local fluctuations. Hence, a residual orientation correlation remains which can decay further down via the RMTD mechanism. Note that the spin couplings can be both dipolar and quadrupolar. The latter has been considered by Fujara *et al.*[30,31] for a formalism showing the analogy of quadrupolar order experiments to quasielastic neutron scattering. These papers, however, are referring to rotational diffusion or jumps of molecules, i.e., to local reorientations.

ACKNOWLEDGMENTS

We thank the Deutsche Forschungsgemeinschaft for financial support and C. Schöll for recording the spectra figure 1.

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