

## Surface fractals probed by adsorbate spin-lattice relaxation dispersion

Tatiana Zavada and Rainer Kimmich

*Sektion Kernresonanzspektroskopie, Universität Ulm, 89069 Ulm, Germany*

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Spin-lattice relaxation of strong adsorbates confined in disordered structures such as porous silica glass is treated on the basis of a relaxation mechanism due to “reorientation mediated by translational displacements.” In such a situation the low-frequency spin-lattice relaxation dispersion beyond the regime where local reorientations dominate reflects molecular dynamics as well as the surface geometry on a length scale longer than 1 nm. It is shown that the power law frequently observed for the spin-lattice relaxation dispersion in porous media can be traced back to surface fractality. The fractal properties of rough surfaces and the statistics governing surface displacements enter explicitly in the expression for the dipolar correlation function. The surface fractal dimension can thus be evaluated from the low-frequency spin-lattice relaxation dispersion accessible by field-cycling NMR relaxometry. [S1063-651X(99)12905-2]

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### I. INTRODUCTION

Adsorbate molecules on surfaces may be subject to fast reorientations about a preferential axis, depending on the local surface orientation and the binding properties. The corresponding correlation times tend to be close to those in the bulk liquid. However, the reorientation of adsorbate molecules on these grounds is restricted to a limited solid-angle range as long as the adsorbate molecules reside at the same surface sites. On the other hand, in the “strong-adsorption limit,” which typically applies to polar liquids confined by polar surfaces, apparent correlation times up to eight orders of magnitude longer than in the bulk have been observed [1,2] using field-cycling NMR relaxometry [3].

It has been shown that the low-frequency spin-lattice relaxation dispersion occurring under such circumstances is closely related to displacements along the surfaces. Intramolecular nuclear dipole-dipole couplings [4,5] as well as nuclear interactions with electron paramagnetic impurities on the surface [6,7] have been discussed. In this study we solely refer to situations where the latter are definitely negligible, as shown in Refs. [1,8], for porous Bioran glasses, for instance.

As a low-frequency adsorbate relaxation mechanism dominating in diamagnetic matrices, “reorientation mediated by translational displacements” (RMTD) has been identified [4]. That is, the low-frequency fluctuations of the spin couplings occur due to adsorbate diffusion effectively taking place along the (rough and shaped) surfaces. The mechanism has also been considered in a recent computer simulation [9]. Spin-lattice relaxation caused by RMTD was shown to be the combined effect of molecular dynamics and of the surface structure. That is, structural and dynamical features contribute to the reorientation process independently. For the description of the surface structure the orientational structure factor has been introduced that is a two-dimensional analogue to the static structure factor known in scattering theory [4,8].

The main objective of this work is to extend the consideration to the case when the surface has fractal properties. Surface fractals describe the roughness in the range of scale invariance  $a_0 \ll r \ll \xi$ , where  $a_0$  is the diameter of the adsor-

bate molecules employed to probe the surface, and  $\xi$  is the correlation length [10–13] whose maximum value is typically determined by the pore size. The surface roughness is considered to consist of height fluctuations of the surface relative to a reference base plane of second order forming a topologically two-dimensional space. The actual rough surface, i.e., the elevations relative to the base plane, is described by the function  $h = h(x, y)$  assumed to be self-affine, where  $x$  and  $y$  are curvilinear coordinates in the base plane, and  $\langle h \rangle = 0$  (see Fig. 1). Self-affinity means that the scaling relation

$$h(\lambda x, \lambda y) = \lambda^H h(x, y) \quad (1)$$

is satisfied, where  $H$  is called the “roughness” (or Hurst) exponent. The parameter  $H$  is related to the “surface fractal dimension”  $D_s$  by  $D_s = 3 - H$ . Experimental data for  $D_s$  in the range  $2 \leq D_s \leq 3$  were measured with the aid of scanning electron microscopy [14], scattering [15,16] and adsorption [17] for different porous materials. The value  $D_s = 2$  indicates a smooth surface, and  $D_s = 3$  a completely compressed “crumpled membrane.”

There is a number of reports in the literature in which NMR parameters of systems such as cross-linked polymers, cement gels, and blood plasma gels have been related to fractals [18–21]. In the present work, we show how the surface fractal dimension  $D_s$  can be deduced from the spin-lattice relaxation dispersion probed by field-cycling NMR relaxometry.

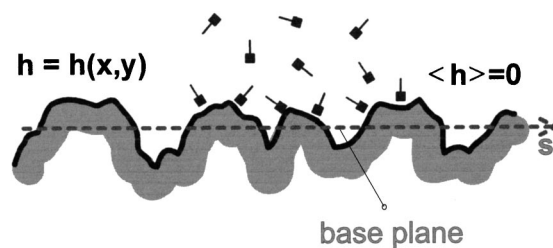


FIG. 1. Schematic representation of a rough surface and adsorbate molecules oriented perpendicular to the surface if adsorbed.

The static structure factor is defined as

$$\tilde{S}_{sc}(\mathbf{k}) \equiv \langle e^{-i\mathbf{k}\cdot\mathbf{r}} \rangle = \int g_{sc}(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} d^3r, \quad (2)$$

where  $g_{sc}(\mathbf{r})$  is the pair correlation function or density-density correlation function (of the random surface) and  $k$  is the wave number. In the limit  $k \gg \xi^{-1}$ , the structure factor and the pair correlation function take the form [15]

$$\tilde{S}_{sc}(k) \propto k^{D_s-6} \quad (3)$$

and

$$g_{sc}(r) \propto 1 - Ar^{3-D_s}, \quad (4)$$

respectively.

In the following, we will translate this approach into the RMTD formalism describing the low-frequency spin-lattice relaxation dispersion of adsorbate molecules on (fractal) surfaces. We will then analyze experimental data obtained with liquid dimethylsulfoxide and malononitrile in a porous silica glass in terms of the surface fractal dimension.

## II. RMTD RELAXATION MECHANISM

Spin-lattice relaxation in adsorbate molecules is assumed to result from intramolecular (dipolar or quadrupolar) spin interactions. The molecular orientation relative to the laboratory frame is given by the azimuthal angle  $\varphi$  and the polar angle  $\vartheta$ . For homonuclear dipolar interaction the spin-lattice relaxation rate  $1/T_1$  is given by the standard expression

$$\frac{1}{T_1} = \left( \frac{\mu_0}{4\pi} \right)^2 \frac{3}{2} \gamma^4 \hbar^2 I(I+1) (\langle |F^{(1)}|^2 \rangle - \langle |F^{(1)}|^2 \rangle [\mathcal{I}(\omega) + 4\mathcal{I}(2\omega)]). \quad (5)$$

$\gamma$  is the gyromagnetic ratio,  $\hbar$  Planck's constant divided by  $2\pi$ , and  $\mu_0$  the magnetic field constant.  $\omega = 2\pi\nu = \gamma B_0$  is the angular Larmor frequency in the external field  $B_0$ .  $F^{(1)}$  is a function of the polar coordinates  $r, \vartheta, \varphi$ , defining the orientation of the internuclear vector relative to the external magnetic field:

$$F^{(1)} = F^{(-1)*} = \frac{1}{r^3} \sin \vartheta \cos \vartheta e^{i\varphi} = \frac{1}{r^3} \sqrt{\frac{8\pi}{15}} Y_{2,-1}(\vartheta, \varphi), \quad (6)$$

where  $Y_{2,-1}(\vartheta, \varphi)$  represents a spherical harmonics of rank two.

The intensity function  $\mathcal{I}(\omega)$  is defined as the cosine Fourier transform of the reduced dipolar correlation function  $G(t)$ ,

$$\mathcal{I}(\omega) = 2 \int_0^\infty G(t) \cos(\omega t) dt. \quad (7)$$

The reduced dipolar correlation function is given by

$$G(t) = \frac{\langle F^{(1)}(0)F^{(-1)}(t) \rangle - \langle |F^{(1)}|^2 \rangle}{\langle |F^{(1)}|^2 \rangle - \langle |F^{(1)}|^2 \rangle}, \quad (8)$$

and decays from the initial value 1 to 0. The brackets indicate averages over all initial and final orientations probed by a molecule on a time of the order of  $T_1$ . In the following we will assume that  $\langle |F^{(1)}|^2 \rangle = 0$  for simplicity.

For intramolecular interactions, the correlation function decay solely reflects molecular reorientations. For quadrupole interaction, the same relationship as given in Eq. (5) between the spin-lattice relaxation rate and the reduced intensity functions applies, apart from different prefactors [3,22].

In the bulklike phase, orientational correlations are cut back by fast, more or less isotropic rotational diffusion. This situation is to be distinguished from that of molecules adsorbed on the surface, for which the RMTD mechanism comes into play on a time scale long compared with that of restricted rotational diffusion occurring locally [3–5]. An adsorbed molecule tends to be oriented in a preferential direction relative to the local surface. If displacements take place effectively along a rough and shaped surface, the adsorbate molecule will change its orientation according to the surface contour.

In the RMTD formalism, the orientational structure of a rough surface is described by the surface orientation correlation function for intramolecular coupling and for a fixed internuclear distance as

$$g(s) = \frac{\langle Y_{2,-1}(\vartheta_0, \varphi_0) Y_{2,+1}(\vartheta_s, \varphi_s) \rangle}{\langle |Y_{2,-1}|^2 \rangle} = 4\pi \langle Y_{2,-1}(\vartheta_0, \varphi_0) Y_{2,+1}(\vartheta_s, \varphi_s) \rangle, \quad (9)$$

where  $\vartheta_0, \varphi_0$  and  $\vartheta_s, \varphi_s$  are the polar coordinates of the surface orientations at  $s=0$  and at a distance  $s$ , respectively.  $g(s)$  is the autocorrelation function of the spatial orientation of surface sites separated by a curvilinear distance  $s$  in the topologically two-dimensional surface space, that is, a second-order plane representing the base on which the surface roughness is measured (see Appendix).

The correlation function given in Eq. (8) can be expressed in terms of the surface orientation correlation function  $g(s)$  (representing the surface structure) and of the surface propagator  $P(s,t)$  (standing for the displacement probability density along the surface):

$$G(t) = \int g(s) P(s,t) d^2s = \int_0^\infty g(s) P(s,t) 2\pi s ds. \quad (10)$$

Using Parseval's theorem for the two-dimensional spatial Fourier transforms of the surface correlation function  $\tilde{S}(\mathbf{k})$  and of the surface propagator  $p(\mathbf{k},t)$ , leads to the  $k$  space picture of this formalism,

$$G(t) = \frac{1}{(2\pi)^2} \int \tilde{S}(\mathbf{k}) p(\mathbf{k},t) d^2k = \frac{1}{(2\pi)^2} \int_0^\infty S(k) p(k,t) dk, \quad (11)$$

where  $k$  is the wave number as the variable conjugate to  $s$ , and

$$S(k) \equiv 2\pi k \tilde{S}(\mathbf{k}). \quad (12)$$

The conjugate  $k$  space variant of the surface correlation function  $g(s)$  is termed the “(static radial) orientational structure factor.” It is given by the Hankel transform

$$S(k) = (2\pi)^2 k \int_0^\infty g(s) J_0(ks) s ds \quad (13)$$

implying the Bessel function of zeroth order,  $J_0(ks)$ . The orientational structure factors  $\tilde{S}(k)$  and  $S(k)$  [Eq. (13)], actually are formal equivalents of the static structure factor known from scattering theory  $\tilde{S}_{sc}(k)$  [see Eq. (2)], as far as surface orientation pair correlations are considered instead of density-density correlations. How far the coincidence extends remains to be discussed below. The corresponding counterpart of the propagator  $P(s, t)$  likewise is

$$p(k, t) = 2\pi \int_0^\infty P(s, t) J_0(ks) s ds. \quad (14)$$

Surface propagators to be examined are a Gaussian displacement probability density

$$P(s, t) = \frac{1}{4\pi} \frac{\exp\{-s^2/(4Dt)\}}{Dt} \quad (15)$$

and a Cauchy distribution

$$P(s, t) = \frac{1}{2\pi} \frac{ct}{[(ct)^2 + s^2]^{3/2}}. \quad (16)$$

The respective displacement rates are determined by the diffusion coefficient  $D$  and the constant  $c$ , which is of the dimension of a velocity.

The Gaussian displacement probability density corresponds to ordinary diffusion. The Cauchy distribution, on the other hand, is expected for Lévy walks [23], as predicted by Bychuk and O’Shaughnessy for adsorbate surface diffusion in the strong-adsorption limit. For this limit, “bulk mediated surface diffusion” (BMSD) was predicted, provided that the surface displacements are short relative to the root mean squared displacements in the bulk on a time scale shorter than the so-called retention time [8,24].

The  $k$  space representation of these surface propagators is commonly given by [25,26]

$$p(k, t) = e^{-t/\tau_k}. \quad (17)$$

The mode correlation times are defined by

$$\tau_k = \frac{1}{Dk^2} (\text{Gauss}), \quad \tau_k = \frac{1}{ck} (\text{Cauchy}), \quad (18)$$

respectively.

The RMTD correlation and intensity functions read

$$G(t) = \frac{1}{(2\pi)^2} \int_0^\infty S(k) e^{-t/\tau_k} dk, \quad (19)$$

$$\mathcal{I}(\omega) = \frac{1}{(2\pi)^2} \int_0^\infty S(k) \frac{2\tau_k}{1 + \omega^2 \tau_k^2} dk, \quad (20)$$

where  $\tau_k = \tau_k(k)$  depends on the propagator effective for surface diffusion according to Eq. (18). Note that any temperature dependence is determined by the respective transport parameter  $D$  or  $c$ .

### III. ORIENTATIONAL STRUCTURE FACTOR FOR FRACTAL SURFACES

The density-density pair correlation function for surface fractals  $g_{sc}(s)$  describes correlations of surface elevations. The orientation-orientation pair correlation function  $g(s)$ , on the other hand, reflects orientational correlations. Both functions are interrelated and indicate how fast the surface properties change when a particle migrates along it. On the other hand, in the case of infinitely extended and planar surfaces, no correlation loss is associated with translations along the surface (compare Ref. [27]).

In this context, surface fractals are characterized by power-law related expressions for the density-density pair correlation function  $g_{sc}(s)$  [Eq. (4)] and the static structure factor  $\tilde{S}_{sc}(k)$  [Eq. (3)]. The densities at a distance  $s$  from the surface position  $s=0$  will only be correlated strongly if  $s < \xi$  where  $\xi$  is the correlation length of the surface. This becomes obvious if the distance vector is a tangent at the surface position  $s=0$ . The probability density that this distance vector points to a more remote element on the surface will be large if the surface is smooth and, hence, slowly varying in its orientation. Conversely, it will be small if the orientation correlation length is shorter than the distance considered.

It is therefore not unreasonable to assume a close relationship between the density-density pair correlation function  $g_{sc}(s)$  [Eq. (4)], and the orientation-orientation pair correlation function  $g(s)$  [Eq. (9)]. A more elaborate consideration of this hypothesis will be presented in the Appendix. The surface correlation function is presumed to scale as

$$g(s) \propto s^{2-D_s}. \quad (21)$$

Likewise the orientational structure factor

$$\tilde{S}(k) = \int g(s) e^{-ik \cdot s} d^2s \quad (22)$$

obeys

$$\tilde{S}(k) \propto k^{D_s-4} \quad (23)$$

in the topologically two-dimensional isotropic space, and, according to the definition given in Eq. (12),

$$S(k) \propto k^{D_s-3}. \quad (24)$$

### IV. SPIN-LATTICE RELAXATION DISPERSION

#### A. Surface displacements by ordinary diffusion

Ordinary surface diffusion is characterized by the Gaussian propagator given in Eq. (15). Such a situation may arise when the liquid adsorbate is permanently residing on the surface, and merely translations along the surface occur. Examples are highly concentrated fine-particle or protein agglomerates [28] and nonfreezing surface layers [8,29]. The

latter arise when the bulklike phase of the adsorbate is frozen, so that liquid adsorbate molecules can only diffuse along the surface.

Under such circumstances the correlation and intensity functions for the RMTD relaxation mechanism on fractal surfaces are found by combining Eq. (7) either with Eq. (10) or (11) using the Gaussian propagator given in Eq. (15) or its  $k$  space counterpart according to Eq. (17) together with the left-hand expression in Eq. (18). Inserting the respective power laws given in Eqs. (21) or (24) provides

$$G(t) \propto (Dt)^{-(D_s-2)/2} \quad (25)$$

and

$$\mathcal{I}(\omega) \propto D^{-(D_s-2)/2} \omega^{(D_s-4)/2}. \quad (26)$$

Therefore, one expects a low-frequency dispersion of the spin-lattice relaxation time following

$$T_1 \propto D^{(D_s-2)/2} \omega^{(4-D_s)/2} \quad (\text{Gauss}). \quad (27)$$

### B. Surface displacements by Lévy walks

Non-Gaussian propagators arise for BMSD [24]. The term ‘‘surface diffusion’’ implies that the adsorbate molecule resides initially as well as finally on the surface irrespective of any bulk excursions in between. This condition is well fulfilled in times shorter than the retention time  $t_h$ . Adsorbate molecules then tend to stay in the vicinity of the surface, provided they were initially adsorbed (compare the computer simulation reported in Ref. [9]).

The correlation and intensity functions for the RMTD relaxation mechanism on fractal surfaces are derived in the same way as before, with the only difference now being that the propagator given in Eq. (16) or its  $k$  space counterpart, Eq. (17), in combination with the right-hand expression in Eq. (18) are used. Again inserting the respective power laws given at Eqs. (21) and (24) yields

$$G(t) \propto (ct)^{-(D_s-2)} \quad (28)$$

and

$$\mathcal{I}(\omega) \propto \begin{cases} c^{-(D_s-2)} \omega^{D_s-3} & \text{if } 2 < D_s < 3, \\ -c^{-(D_s-2)} \ln(\omega\tau_u) & \text{if } D_s = 3, \end{cases} \quad (29)$$

where  $\tau_u = 1/(ck_u)$  is the surface displacement correlation time corresponding to the upper wave-number cutoff value,  $k_u$ , i.e., to the static surface mode with the shortest wavelength (compare Refs. [4,8]). The low-frequency spin-lattice relaxation dispersion thus obeys

$$T_1 \propto \begin{cases} c^{D_s-2} \omega^{3-D_s} & \text{if } 2 < D_s < 3, \\ -c^{D_s-2} \frac{1}{\ln(\omega\tau_u)} & \text{if } D_s = 3. \end{cases} \quad (\text{Cauchy}) \quad (30)$$

### C. Limiting cases

In the limit  $D_s = 2$ , the spin-lattice relaxation dispersion for both the Cauchy and the Gaussian probability densities approaches  $T_1(\omega) \propto \omega$ . Corresponding dispersion slopes, indicating  $D_s \approx 2.0-2.1$ , were observed for densely packed

silica particle agglomerates [5]. These results, obtained for surface displacements of water molecules, ranging from  $10^1$  to  $10^2$  nm, are consistent with the observations of Avnir *et al.* [17] for such systems, valid on a nanometer scale.

Note that both Cauchy and Gaussian distributions predict the same frequency dependence of  $T_1$  for smooth surfaces. Hence, the statistics of surface diffusion cannot be distinguished in this case. A very remarkable feature of this limit is that spin-lattice relaxation becomes independent of temperature because the displacement parameters  $D$  and  $c$  do not show up anymore [see Eqs. (27) and (30)]. As a matter of fact, the temperature dependences found in porous media are often strikingly weak (compare the data reported in Ref. [29], for instance).

The opposite limit,  $D_s \rightarrow 3$ , indicates an extremely rough and rugged surface so that practically the whole Euclidean space is filled with the completely compressed ‘‘crumpled membrane’’ representing the surface. In this case, the spin-lattice relaxation dispersion is expected to display a square root frequency dependence  $T_1 \propto \omega^{1/2}$  and a logarithmic relationship  $T_1 \propto -1/\ln(\omega\tau_u)$  (where  $\omega\tau_u \ll 1$ ), for the Gauss and the Cauchy surface propagators, respectively. A square root frequency dependence of the deuterium spin-lattice relaxation time was actually found in globular protein agglomerates completely hydrated with heavy water in such a way that no bulklike water phase existed [4,30]. In this case the distribution of the static surface modes tends to be uniformly random in a certain range.

## V. APPLICATION TO A POROUS GLASS AND DISCUSSION

The RMTD low-frequency spin-lattice relaxation mechanism links dynamic properties of adsorbate molecules with the structural details of the adsorbent surface. This in particular means that the fractal surface dimension can be evaluated from the low-frequency  $T_1$  dispersion provided that fractal behavior exists. Typical systems where this may be pertinent are porous media with a relatively high surface-to-volume ratio. In our previous work we have studied a number of porous silica glasses [1,2,8] and fine-particle agglomerates [4,5] using field-cycling NMR relaxometry [3].

Let us now consider the systems dimethylsulfoxide (DMSO) and malononitrile filled into porous silica glass B10 with a mean pore dimension of 10 nm. Experimental details can be found in Ref. [8]. Figure 2 shows the proton  $T_1$  dispersion measured in DMSO and in the adsorbate diluted by its deuterated version. The coincidence of the two data sets proves that the spin interactions dominating spin-lattice relaxation in DMSO are of an intramolecular nature. Two different temperatures have been examined.

At 270 K the bulklike DMSO in the pores is frozen and does not perceptibly contribute to the spin-lattice relaxation rate. It rather is the nonfreezing interfacial liquid existing in the form of a one to two molecular diameters thick nonfreezing surface layer that is responsible for the observed  $T_1$  dispersion. In such a situation one expects that diffusion along the surface is normal, that is, it is governed by a Gaussian propagator.

On the other hand, at 291 K when all DMSO molecules are in the liquid state, the bulklike adsorbate phase contrib-

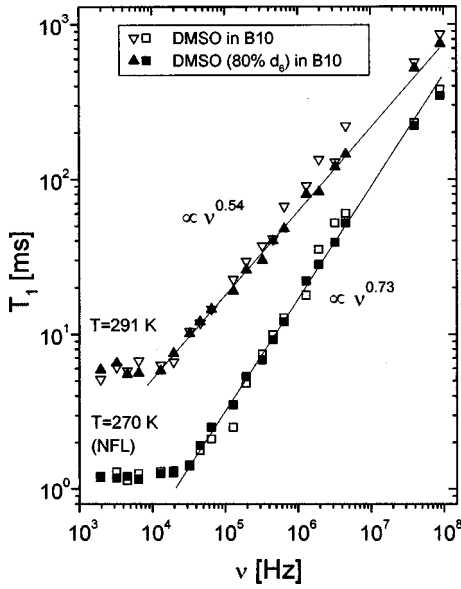


FIG. 2. Frequency dependence of the proton spin-lattice relaxation time of dimethylsulfoxide (DMSO) in porous glass B10 above and below the freezing temperature of the bulklike liquid. Data for an isotopically diluted sample (80% DMSO- $d_6$ ) are also included. The relaxation times of the partially frozen sample at 270 K refer to the slowly decaying component of the NMR signal corresponding to the nonfreezing surface layers.

utes, and the “bulk-mediated surface diffusion” mechanism can occur [24]. As already outlined above, the consequence is that in the strong-adsorption limit (which is pertinent here) and for surface displacements short relative to diffusion in the bulk, a Cauchy distribution applies for the propagation of adsorbate molecules along the surface.

At both temperatures a power-law behavior was found over three to four decades of the Larmor frequency. The results are

$$T_1 \propto \nu^{0.73 \pm 0.04} \quad \text{for } T = 270 \text{ K} \quad (31)$$

and

$$T_1 \propto \nu^{0.54 \pm 0.04} \quad \text{for } T = 291 \text{ K}. \quad (32)$$

Evaluating these power laws according to the Gaussian and Cauchy distributions, respectively, leads to a common orientational structure factor obeying

$$S(k) \propto k^{-0.5 \pm 0.04}. \quad (33)$$

We infer a surface fractal dimension of

$$D_s = 2.5 \pm 0.04. \quad (34)$$

This value very favorably fits the range of typical literature data evaluated for controlled porous glass on the basis of x ray and neutron scattering experiments [31].

Consistent results are obtained with malononitrile filled into the same porous glass. Figure 3 shows the proton spin-lattice relaxation time as a function of the frequency for malononitrile in Bioran B10 at 275 K (nonfreezing surface layers) and 291 K (adsorbate unfrozen). Approaching the dispersion slopes by power laws again suggests the same

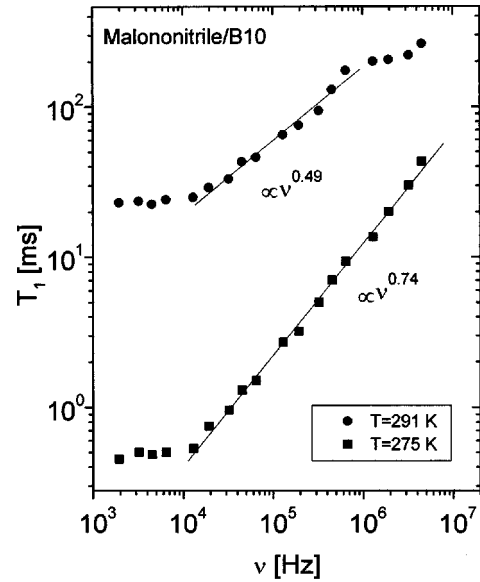


FIG. 3. Frequency dependence of the proton spin-lattice relaxation time of malononitrile in porous glass B10 above and below the freezing temperature of the bulklike liquid. The relaxation times of the partially frozen sample at 275 K refer to the slowly decaying component of the NMR signal corresponding to the nonfreezing surface layers.

orientational structure factor. The exponent is estimated to be  $-0.49 \pm 0.05$ , in coincidence with that given in Eq. (33). Thus it is demonstrated that the same surface fractal dimension comes out for a very different adsorbate species, but the same adsorbent.

Note that similar  $T_1$  dispersion slopes have also been observed with several other polar liquids in porous glass Bioran B30 [29] with a mean pore dimension of 30 nm. This again indicates that the surface structure acts on all adsorbate liquids the same way. The only exception found in this context is water on polar surfaces. The water anomaly in this and other respects will be the subject of another study to be published elsewhere.

## ACKNOWLEDGMENTS

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## APPENDIX

In this appendix a simplified model of the surface correlation function illustrating our working hypothesis will be presented. Fractal surface structure can be studied using a profile analysis [11]. For simplicity, we will restrict ourselves to the consideration of a one-dimensional profile line function  $h = h(x)$  across the surface. The quantity  $h(x)$  is the altitude of the surface measured as a function of the position  $x$  along the baseline. This baseline is chosen in such a way that  $\langle h(x) \rangle = 0$ . A schematic illustration is given in Fig. 1.

The profile line  $h = h(x)$  is a random self-affine function

whose variance scales with the length of a section  $\Delta x$  on the baseline according to

$$\langle h^2(\Delta x) \rangle \propto |\Delta x|^{2H}. \quad (\text{A1})$$

The length  $l$  of a self-affine curve can be measured with a certain resolution defined, in our case, by the diameter of an adsorbate molecule.  $l$  scales with  $\Delta x$  (i.e., with the linear size of the system) as [10,13]

$$l(\Delta x) \propto (\Delta x)^{d_H}, \quad (\text{A2})$$

where  $d_H$  is the Hausdorff dimension of the surface profile which is related to the Hurst exponent  $H$  by

$$d_H = 2 - H. \quad (\text{A3})$$

The Hausdorff dimension  $d_H$  refers to a topologically one-dimensional object embedded in the two-dimensional space; hence,  $1 \leq d_H \leq 2$ . A surface, on the other hand, is a topologically two-dimensional object whose surface area  $A$  scales with the area  $(\Delta x)^2$  on the base plane according to

$$A(\Delta x) \propto (\Delta x)^{D_s}. \quad (\text{A4})$$

The range of the exponent, that is, the surface fractal dimension  $D_s$ , is  $2 \leq D_s \leq 3$ . All these characteristic parameters are now related to each other by the known lemma [13,32]

$$D_s = d_H + 1 = 3 - H. \quad (\text{A5})$$

The surface orientation correlation function  $g(s)$  was introduced in terms of second-order spherical harmonics taken for the orientations of the surface normals at a (curvilinear) distance  $s$  [see Eq. (9)].  $s$  is the displacement in the (topologically two-dimensional) second-order base plane corresponding to the average spatial orientation of the (rough) surface. In the present approach we consider a planar base plane and interpret the surface correlation function directly as the correlation function of the normal vectors on a one-dimensional profile line,  $\vec{n}$ , separated by the Euclidean distance  $\Delta x$ .

This simplification appears to be justified as long as one restricts oneself to the scaling-law discussion of this paper. In particular, if the external magnetic field is assumed to be perpendicular to the base line, the azimuth angle in the second-order spherical harmonics has a fixed value. The corresponding term in correlation functions of the type given in Eq. (9) hence cancels. Furthermore, the terms referring to the polar angle  $\vartheta$  can be rewritten in the forms  $\sin \vartheta \cos \vartheta = \frac{1}{2} \sin(2\vartheta) = \frac{1}{2} \sin \tilde{\vartheta}$  and  $\sin^2 \vartheta = \frac{1}{2} [1 - \cos(2\vartheta)] = \frac{1}{2} (1 - \cos \tilde{\vartheta})$ . That is, the polar-angle terms in the second-order spherical harmonics can be traced back to linear trigonometric functions of the double polar angle.

Keeping this in mind and identifying the distance  $s$  with the baseline section  $\Delta x$  introduced above, we consider the correlation function of the normal vectors separated by a distance  $\Delta x$ ,

$$\begin{aligned} g(\Delta x) &= \langle \vec{n}(x) \cdot \vec{n}(x + \Delta x) \rangle \\ &= \langle \cos[\vartheta(x + \Delta x) - \vartheta(x)] \rangle \\ &= \langle \cos[\vartheta(x + \Delta x)] \cos[\vartheta(x)] \rangle \\ &\quad + \langle \sin[\vartheta(x + \Delta x)] \sin[\vartheta(x)] \rangle, \end{aligned} \quad (\text{A6})$$

where  $\vartheta$  in this context means the angle between the normal vectors on the baseline and on the profile line  $h = h(x)$ . The brackets denote averages over the baseline segment  $\Delta x$ . Note that this is equivalent to averaging over any profile curve section because of the self-affinity property.

We now make use of the relations

$$\tan[\vartheta(x)] = \frac{dh}{dx} \equiv h'(x), \quad (\text{A7})$$

$$\cos[\vartheta(x)] = \frac{1}{\sqrt{1 + h'^2(x)}} = \frac{dx}{dl}, \quad (\text{A8})$$

$$\sin[\vartheta(x)] = \frac{h'(x)}{\sqrt{1 + h'^2(x)}} = h'(x) \frac{dx}{dl}, \quad (\text{A9})$$

where  $l$  is the length measured along the profile line (in ‘yardstick’ units). The correlation functions in Eq. (A6) can then be evaluated according to

$$\begin{aligned} &\langle \cos[\vartheta(x + \Delta x)] \cos[\vartheta(x)] \rangle \\ &= \frac{1}{l(\Delta x)} \int_{l(\Delta x)} \cos[\vartheta(x + \Delta x)] \cos[\vartheta(x)] dl \\ &= \frac{1}{l(\Delta x)} \int_0^{\Delta x} \cos[\vartheta(x + \Delta x)] dx \\ &= \frac{1}{l(\Delta x)} \int_0^{\Delta x} \frac{1}{\sqrt{1 + h'^2(x + \Delta x)}} dx \end{aligned} \quad (\text{A10})$$

[ $l(\Delta x)$  is the length of the curve  $h(x)$  on the line segment  $\Delta x$ ],

$$\begin{aligned} &\langle \sin[\vartheta(x + \Delta x)] \sin[\vartheta(x)] \rangle \\ &= \frac{1}{l(\Delta x)} \int_{l(\Delta x)} \sin[\vartheta(x + \Delta x)] \sin[\vartheta(x)] dl \\ &= \frac{1}{l(\Delta x)} \int_0^{\Delta x} \frac{h'(x) h'(x + \Delta x)}{\sqrt{1 + h'^2(x + \Delta x)}} dx. \end{aligned} \quad (\text{A11})$$

Assuming small tilt angles, so that  $h'^2(x) \ll 1$ , the integrands in Eqs. (A10) and (A11) can be expanded and approximated to the lowest nontrivial order. Furthermore, inserting Eq. (A2) thus leads to

$$\langle \cos[\vartheta(x + \Delta x)] \cos[\vartheta(x)] \rangle \propto (\Delta x)^{1 - d_H} - O_1((\Delta x)^{3(1 - d_H)}), \quad (\text{A12})$$

$$\langle \sin[\vartheta(x + \Delta x)] \sin[\vartheta(x)] \rangle \propto (\Delta x)^{3(1 - d_H)}, \quad (\text{A13})$$

where we have used the fact that the mean squared fluctuation of the profile line function scales according to Eq. (A1). In the frame of this simplified consideration, it becomes clear that the leading term of the orientation correlation function of fractal surfaces scales as

$$g(\Delta x) \propto (\Delta x)^{2-D_s}. \quad (\text{A14})$$

In this derivation we have tacitly assumed that the profile line is a random function  $h = h(x)$  relative to a straight baseline with the coordinate axis  $x$ . In reality, the roughness of surfaces in porous glasses, for instance, is to be considered relative to a baseline curvilinearly representing the mean cur-

vature of the pore. In two topological dimensions, the surface roughness is to be measured based on a second-order plane, which ideally may take the form of a cylinder or a sphere.

Since the second-order base plane also effects the surface orientation in addition to the random roughness in the sense of the above treatment, the validity of our formalism is intrinsically restricted to the correlation length  $\xi$  of that second-order base plane. Therefore, diffusive displacements along the surface are to be measured in curvilinear coordinates  $s$  on the second-order base plane instead of the Euclidean distance  $\Delta x$  in Eq. (A14). The range of relevant distances is then restricted to  $a_0 < s < \xi$ .

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