

Propagator representation of anomalous diffusion: The orientational structure factor formalism in NMR

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(Received 3 March 1999)

The radial Fourier transform for the isotropic space with a fractal dimension is discussed. The moments of diffusive displacements with non-Gaussian propagators arising as solutions of fractional diffusion equations are calculated. The Fourier propagator is applied to NMR correlation and spectral density functions in context with the orientational structure factor formalism. It is shown that the low-frequency molecular fluctuations of liquids in porous media with strong or forced adsorption at surfaces are due to reorientations mediated by translational displacements caused by surface diffusion of the adsorbate molecules. In terms of this formalism, field-cycling NMR experiments provide information on the static and dynamic fractal dimensions related to surface diffusion. The experimental results for liquids in porous silica glass can be explained by a surface fractal dimension $d_f=2.5$, where the mean squared displacement scales as $\langle r^2(t) \rangle \propto t^{2/d_w}$ with $d_w=1$ (ballistic transport), if the surface population can exchange with the bulklike phase in the pores, and with $d_w=2$, if the bulklike phase is frozen. The former dynamics is interpreted in terms of bulk-mediated surface diffusion. [S1063-651X(99)08807-8]

PACS number(s): 05.40.-a, 61.43.Hv, 68.35.Ct, 68.35.Fx

I. INTRODUCTION

The anomalous transport in disordered media can be discussed either in terms of a random walk (or statistical) approach or on the basis of a fractional diffusion equation (FDE). Fractional or enhanced diffusion is characterized by the mean squared displacement law

$$\langle r^2(t) \rangle \propto t^{2/d_w}, \quad (1)$$

where the dynamic parameter d_w (usually called the anomalous diffusion exponent) of the corresponding (anomalous) random process deviates from Einstein's classical result $d_w=2$. Non-Gaussian propagators arise as the solutions of fractional diffusion equations, which are mostly discussed for $d_w > 2$ (see Refs. [1–3]). However, it can be shown [4–6] that this type of equation can be solved for the superdiffusive regime $1 \leq d_w < 2$ as well.

With respect to the exponent d_w , anomalous diffusion can be classified [5,6] as follows.

(i) $d_w=2$ corresponds to the classical Brownian motion described by a Gaussian propagator. From the statistical point of view, this random process is characterized by fixed step length and waiting time [1].

(ii) $d_w > 2$ corresponds to the dispersive diffusion regime described by a non-Gaussian displacement probability density. In the frame of the continuous time random walk (CTRW) model, processes of this kind are due to temporal disorder, characterized by power-law distributions of the waiting times [1].

(iii) $1 < d_w < 2$ defines the intermediate region of superdiffusion. Enhanced transport of this sort results from long-tailed step-length and waiting-time distributions (i.e., spatial or/and temporal disorder of the random process).

(iv) $d_w=1$ indicates ballistic transport. In this case, the fractional diffusion equation adopts the form of a wave equation.

In the present study, the reciprocal-space solutions for displacement distributions are employed in the frame of the orientational structure factor formalism [7,8] in order to calculate the NMR correlation and intensity functions and the frequency dependence of the spin-lattice relaxation rate for molecular dynamics dominated by reorientation mediated by translational displacements (RMTD) along surfaces [9]. The static and dynamic fractal dimensions, d_f and d_w , respectively, which are related to diffusion of strongly adsorbed molecules along fractal surfaces of porous glass, are evaluated. The experimental data provide evidence for superdiffusive surface displacements with $d_w=1$ if the surfacelike and bulklike phase are in fast exchange. This result is consistent with the model of bulk-mediated surface diffusion developed by Bychuk and O'Shaughnessy [10]. That is, on the time scale of the so-called retention time, surface diffusion takes place in the form of Lévy walks.

II. ANOMALOUS DIFFUSION: A FRACTIONAL CALCULUS APPROACH

Fick's second diffusion law reads

$$\frac{\partial}{\partial t} P(r,t) = \lambda \nabla^2 P(r,t), \quad (2)$$

where λ is equal to the diffusion coefficient, and ∇ is the nabla operator. $P(r,t)$ is the probability density of diffusive displacements r in a time t (the propagator). The well-known solution of Eq. (2) is the Gaussian probability density.

Anomalous diffusion processes on fractal structures can be treated using the fractional diffusion equation [4,6]. The integral representation of the FDE reads

$$P(r,t) - P(r,0) = \int_0^t \Lambda(t-t') \nabla^2 P(r,t') dt'. \quad (3)$$

The memory kernel $\Lambda(t-t')$ reflects temporal disorder of an anomalous transport process. Assuming $\Lambda(t-t') = \lambda (t-t')^{\beta-1}/\Gamma(\beta)$, one gets [4,6]

$$P(r,t) - P(r,0) = \lambda {}_0D_t^{-\beta} \nabla^2 P(r,t), \quad (4)$$

where ${}_0D_t^{-\beta}$ is the Riemann-Liouville integral operator [11]. The units of the transport constant λ are related to that of the ordinary diffusion coefficient D_0 : $[\lambda] = [D_0/\tau^{\beta-1}]$. The differential form of this equation can be expressed by the following time-fractional diffusion equation

$$\frac{\partial^\beta}{\partial t^\beta} P(r,t) - \frac{\partial^\beta}{\partial t^\beta} P(r,0) = \lambda \nabla^2 P(r,t). \quad (5)$$

Note that the important term $(\partial^\beta/\partial t^\beta)P(r,0) = P(r,0)t^{-\beta}/\Gamma(1-\beta)$, accounting for the initial-value condition $P(r,0) = \delta(r)$, is often not mentioned explicitly in the literature [3,5,12,13]. Actually, this term can be omitted only in the case $\beta \in \mathcal{N}_0$ but is essential if the diffusion equation really has a fractional character. Obviously, for $\beta=1$, we have $(\partial/\partial t)P(r,0) = 0$, and hence the conventional diffusion equation, Eq. (2), is recovered. If $\beta=2$, i.e., $(\partial^2/\partial t^2)P(r,0) = 0$, Eq. (5) takes the form of a wave equation and describes the ballistic transport regime.

The geometry of the fractal structure and the dynamics of the corresponding random process are described by the static fractal dimension d_f and by the dynamic fractal dimension d_w (i.e., the anomalous diffusion exponent), respectively. Note that ∇ in the FDE Eq. (5) represents the nabla operator in D dimensions [3,5]. The order of the fractal time derivative, β , is related to d_w by $\beta = 2/d_w$ and is independent of the static parameter d_f .

Occasionally, the operator ∇^α is discussed in the literature [6,12] instead of ∇^2 . The FDE is then certainly treatable in one dimension, and leads to solutions in the form of Lévy distributions [6]. However, the interpretation of the fractional spatial derivative in more dimensions remains unclear, whereas the use of the operator ∇^2 in Eqs. (4) or (5) is motivated by the radial symmetry of the (fractal) space under consideration: In the reciprocal space, Eqs. (4) or (5) are converted into

$$\frac{\partial}{\partial t} p(k,t) = -\lambda k^2 {}_0D_t^{1-\beta} [p(k,t)]. \quad (6)$$

The square of the wave number, $k^2 = |\mathbf{k}|^2$, is equal to the sum of the d components of \mathbf{k} if the space in which the random motion takes place is defined by d Euclidean dimensions. On the other hand, if the random-walk space is of a fractal dimensionality, the number of the \mathbf{k} components is defined by the global dimension D (e.g., $D=2$ for a fractal surface, $D=3$ for a fractal volume).

Schneider and Wyss [4] solved Eq. (5) after rescaling it so that $\lambda = 1$. However, the parameter λ is important for experiments since it is related to the diffusion coefficient D_0 , and, as a consequence, to the temperature dependence of the diffusion process.

The solution [4] of Eq. (6) is given by the Mittag-Leffler function

$$p(k,t) = E_{\beta,1}[(-\lambda t^\beta k^2)] = \sum_{j=0}^{\infty} \frac{(-\lambda t^\beta k^2)^j}{\Gamma[1+\beta j]}, \quad (7)$$

where $\beta = 2/d_w$ can be found with the approach suggested by Metzler and Nonnenmacher [5]. The inverse D -dimensional Fourier transformation (see Appendix) of the characteristic function given in Eq. (7) leads to the real-space propagator in terms of Fox's \mathcal{H} function [14],

$$P(r,t) = 2^{-1-D} \pi^{-D/2} t^{-D/d_w} \lambda^{-D/2} \times \mathcal{H}_{1,2}^{2,0} \left[\frac{r}{2\sqrt{\lambda} t^{1/d_w}} \left| \begin{array}{c} \{ \} \\ \left\{ \left\{ 1 - \frac{D}{d_w}, \frac{1}{d_w} \right\} \right\} \end{array} \right. \right]. \quad (8)$$

Note that the space dimension D does not enter in the expression for $p(k,t)$ [Eq. (7)], in contrast to the real-space propagator [Eq. (8)]. Thus, in this model, $p(k,t)$ exclusively provides the dynamical information indicated by d_w , regardless of the structure of the r space. For $D=2$, Eq. (8) represents our surface propagator.

The m th moment of the propagator at Eq. (8) reads (see Appendix)

$$\langle r^m(t) \rangle = 2^{m-1} D \lambda^{m/2} \frac{\Gamma[(2+m)/2] \Gamma[(m+D)/2]}{\Gamma[(2+D)/2] \Gamma[1+m/d_w]} t^{m/d_w} \quad (9)$$

so that the second moment takes the form

$$\langle r^2(t) \rangle = \frac{2D\lambda}{\Gamma[1+2/d_w]} t^{2/d_w}. \quad (10)$$

In the limit $\lambda t^{2/d_w} k^2 \ll 1$, the propagator given in Eq. (7) approaches

$$p(k,t) = \exp\left(-\frac{\lambda t^{2/d_w} k^2}{\Gamma[1+2/d_w]}\right). \quad (11)$$

With this expression, one finds

$$\langle r^m(t) \rangle = 2^{m-1} D \lambda^{m/2} \frac{\Gamma[(m+D)/2]}{\Gamma[(2+D)/2]} \frac{t^{m/d_w}}{\Gamma[1+2/d_w]^{m/2}}, \quad (12)$$

in general, and

$$\langle r^2(t) \rangle = \frac{2D\lambda}{\Gamma[1+2/d_w]} t^{2/d_w} \quad (13)$$

for the second moment. Comparing Eqs. (10) and (13), one realizes that the asymptotic form of the Mittag-Leffler propagator given in Eq. (11) can be used to calculate the mean squared displacement instead of the exact solution at Eq. (7). This finding is of relevance for practical applications since the asymptotic form of $p(k,t)$ is more obvious than the exact Mittag-Leffler representation of the propagator.

In Ref. [6], an alternative approach to superdiffusion was considered for the fractional diffusion equation in one dimension. In that case, the k -space solution turns out to be equal to the characteristic Kohlrausch-Williams-Watts function,

$$p(k,t) = \exp(-at|k|^\alpha), \quad 0 < \alpha < 2 \quad (14)$$

where ($a > 0, t > 0$). By means of $p(k,t)$ given in Eq. (14), Lévy distributions $\tilde{p}(r,t)$ in the real space can be generated with the aid of the inverse Fourier transform [6]. For large r , one obtains $\tilde{p}(r,t) \propto t/r^{\alpha+1}$ as the limiting form of the Lévy α -stable process in a one-dimensional space.

III. THE RMTD RELAXATION MECHANISM AND THE ORIENTATIONAL STRUCTURE FACTOR

Proton spin-lattice relaxation in liquids is predominantly due to fluctuations of the intramolecular dipole-dipole interaction among the spin-bearing nuclei. That is, molecular dynamics reorients the molecules so that dipolar coupling is modulated. In context with adsorbate diffusion along rough surfaces, fluctuations slow compared with bulk correlation times are governed by reorientations mediated by translational displacements along rough and curved surfaces [8,15–18].

Molecular fluctuations are described by the autocorrelation function $G(t)$, and, in the frequency domain, by the intensity function $\mathcal{I}(\omega)$. The latter is defined as the cosine Fourier transform of $G(t)$,

$$\mathcal{I}(\omega) = 2 \int_0^\infty G(t) \cos(\omega t) dt. \quad (15)$$

The spin-lattice relaxation rate is given by

$$\frac{1}{T_1} = \left(\frac{\mu_0}{4\pi} \right)^2 \frac{3}{2} \gamma^4 \hbar^2 I(I+1) \langle |F^{(1)}|^2 \rangle [\mathcal{I}(\omega) + 4\mathcal{I}(2\omega)]. \quad (16)$$

A technique suitable to record the frequency dependence of this function over several orders of magnitude is field-

cycling NMR relaxometry [9]. The information probed in this way refers to the autocorrelation function via the intensity function.

The correlation function $G(t)$ virtually reflects the correlation of molecular orientations at the moments t' and $t' + t$. Molecular reorientations in bulk liquids are a consequence of rotational diffusion. If the molecule is adsorbed on a surface, this rotational diffusion is hindered and incomplete with respect to the solid angle range covered. That is, residual orientational correlations persist on a time scale much longer than that of ordinary rotational diffusion. The mechanism coming at longer times into play is ‘reorientation mediated by translational displacements’ along rough surfaces. The formalism is described in more detail in Refs. [7–9,15,16,18]. Thus, on a correspondingly long time scale, nuclear spin-lattice relaxation is dominated by surface diffusion.

Displacements of the adsorbed molecule along the surface are characterized by the propagator $P(s,t)$ on the one hand, and the orientational correlation at sites separated by the distance s on the other. The latter is described by the surface orientation correlation function $g(s)$ which can be expressed in terms of second-order spherical harmonics $Y_{2,-1}(\mathbf{\Omega})$,

$$\begin{aligned} g(s) &= 4\pi \langle Y_{2,-1}(\mathbf{\Omega}_0) Y_{2,-1}(\mathbf{\Omega}_s) \rangle_{s_0 \mathbf{\Omega}_0 \mathbf{\Omega}_s} \\ &= \frac{4\pi}{A} \int d^2 s_0 \int d\mathbf{\Omega}_0 \int d\mathbf{\Omega}_s Y_{2,-1}(\mathbf{\Omega}_0) \\ &\quad \times Y_{2,-1}(\mathbf{\Omega}_s) \Phi(\mathbf{\Omega}_0, \mathbf{\Omega}_s, s). \end{aligned} \quad (17)$$

The quantity A is the surface area accessible by surface diffusion on a time scale of the order T_1 . The vectors $\mathbf{\Omega}_0$ and $\mathbf{\Omega}_s$ denote the surface orientations at the initial and final positions on the surface, s_0 and $s_0 + s$, respectively. The function $\Phi(\mathbf{\Omega}_0, \mathbf{\Omega}_s, s) d\mathbf{\Omega}_0 d\mathbf{\Omega}_s$ is the conditional probability that the surface orientation at the position s is within $\mathbf{\Omega}_s$ and $\mathbf{\Omega}_s + d\mathbf{\Omega}_s$ if the surface orientation at the position s_0 is within $\mathbf{\Omega}_0$ and $\mathbf{\Omega}_0 + d\mathbf{\Omega}_0$. Expressing $\Phi(\mathbf{\Omega}_0, \mathbf{\Omega}_s, s)$ by the product of δ functions averaged over all possible initial positions, $\Phi(\mathbf{\Omega}_0, \mathbf{\Omega}_s, s) = \langle \delta(\mathbf{\Omega}(s_0) - \mathbf{\Omega}_0) \delta(\mathbf{\Omega}(s_0 + s) - \mathbf{\Omega}_s) \rangle_{s_0}$, leads to

$$g(s) = 4\pi \langle Y_{2,-1}(\mathbf{\Omega}(s_0)) Y_{2,-1}(\mathbf{\Omega}(s_0 + s)) \rangle_{s_0}. \quad (18)$$

Random surfaces may be discussed by considering a one-dimensional surface profile [18]. Furthermore, it can be shown that the surface correlation function given above in terms of second-order spherical harmonics essentially decays the same way as the correlation function of the normal vectors, $g(x) \approx \langle \mathbf{n}(x_0) \cdot \mathbf{n}(x_0 + x) \rangle_{x_0}$. On the basis of fractal scaling relations, the proportionality $g(x) \propto x^{H-1}$ can be obtained, where H is the roughness exponent of the surface profile related to the surface fractal dimension by $H = 3 - d_f$.

On these grounds and assuming radial symmetry, we suggest that for fractal surfaces characterized by the fractal dimension d_f , the surface correlation function scales as

$$g(s) \propto s^{2-d_f}, \quad (19)$$

where s is the curvilinear displacement within the two-dimensional (2D) space of the second-order base plane relative to which the surface roughness is considered. Equation (19) is valid in the scale-invariance range $\xi_0 < s < \xi_1$, where ξ_0 is of the order of the molecular diameter, and ξ_1 is of the order of the mean pore size.

For the analysis in the following, we recall that $g(s)$ reflects the geometry of the surface, whereas $P(s, t)$ accounts for the dynamics on the surface. That is, we have to set $D = 2$ in Eq. (8). The same applies to the correlation function $G(t)$, which is calculated in the base-plane space of the dimension $D=2$. In the isotropic case, $G(t)$ can be expressed by [8]

$$G(t) = \int_0^\infty g(s)P(s, t)2\pi s ds. \quad (20)$$

This is the real-space variant. In the reciprocal space, the correlation function reads

$$G(t) = \frac{1}{(2\pi)^2} \int_0^\infty S(k)p(k, t)dk, \quad (21)$$

where the orientational structure factor $S(k)$ is introduced as a counterpart to the surface correlation function $g(s)$. The two functions are related by the spatial Hankel transform

$$S(k) = (2\pi)^2 k \int_0^\infty s g(s) J_0(ks) ds, \quad (22)$$

with $J_0(ks)$ the Bessel function of zeroth order. The Hankel transform is a special case of the radial Fourier transform for an isotropic space with two dimensions (see, also, Appendix).

Actually, $S(k)$ in the RMTD model is analogous to the static structure factor used in scattering theories. The only difference is that the orientational structure factor in context of NMR reflects orientational rather than material density correlations [18]. For fractal surfaces, $S(k)$ is a power law $S(k) \propto k^{d_f-3}$, leading to power-law decays of $G(t)$ and $\mathcal{I}(\omega)$.

Equation (21) stipulates the availability of $p(k, t)$ in the whole wave number range. However, the orientational structure factor is a power law only in the scale-invariance range of the surface. Therefore, the decays of the correlation and intensity functions calculated below apply in correspondingly limited time and frequency ranges, respectively. This should be kept in mind when contemplating the examples in the following.

The correlation function $G(t)$ can be calculated for the RMTD mechanism with the help of Eq. (20) using the exact representation of a real-space propagator Eq. (8). Alternately, the calculation can be performed in the k space [Eq. (21)] using the asymptotic k -space distribution given by Eq. (11). Thus, in terms of the fractional-time diffusion equation approach, one finds

$$G(t) \propto t^{-(d_f-2)/d_w}, \quad (23)$$

provided that the displacements along the surface correspond to the scale-invariance length scale of the surface.

On the other hand, in context with Lévy walks and a fractal-space diffusion equation, one gets

$$G(t) \propto t^{-(d_f-2)/\alpha}. \quad (24)$$

This suggests that α has the character of a fractal dimension as already pointed out by Klafter *et al.* [1] for the same parameter in Eq. (14). Comparing $G(t)$ calculated in terms of the time-fractal and space-fractal FDE, Eqs. (23) and (24), respectively, indicates indeed that the exponent α in Eq. (14) corresponds to d_w in the context of the fractional diffusion theory. This conclusion thus elucidates the nature of a very fundamental parameter.

The counterpart of the correlation function $G(t)$ is the intensity function. In the present context, it reads

$$\mathcal{I}(\omega) \propto \omega^{-(2+d_w-d_f)/d_w} \quad (25)$$

according to Eq. (15).

In the case of normal two-dimensional diffusion, i.e., $d_w = \alpha = 2$, the RMTD correlation and intensity functions scale as

$$G(t) \propto t^{-(d_f-2)/2} \quad (d_f > 2) \quad (26)$$

and

$$\mathcal{I}(\omega) \propto \omega^{-(4-d_f)/2} \quad (2 \leq d_f \leq 3), \quad (27)$$

respectively. Normal 2D diffusion is expected, for example, in the thin interfacial liquid layer arising between the matrix and the frozen bulklike adsorbate at temperatures below the freezing point. In that case, bulk-mediated surface diffusion is prevented, and we are dealing with ordinary diffusion in a two-dimensional system.

On the other hand, at temperatures above the freezing point and under strong-adsorption conditions, the adsorbate molecules perform random walks along the surface as a consequence of intermittent excursions into the bulklike phase. Surface diffusion on this basis was shown to be anomalous within the so-called retention time (see Refs. [10,19]). The character of surface diffusion then turns out to be of the ballistic type, i.e., $d_w = 1$. This sort of random displacement is also known as Lévy walk. The corresponding RMTD functions are

$$G(t) \propto t^{-(d_f-2)} \quad (2 < d_f \leq 3) \quad (28)$$

and

$$\mathcal{I}(\omega) \propto \omega^{-(3-d_f)} \quad (2 \leq d_f < 3). \quad (29)$$

IV. COMPARISON WITH EXPERIMENTAL DATA AND DISCUSSION

The RMTD low-frequency spin-lattice relaxation mechanism links dynamic properties of adsorbate molecules with the structural details of the adsorbent surface, characterized by the dynamic fractal parameter d_w of the random process and, for fractal surfaces, by the static fractal dimension d_f of the surface, respectively. According to Eq. (25), these parameters can be evaluated from the power-law low-frequency T_1 dispersion curves, which were observed for polar liquids in

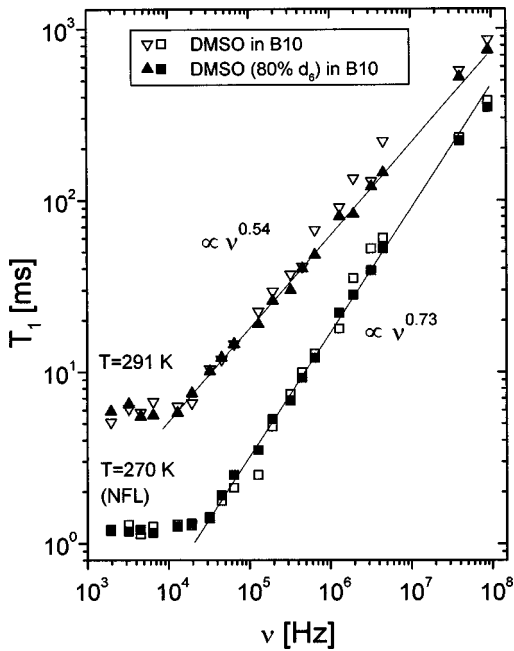


FIG. 1. Frequency dependence of the proton spin-lattice relaxation time of dimethylsulfoxide (DMSO) in porous glass B10 above and below the freezing temperature of the bulklike liquid. Data for an isotopically diluted sample (80% DMSO- d_6) are also shown. The relaxation times of the partially frozen sample at 270 K refer to the slowly decaying component of the NMR signal corresponding to the nonfreezing surface layers.

porous glasses [16], for instance.

A clear example for a power-law frequency dependence of the spin-lattice relaxation time T_1 is shown in Fig. 1. It refers to the system dimethylsulfoxide (DMSO) filled into porous silica glass with a mean pore dimension of 10 nm. Experimental details can be found in Ref. [8]. Figure 1 also shows the proton T_1 dispersion measured in the adsorbate diluted by its deuterated form so that any intermolecular dipolar interactions are reduced. The coincidence of the two data sets proves that the spin interactions dominating the low-frequency spin-lattice relaxation in DMSO are of an intramolecular nature.

Two different temperatures have been examined. At 270 K the bulklike adsorbate in the pores is frozen and does not perceptibly contribute to the spin-lattice relaxation rate. The observed T_1 dispersion is rather caused by the nonfreezing interfacial liquid existing in the form of a one to two molecular diameter thick nonfreezing surface layer. In such a situation, one expects that diffusion along the surface is normal, that is, $d_w = 2$.

On the other hand, at 291 K when all adsorbate molecules are in the liquid state, the bulklike adsorbate phase contributes, and the ‘‘bulk-mediated surface diffusion’’ mechanism can occur [10]. 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 the dynamic parameter $d_w = 1$ applies for the propagation of adsorbate molecules along the surface.

At both temperatures a power-law behavior is observed over three to four decades of the frequency $\nu = \omega_0/2\pi$ (ω_0 is the Larmor frequency). The results are

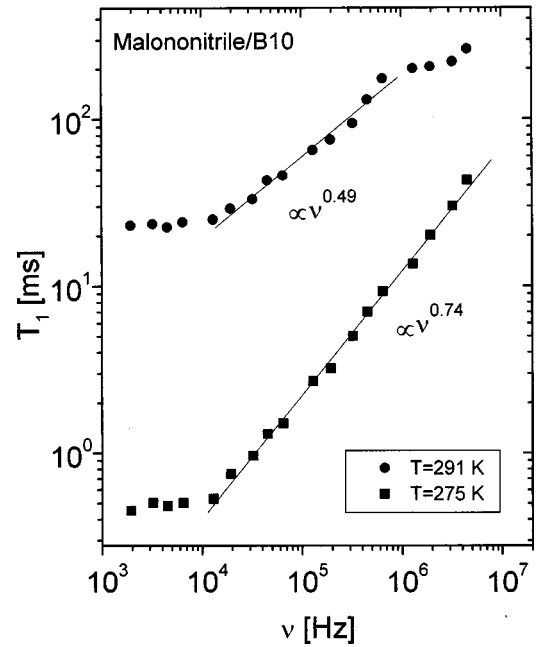


FIG. 2. Frequency dependence of the proton spin-lattice relaxation time of malononitrile in porous glass B10 above and below the freezing temperature of the bulklike liquid. The relaxation times of the partially frozen sample at 275 K refer to the slowly decaying component of the NMR signal corresponding to the nonfreezing surface layers.

$$T_1 \propto \nu^{0.73 \pm 0.04} \quad \text{for } T = 270 \text{ K}, d_w = 2 \quad (30)$$

and

$$T_1 \propto \nu^{0.54 \pm 0.04} \quad \text{for } T = 291 \text{ K}, d_w = 1. \quad (31)$$

Note that similar T_1 dispersion slopes have also been observed [16] with several other polar organic liquids in a porous glass with 30 nm pores. This indicates that the surface structure acts on all adsorbate liquids the same way.

As another example, Fig. 2 shows malononitrile in the same nanoporous glass at 275 K (8 K below the melting region of the bulklike liquid in the pores) and at 291 K (18 K above the freezing point), respectively. The power-law frequency dispersions of the spin-lattice relaxation time are evaluated as

$$T_1 \propto \nu^{0.74 \pm 0.04} \quad \text{for } T = 275 \text{ K}, d_w = 2 \quad (32)$$

and

$$T_1 \propto \nu^{0.49 \pm 0.04} \quad \text{for } T = 291 \text{ K}, d_w = 1. \quad (33)$$

Interpreting these power laws according to Eq. (25) and the propagator Eq. (8) suggests a common orientational structure factor of this particular porous glass independent of the adsorbate species. The result is

$$S(k) \propto k^{-0.5 \pm 0.04}. \quad (34)$$

The surface fractal dimension to be inferred from this is

$$d_f = 2.5 \pm 0.04. \quad (35)$$

This value very favorably fits to the range of typical literature data evaluated for controlled porous glass on the basis of x-ray and neutron scattering experiments [20].

In this work, we have described fractional dynamics in fractal spaces in a comprehensive way. The two sources of anomalous scaling laws are clearly distinguished in the formalism presented. It was shown that fractional scaling laws in space and time can be identified experimentally using field-cycling NMR relaxometry. Furthermore, it was elucidated that the physical meaning of the exponents α [see Eq. (14)] and d_w [see Eq. (1)] coincides so that the formalism can consistently be expressed in a closed form.

ACKNOWLEDGMENTS

We thank R.-O. Seitter for cooperation in the course of this work, and R. Metzler and N. Fatkullin for useful discussions. Financial support by the Graduiertenkolleg ‘‘Molekulare Dynamik an Grenz- und Oberflachen,’’ the Deutsche Forschungsgemeinschaft (SFB 239, Project Nos. B5 and B10), and the Volkswagen-Stiftung is gratefully acknowledged.

APPENDIX: THE FOURIER TRANSFORM IN THE FRACTAL SPACE WITH RADIAL SYMMETRY

The radial part of the Fourier transform in the isotropical D -dimensional fractal space reads

$$p(k, t) = \int P(r, t) e^{-ikr \cos \theta} d^D r, \quad (\text{A1})$$

where $r = |\mathbf{r}|$, $k = |\mathbf{k}|$, and the angle θ is spanned by \mathbf{r} and \mathbf{k} . Furthermore,

$$d^D r = d\Omega_D r^{D-1} dr, \quad (\text{A2})$$

$$\int_{\Omega} d\Omega_D = \frac{2\pi^{D/2}}{\Gamma(D/2)}. \quad (\text{A3})$$

This result can be obtained for radial symmetry with the ansatz

$$d\Omega_D = \frac{2\pi^{(D-1)/2}}{\Gamma[(D-1)/2]} (\sin \theta)^{D-2} d\theta, \quad D > 1 \quad (\text{A4})$$

for $\theta \in [0, \pi]$. Experimentally, only the range $1 < D \leq 3$ is relevant, so that we can restrict ourselves to this case. The fractal space with the non-Euclidean (fractal) dimension D has a global dimension n , defined by the number of the independent variables describing the behavior of self-affine functions in the space under consideration. For instance, n

$= 2$ for a rough surface with the surface fractal dimension $1 < D \leq 3$, and $n = 3$ for a fractal pore space with the (volume) fractal dimension $2 < D \leq 3$. The number of angle variables depends on the global dimension n . In two global dimensions (on the fractal surface), only one angle variable is necessary. In three dimensions (in the fractal volume), polar and azimuthal angles (θ and φ , respectively) are needed. In the latter case, $\int_0^{2\pi} d\varphi = 2\pi$ as a consequence of the radial symmetry assumed above. One can choose the coordinate system so that the angle θ between \mathbf{r} and \mathbf{k} in Eq. (A1) coincides with the polar angle of the system. Hence, if $\theta \in [0, \pi]$, the volume elements for $D = 2$ and 3 read

$$d^2 r = r dr d\Omega_2 = 2r dr d\theta, \quad (\text{A5})$$

$$d^3 r = r^2 dr d\Omega_3 = 2\pi r^2 dr \sin \theta d\theta.$$

Note that according to the integral representation of the Bessel function [21],

$$\int_0^{\pi} e^{\pm ikr \cos \theta} (\sin \theta)^{D-2} d\theta = 2^{D/2-1} \pi^{1/2} \Gamma\left(\frac{D-1}{2}\right) \times (kr)^{1-D/2} J_{D/2-1}(kr), \quad (\text{A6})$$

the radial part of the Fourier transform in the statistically isotropic fractal space takes the form

$$p(k, t) = (2\pi)^{D/2} k^{1-D/2} \int_0^{\infty} r^{D/2} J_{D/2-1}(kr) P(r, t) dr. \quad (\text{A7})$$

Schneider and Wyss [4] pointed out that the radial Fourier transform of this type applies to $D = n \in \{1, 2, 3\}$. As shown above, Eq. (A7) is valid for any space with the static fractal dimension $D \in \mathcal{R}$, $D > 1$. Note that the Fourier transform given in Eq. (A7) is self-inverse. The real-space propagator $P(r, t)$ can be calculated from $p(k, t)$ as the inverse Fourier transform

$$P(r, t) = (2\pi)^{-D/2} r^{1-D/2} \int_0^{\infty} k^{D/2} J_{D/2-1}(kr) p(k, t) dk. \quad (\text{A8})$$

Using Eqs. (A2) and (A4), the m th moment of r is found to be

$$\langle r^m(t) \rangle = \frac{2\pi^{D/2}}{\Gamma[D/2]} \int_0^{\infty} r^{D-1} r^m P(r, t) dr. \quad (\text{A9})$$

Equation (9) is reproduced by inserting the propagator Eq. (8) in Eq. (A9).

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