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Fractal Effects in Magnetic Resonance

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Effects of fractal structure on the magnetic resonance phenomena are discussed. Fractal theory is a mathematical tool used to describe geometrically complex disordered systems. In principle, one can get characteristic information about a fractal system *via* measurements of the relevant spectroscopic parameters, which are related to the fractal structure and fractal dynamics. Here, it is demonstrated that the surface fractal dimension, fracton dimension and the random walk dimension can be measured by means of nuclear magnetic resonance and electron paramagnetic resonance spectroscopy. It is further shown that nuclear magnetic resonance relaxation data allow determination of the non-exponential correlation functions, which reveal the fractal structure of the potential and of the corresponding free energy. The concept of the time fractal sequences of events, leading to the stretched exponential correlation functions, is also discussed.

INTRODUCTION

The aim of this paper is to discuss the effects of the fractal structure on the magnetic resonance phenomena. Fractal theory is a mathematical tool used to describe geometrically complex disordered systems. Geometrical description of an ordered crystal structure is based on translational symmetry. The crystal is completely described in terms of one unit cell. Less symmetrical systems do not allow such a simple description. However, such systems may posses dilation symmetry. This means that a part of the object is similar to the whole object at an appropriate magnification (Figure 1). If the resemblance is complete, the object is called a mathematical or non-random fractal. In nature, however, there are many objects where similarity holds only in some average way. These refer to such diverse examples as the shape of a cloud or a coastline, sandstones, polymer melts and solutions, aggregates, lung tissue, different gels and other amorphous systems or the mass distribution in the universe. These objects are called physical or random fractals. A fractal object[1,2,3] can be described in terms of at least three different parameters, namely the dimension of the embedding Euclidean space d, the fractal dimension $\overline{d}$ and the spectral (fracton) dimension $\tilde{d}$. For regular non-fractal objects, all these dimensions are equal ($d = \overline{d} = \tilde{d}$). The same is true if the observation is made on a length scale R that exceeds the coherence length ξ of the fractal system, *i.e.*, for $R > \xi$. For $R < \xi$, however, $d \neq \overline{d} \neq \tilde{d}$ where $\overline{d}$ and $\tilde{d}$ may

be non-integral. In fractal systems, the fractal dimension describes the geometrical structure of the object , namely the dependence of the mass on the length scale: $m \propto R^{\bar{d}}$, where m is the mass of the sphere with radius R. The spectral dimension describes the density of vibrational states on a fractal lattice $\rho(\omega) \propto \omega^{\tilde{d}-1}$ and reflects the topological structure of the fractal, which is in general different from the geometrical structure: $\tilde{d} \leq \bar{d}$ (see Figure 1).

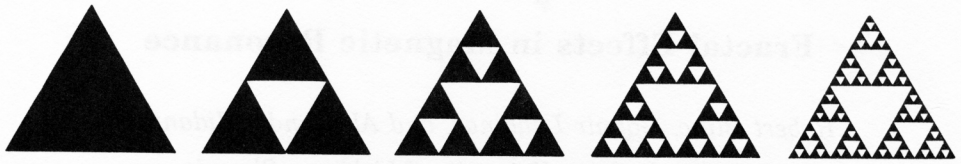

Figure 1. Sierpinski gasket. The fractal triangular Sierpinski gasket is constructed from a filled triangle in terms of a recursive procedure. At each step, all the central triangles are removed, as shown. After an infinite number of iterations, the remaining object[2] will have the fractal dimension of $\ln 3/\ln 2 \approx 1.585$ and the fracton dimension of $2 \ln 3/\ln 5 \approx 1.365$, the latter being close to the value for an infinite percolation cluster $\tilde{d} = 4/3$.

In irregular, but self-similar systems, there is no translational invariance but scale invariance and dilation symmetry. Scale invariance for a fractal system implies that if $m \propto R^{\bar{d}}$, then for a change of scale $R \rightarrow \lambda R$ one has

$$m(\lambda R) = \lambda^{\bar{d}}\, m(R)\,. \tag{1}$$

In addition, the fractal dimensionality of a random walk[2] constrained to the fractal is

$$d_w = 2\bar{d}/\tilde{d}\quad . \tag{2}$$

Fractal Potentials

If one observes thermodynamic quantities in a fractal system at the proper scale, the structure of the thermodynamic potential may also be fractal. Diffusion of a particle in a fractal system can be modified by the fractal structure of the potential.[4] An illustration of a random fractal potential is given in Figure 2, where each potential well is a microstructure of larger wells. The fractal potential, therefore, consists of an infinite number of local minima and the fractal dimension of a potential is defined by the following relation

$$N(\varepsilon) \propto \varepsilon^{-d_p}\,, \tag{3}$$

where ε is the length scale and $N(\varepsilon)$ is the number of local minima observed on scale ε. Here scale ε is a parameter characterizing the potential, and the above relation is valid only in a limited interval of ε. However, in such an interval, one may have molecular motion which accounts for the magnetic resonance relaxation.

The fractal dimension of a random potential d_p can take on any value between 0 and 1. For the description of motion in a fractal potential, it is essential to know the

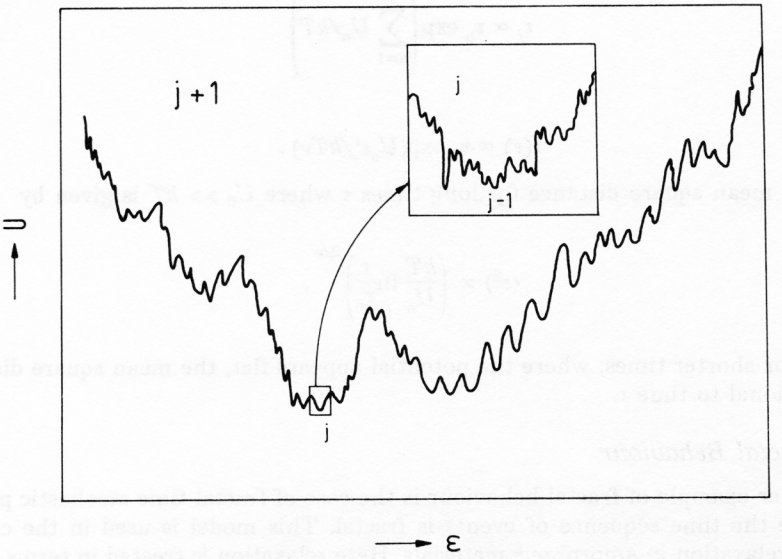

Figure 2. Random fractal potential. Each potential well is made up of smaller wells that are similar to the original one. Here, small wells at level $j-1$ (see insert) are joined together into a larger well at level j. The wells at level j make together a larger well at level $j+1$. On a very short length scale, the potential barriers become smaller than the average thermal energy kT. Thus, the particle does not feel the details of the potential and the level is denoted as $j=1$.

potential relief. In the case of a scaling fractal potential, the potential barriers are described by the scaling relation

$$U \propto U_0 \varepsilon^{\nu}, \tag{4}$$

where U_0 is a constant and ν is the scaling exponent. In this case, one deals with a mountainlike potential relief.

Therefore, such a potential, has a hierarchical structure of local minima and diffusion proceeds from the largest wells down to the smaller ones. At a given temperature T_o, cutoff is made so that the potential is smooth for the distances where the potential barrier U_0 is smaller than the thermal energy kT. The potential wells are labelled by subscript j which takes on value 1 at the smallest wells and value j for larger wells which are made up of the subwells labelled by $j-1$ (see Figure 2). The lifetime of a particle in a given potential well at level j is expressed in terms of the lifetime in the subwell at level $j-1$ as

$$\tau_j \propto \tau_{j-1} \exp(U_j/kT). \tag{5}$$

Here, relaxation times are independent of the fractal dimension, only the potential barriers are important. Taking into account the lower cutoff where $j = 1$, the relaxation time τ_j can be expressed as

$$\tau_j \propto \tau_0 \exp\left(\sum_{n=1}^{j} U_n/kT\right) \tag{6}$$

or

$$\tau(\varepsilon) \propto \tau_0 \exp(U_0 \varepsilon^{\nu}/kT\nu)\,. \tag{7}$$

Then, the mean square distance for long times τ where $U_0 >> kT$ is given by

$$\langle \varepsilon^2 \rangle \propto \left(\frac{kT}{U_0} \ln \frac{\tau}{\tau_0}\right)^{2/\nu}, \tag{8}$$

whereas for shorter times, where the potential appears flat, the mean square distance is proportional to time τ.

Time Fractal Behaviour

Another example of fractal behaviour is the case of fractal time stochastic processes, where the time sequence of events is fractal. This model is used in the case of dielectric relaxation in amorphous materials. Here relaxation is treated in terms of the defect-diffusion model, governed by a fractal time stochastic process, where the mean duration between defect movements is infinite.[5] Let us consider a process where the time between events is a random variable and $\psi(\vartheta)$ is the probability density that an event occurs at time ϑ after the previous event. Here, ϑ is a dimensionless time, defined as the ratio between the real time t and a given time constant t_0. The mean time between events is

$$\langle \vartheta \rangle = \int_0^{\infty} \vartheta \psi(\vartheta)\, \mathrm{d}\vartheta \tag{9}$$

and the median time ϑ_m is defined as

$$\int_0^{\vartheta_m} \psi(\vartheta)\, \mathrm{d}\vartheta = \frac{1}{2} \tag{10}$$

If $\langle \vartheta \rangle$ is finite, a natural time scale exists in which we can measure time events ($\langle \vartheta \rangle = \tau$). If $\langle \vartheta \rangle$ is infinite, no natural time scale exists, though events do occur and ϑ_m is finite. In this case, the time sequence of events occurs in self-similar clusters, like points in a Cantor set (Figure 3). Such a self-similar time event probability density is, for instance, a sum of Poisson terms:

$$\psi(\vartheta) = \frac{(1-p)}{p} \sum_{n=1}^{\infty} p^n \lambda^n \exp(-\lambda^n \vartheta), \qquad \lambda < p < 1\,. \tag{11}$$

Here, λ is the inverse expectation time $\langle \vartheta \rangle^{-1}$ for the first random process ($n = 1$), which occurs with the probability $1-p$. λ is also the ratio of the time scales for the random processes where the difference in n equals 1. An order of magnitude longer duration

between events (λ^n *versus* λ^{n-1}) is by an order of magnitude less probable (p^n compared with p^{n-1}). This mirrors the spacings of a Cantor set.

In Laplace transform space one finds the relation

$$\psi^*(s) = \int_0^\infty \psi(\vartheta)\, e^{-s\vartheta}\, d\vartheta = \frac{1-p}{p} \sum_{n=1}^{\infty} \frac{p^n \lambda^n}{s+\lambda^n} = p\psi^*(s/\lambda) + \frac{1-p}{1+(s/\lambda)}. \tag{12}$$

This scaling equation has the solution[5]

$$\psi^*(s) = 1 + s^\alpha K(s) + (1-p) \sum_{n=1}^{\infty} \frac{(-s)^n}{\lambda^n - p}, \qquad \alpha = \ln p / \ln \lambda \tag{13}$$

where $K(s)$ is an oscillatory function periodic in $\ln s$ with a period $\ln \lambda$. If $0 < \alpha < 1$, then

$$\langle \vartheta \rangle = -\frac{\partial \psi^*(s=0)}{\partial s} = \infty \tag{14}$$

and α has the role of a fractal time dimension.

It has been recently realized that for many glasses, polymers and other random media, the time decay of the correlation function follows the same stretched exponential law

$$g(\tau) = \exp[-(\tau/\tau_0)^\alpha], \tag{15}$$

i.e. the correlation function has the Kohlrausch-Williams-Watts form. Here the exponent α equals the time fractal dimension α. The above form of the auto-correlation function has been derived for:

(i) Direct excitation transfer from donor to receptor (defect) on a fractal structure;
(ii) Hierarchically constrained dynamics, where relaxation occurs in stages and the constant imposed by a faster degree must relax before a slower degree of freedom can relax;

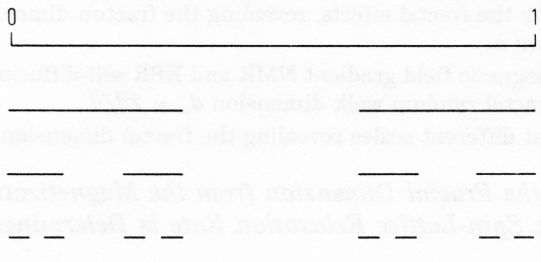

Figure 3. Three iterations on the Cantor bar. If the spacing between the remaining bars is considered to represent the time between events in a process, then a self-similarity of event times is introduced. After an infinite number of iterations of the Cantor bar, the remaining Cantor set will have a regular self-similarity and a fractal dimension of ln 2/ln 3.

(iii) Fractal time defect diffusion, where migrating defects trigger relaxation of *e.g.*, frozen dipoles on a fractal, self-similar structure;
(iv) The dynamics of a random Ising model.

Spatial Fractal Dimension

While the physics behind these models is very different, the underlying unifying concept is a scale invariant distribution of relaxation times.

Spatial fractal dimension is usually determined by measuring the length, surface area or volume of the object on different length scales. For natural objects, the relation $m \propto R^{\bar{d}}$ holds only in a limited length scale interval. An example is the measurement of the fractal dimension of a coastline. Here, the line is more or less rough so that the apparent length is larger if measured on a smaller scale. If the fractal dimension of the coast is $\bar{d}$, then its length is proportional to $R^{\bar{d}}$, where R is the length scale. One can define a $\bar{d}$ – dimensional volume $L_{\bar{d}} = N(R)\, R^{\bar{d}}$ which is a constant but cannot be measured directly. Instead, one measures the length at different length scales: $L(R)=N(R)R$ where R is the length of the measuring stick and N is the number of sticks that can be placed on the object. Since the number $N(R)$ is of the same order of magnitude for one dimension as for $\bar{d}$ dimensions, $L(R)$ is proportional to $R^{1-\bar{d}}$ and $\bar{d}$ can be determined from the slope of the logarithmic plot of $L(R)$ *versus* R. In this way, fractal dimensions of different coastlines have been measured.[1] The value is between 1 and 2, depending on the roughness of the line.

Fractal dimension can also be measured by means of nuclear magnetic resonance[6] (NMR) and electron paramagnetic[6] (EPR) techniques. The rest of the paper is devoted to the analysis of the effects observed in magnetic resonance arising from the fractal nature of the systems studied.

THEORY OF NMR IN FRACTAL SYSTEMS

Fractal geometry produces a number of unconventional effects in magnetic resonance (MR) experiments which can be exploited to reveal the fractal and fracton dimension of the system. These effects can be classified into four different groups, namely

(i) non-exponential magnetization decay or recovery in systems where the spin-lattice relaxation rate is caused by dipolar interactions, revealing the fractal dimension $\bar{d}$,
(ii) anomalies in the frequency and temperature dependence of the spin-lattice relaxation rate produced by the fractal effects, revealing the fracton dimension $\tilde{d}$ or the time fractal dimension α,
(iii) anomalies in magnetic field gradient NMR and EPR self-diffusion measurements revealing the fractal random walk dimension $d_w = 2\bar{d}/\tilde{d}$,
(iv) NMR imaging at different scales revealing the fractal dimension *via* $m \propto R^{\bar{d}}$.

Determination of the Fractal Dimension from the Magnetization Recovery in Systems where the Spin-Lattice Relaxation Rate is Determined by Dipolar Interactions

Contrary to the small-angle scattering techniques conventionally used to characterize the geometrical arrangement of the fractal systems *via* an analysis of the scattering intensity in reciprocal space, NMR is capable of determining the mass-to-distance relation in real space, $m(r) \propto r^{\bar{d}}$, with $\bar{d}$ being the fractal dimension. In the NMR

experiment of Devreux *et al.*,[7] a magic angle spinning (MAS) NMR probe has been used to eliminate spin-diffusion between ^{29}Si nuclear spins of the fractal silica aerogel sample, so that the recovery of the ^{29}Si magnetization is left to reflect the spatial repartition of the ^{29}Si nuclear spins which relax to their equilibrium polarization by dipolar flipping with paramagnetic ions diluted in a fractal lattice. In the absence of other contributions to the relaxation, the magnetization at time t after saturation relaxes towards the equilibrium value as

$$M(t) \propto \int_0^\infty \left[1 - \exp(-At/r^6)\right] \rho(r)\, dr . \tag{16}$$

Here, $\rho(r)dr$ is the equilibrium ^{29}Si magnetization within a small slice at a distance r from an electronic spin of the paramagnetic ion. The nuclear spin relaxation rate due to direct dipolar coupling with a fixed paramagnetic impurity located at a distance r is given as

$$1/T_1 = A/r^6 , \tag{17}$$

where constant A is independent of r. Hence, as the time constant for the dipolar coupling relaxation increases with the distance as r^6 (17), the recovered magnetization at time t after saturation will be that of the spins contained within a sphere of radius $r = (At)^{1/6}$. The exponential function under integration is assumed to take the value zero inside the sphere and 1 outside the sphere. The recovered magnetization is, thus, proportional to the equilibrium magnetization $M_0(r)$ inside the sphere of radius r:

$$M(t) \propto M_0 [r = (At)^{1/6}] . \tag{18}$$

The equilibrium magnetization $M_0(r)$ is proportional to the number of spins inside the sphere and, hence, to mass $m(r)$:

$$M_0(r) \propto m(r) \propto r^{\bar{d}} = (At)^{\bar{d}/6} . \tag{19}$$

In view of (18), the magnetization recovery $M(t)$ will show the time dependence

$$M(t) \propto t^{\bar{d}/6} . \tag{20}$$

Measuring the magnetization recovery over a long period of time, enables one to determine the fractal dimension $\bar{d}$, provided the effect of spin-diffusion can be eliminated.

The measured ^{29}Si magnetization recovery in aerogels and alcogels is found to exhibit a power law behaviour (20) over a very large time range up to five orders of magnitude, which reflects the mass distribution $m(r) \propto r^{\bar{d}}$, providing information about the fractal dimension $\bar{d}$. In particular, a value $\bar{d}$ of 2.2 is found in agreement with that determined by small angle X-ray scattering.[7]

Spin-lattice Relaxation in Fractal Systems

Nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) relaxation in a disordered system exhibit some peculiar characteristics. Since the high

energy vibrational states of the system are highly localized fractons, one expects a broader distribution of the relaxation rates leading to a non-exponential magnetization decay. In crystals, where the vibrations of the lattice are described with phonons, the nuclear or electron spin relaxes *via* direct (one phonon) or Raman (two phonon) processes. In the Raman process, the electron or nuclear spin relaxes by absorbing one quantum of vibrational energy at ω_1 and emitting another quantum at ω_2 so that their energy difference equals the Larmor energy, $\hbar(\omega_2 - \omega_1) = \hbar\omega_L$.

In electron paramagnetic relaxation, the Raman process is faster than the direct process when the temperature is high enough to populate the vibrational states with energy higher than the Larmor energy. The corresponding temperature is usually a few K. On the other hand, in the nuclear spin-lattice relaxation, direct processes will be generally dominant for overdamped modes, whereas for underdamped modes Raman processes will dominate.

In disordered systems, the same description can be applied if the phonons are replaced by localized oscillation states, known as fractons. This leads to changes in temperature and Larmor frequency dependence of the spin-lattice relaxation rates. Here, two different cases should be distinguished:

Direct Processes

The spin-lattice relaxation rate for the underdamped modes is proportional to the temperature and some power of the Larmor frequency. The calculation of Orbach *et al*[8] gives the following expression

$$\frac{1}{T_1} \propto N(\omega_L)\, \omega_L^{2q-1} \coth\left(\frac{\hbar\omega_L}{2kT}\right), \qquad q = d_\phi\, \bar{d}/\bar{d}, \tag{21}$$

where parameter d_ϕ describes the range dependence of the fracton wave function: $\Phi \propto \exp(-r^{d_\Phi})$. The value of d_ϕ can be greater than 1 due to the fact that an exponential decay on the fractal is distorted in real space, but it cannot be greater than dimension d_{min} of the shortest path between the two points. d_{min} is defined so that the shortest path between the points at a distance R is proportional to $R^{d_{min}}$ and it is usually not greater than the fractal dimension. For phonons, $q = d_\phi = 1$. An example of the fractal system is a three dimensional percolation network where $\bar{d} = 4/3$ and $q = 0.74$. Other fractal systems can generally be characterized by non-integer values of the above parameters. In the high temperature approximation $kT >> \hbar\omega_L$, relation (21) is simplified to

$$\frac{1}{T_1} \propto T\, \omega_L^{2q + \bar{d} - 3}. \tag{22}$$

Raman Processes

Raman processes at low temperatures can reveal information about the fracton dimension of the system. At low temperatures, below the Debye temperature, the EPR spin-lattice relaxation rate is proportional to some power of temperature

$$\frac{1}{T_1} \propto T^{3 + 2d} \tag{23}$$

if relaxation between time reversed magnetic states of half integral spin takes place (Kramers process). Here, d is dimensionality of the sample. The low temperature EPR spin-lattice relaxation data on different biopolymers[9] were explained by non-integer dimensions of d between 1 and 2.

However, in this case, the localization of the fracton wave function should also be taken into account so that the above expression for disordered systems is in fact given by[10]

$$\frac{1}{T_1} \propto T^{4q - 1 + 2\tilde{d}}. \tag{24}$$

It means that the non-integer exponent reveals the fractal nature of the observed system, but this is not sufficient for the determination of the fracton dimension. However, one can test two different hypotheses, *viz.* that the vibrational states can be described classically ($\tilde{d} = 1$) or that the fractal dimension takes the value $\tilde{d} = 4/3$, which is characteristic of a large class of fractal objects.[2] Here, the ratio $d_\phi/\tilde{d}$ can be determined for both values of the fracton dimension $\tilde{d}$. The correct value of the fracton dimension is chosen so that the ratio $d_\phi/\tilde{d}$ is smaller than one and larger than $1/\tilde{d}$.

It is worth noting that the exponent for non-Kramers processes is the one calculated above minus 2. This type of behaviour has indeed been observed for nuclear quadrupolar relaxation in glasses.[10,11]

Since the above equation (24) connects three different fractal parameters, one should measure two of them separately in order to determine the remaining one.

Time Fractal Sequences of Events

The spin-lattice relaxation rate T_1^{-1} depends on the spectral density of the autocorrelation function $g(\tau)$ at the nuclear Larmor frequency ω_L:

$$\frac{1}{T_1} \propto J(\omega_L) = 2 \int_0^\infty \cos(\omega_L t)\, g(\tau)\, \mathrm{d}t\,. \tag{25}$$

In the case of organic glasses, the stretched exponential correlation function (15)

$$g(\tau) = \exp[-(\tau/\tau_0)^\alpha] \tag{26}$$

can be used. In the fast motion regime, where $\omega_L\tau_0 << 1$, one finds

$$J(\omega_L) = 2\frac{\tau_0}{\alpha}\Gamma(1/\alpha)\,, \qquad \omega_L\tau_0 << 1\,. \tag{27}$$

Here, Γ is the Euler gamma function. On the other hand, in the slow motion regime, where $\omega_L\tau_0 >> 1$, one finds:

$$J(\omega_L) = \frac{2\alpha}{\omega_L^{1+\alpha}\,\tau^\alpha}\Gamma(\alpha)\sin\left(\frac{\alpha\pi}{2}\right), \qquad 0<\alpha<1\,. \tag{28}$$

For the intermediate case, one cannot find an analytical expression for $J(\omega_L)$ for a general value of α. Thus, the value of α can be determined by measuring the Larmor frequency dependence of the spin-lattice relaxation rate in the slow motion regime.

Fractal Dimension and the Collapse Transition in Gels

The fractal dimension can be measured in a system that changes the length scale during observation. Gels[12] can change their volume and, thus, also the length scale very rapidly due to a small change in external conditions. Gels consist of a polymer network immersed in a liquid (*e.g.* water). The water prevents the polymer network from collapsing and the network prevents the water from flowing away. Drastic changes in volume can be obtained by small changes in temperature, electric field, pH or in some cases simply by detaching the gel from the test tube surface. Such a change is termed a collapse transition.

The increase in the surface to volume ratio at the collapse transition of gels can be exploited to allow an NMR determination of the fractal dimension of the gel surface in the liquid state, where this quantity is hard to measure with other techniques. In this approach,[12,13] one measures the ratio between the spin-lattice and the spin-spin relaxation times T_1/T_2 of the liquid component (*e.g.* water), and the ratio of the masses or volumes of the gel before and after the a collapse transition.

The method is based on the fact that in the fast exchange two site model the knowledge of all the relaxation rates allows determination of the bound water fraction which is proportional to the surface area of the gel. Namely, in this case, the observed relaxation rate is a weighted average of the relaxation rates for a given phase:

$$\frac{1}{T_i} = \eta \frac{1}{T_{i,b}} + (1 - \eta) \frac{1}{T_{i,f}} . \tag{29}$$

Here, i can be either 1 or 2, denoting the spin-lattice relaxation and the spin-spin relaxation, respectively. The bound water fraction η is determined as the number of bound water molecules divided by the number of all water molecules present in the system. Subscripts b and f stand for the relaxation rates of the bound and the free water phases, respectively. If one measures the relaxation rate $1/T_i$ of the gel, the relaxation rate $1/T_{i,b}$ of the bound water phase and the relaxation rate $1/T_{i,f}$ of the free water phase, the bound water ratio η can be determined directly from (29). If the bound water layer is uniformly distributed over the gel surface, the bound water fraction η is proportional to the surface area S

$$\eta = \frac{KS}{V} , \tag{30}$$

where V is the volume of water inside the gel and K is the thickness of the adsorbed water layer. Since water occupies almost the whole volume of the gel, the water volume can be assumed to be three dimensional and

$$\eta \propto R^{D_S - D_V} , \tag{31}$$

where D_S is the unknown surface fractal dimension and D_V is the water volume dimension which is assumed to be 3. Since the volume of the water is also proportional to its mass, one can determine the surface fractal dimension D_S by measuring the change

in the bound water ratio η and the change in mass m at two different scales (*i.e.* at the collapse). The surface fractal dimension is then given as

$$D_S = D_V \left[1 - \frac{\ln(\eta_1/\eta_2)}{\ln(m_2/m_1)}\right] . \tag{32}$$

Here, η_1 and m_1 are quantities measured before, and η_2 and m_2 are those measured after the collapse transition.

In the actual experiment, the bound water relaxation rates are difficult to measure, so they are calculated by means of the BPP approximation for the relaxation with a single correlation time.[13] The surface fractal dimensions for fibrin gels, blood and plasma clots have been determined in this way making use of the collapse transition.[12,13]

Stretched Exponential Correlation Functions Observed by NMR

Relaxation in organic glasses depends on the correlation functions for the characteristic motions of the system. The details about the correlation function can be revealed by the temperature dependence of the NMR lineshape and the spin-lattice relaxation. The lineshape can be expressed with the help of the correlation function $g(\tau)$ as[14]

$$I(\omega) = \int_0^\infty \widetilde{G}(t)\, e^{-i\omega t}\, dt , \tag{33}$$

$$\widetilde{G}(\omega) = G(t)\, e^{i\omega_0 t} , \tag{34}$$

where

$$G(t) = \exp\left[-\omega_p^2 \int_0^t (t - \tau)\, g_\omega(\tau)\, d\tau\right] \tag{35}$$

with $\omega_p^2 = \langle\omega^2\rangle$. Measured lineshapes can be fitted to the above expressions. In the experimental case where the lineshapes of the organic glass COANP have been fitted for a large temperature interval,[15] the best agreement has been obtained with the stretched exponential correlation function $g(\tau)$ (15,26) for $\alpha = 0.28$ and a thermally activated correlation time $\tau_0 = \tau_\infty \exp(E_a/kT)$ with $E_a = 1.39$ eV and $\tau_\infty = 5 \cdot 10^{-31}$s.

NMR and EPR Self-Diffusion Measurements and the Fractal Random Walk Dimension

NMR and EPR self-diffusion measurements are usually performed by means of pulse field gradient (PFG) technique. The nuclei or electrons are labelled by their Larmor precession frequencies in a spatially varying magnetic field and one observes signal attenuation due to translational self-diffusion. The magnetic field gradient is applied in the form of two pulses of magnitude G, duration δ and separation Δ, which thus represents the diffusion time. The field gradient pulse sequence is superposed on the Hahn spin echo sequence. The translational self-diffusion coefficient

$$D = \frac{1}{3} \int_0^\infty \langle v(0)v(t) \rangle \, dt \tag{36}$$

and the ensemble averaged mean square nuclear or electron displacement in the direction of the field gradient $\langle x^2 \rangle$ are conventionally determined from the echo attenuation

$$A(G)/A(0) = \exp(-\tfrac{1}{2} \gamma^2 G^2 \delta^2 \langle x^2 \rangle) \tag{37}$$

or

$$A(G)/A(0) = \exp[-\gamma^2 G^2 D \delta^2 (\Delta - \delta/3)] \, . \tag{38}$$

Here, the magnitude of gradient G or duration δ can be varied in order to determine the diffusion coefficient D. Here, v is the velocity of the particle and γ is the gyromagnetic ratio.

In a continuous wave (cw) field gradient experiment, where the field gradient is on for a time t, the echo attenuation is given by

$$A(G)/A(0) = \exp(-\gamma^2 G^2 D t^3/12) \, . \tag{39}$$

The above expressions are correct only for classical unrestricted diffusion at times that are long on a microscopic scale.

The relation between the mean square displacement $\langle x^2 \rangle$ and diffusion time t for long time is given by the Einstein relation $\langle x^2 \rangle \propto t^{2/d_w}$ $(t \to \infty)$, where for Euclidean space $\bar{d} = \bar{d}$ and $d_\omega = 2$. For a fractal system with $R < \xi$, on the other hand, one has $d_\omega = 2\, \bar{d}/\bar{d}$, where the spectral dimension $\bar{d}$ is generally smaller than the fractal dimension $\bar{d}$, so that $d_\omega \geq 2$.

From the Einstein relation, the apparent self-diffusion coefficient can be defined as

$$D(t) = \frac{1}{2} \frac{d\langle x^2 \rangle}{dt} \propto t^{2/d_w - 1} \, . \tag{40}$$

For Euclidean geometry ($d_\omega = 2$), the self-diffusion coefficient D is obviously not time dependent. On the other hand, for a fractal system, the apparent self-diffusion coefficient can be time dependent, if $R < \xi$, but it becomes time independent for very long times when a crossover to Euclidean behaviour occurs ($R > \xi$). The time dependence of the echo attenuation and the random walk dimension d_ω is determined by fitting the self-diffusion coefficient to the power law $D \propto t^{2/d_w - 1}$.

NMR Imaging at Different Scales

The simplest way to determine the fractal dimension by NMR is to use NMR imaging at different scales. Such a study has been recently performed in hydrating cement pastes where NMR imaging at different scales was used to determine the volume fractal dimension D_V, whereas the surface fractal dimension D_S was determined from the spin-lattice relaxation induced by the internal surface of the cement gel.[16]

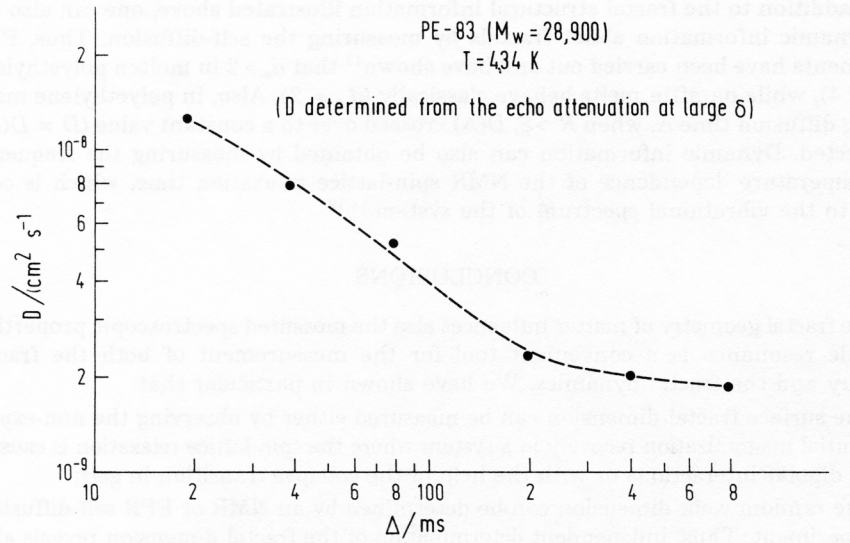

Figure 4. Dependence of the apparent self-diffusion coefficient D on the diffusion time Δ for a polyethylene melt[17] at T = 434 K (polyethylene molecular weight $M_W \approx 28900$).

SOME EXPERIMENTAL RESULTS AND DISCUSSION

The first evidence for the fractal behaviour of matter detected by MR came from EPR measurements of temperature dependence of the spin-lattice relaxation time in various proteins.[9] Since that time, many different techniques for measuring the fractal properties by MR have been developed. For example, the fractal dimension of gels can be measured by inducing the collapse transition of the gel. The surface fractal dimension of different fibrin gels, blood clots and plasma clots have been measured in this way.[12,13] The results show that the measured relaxation rates allow characterization of the state of water leading to determination of the gel surface area ratio before and after the collapse transition. The fibrin network in blood and plasma clots forms a self-similar porous fractal structure characterized by a surface fractal dimension of 1.7 to 1.9 in plasma clots and of 1.3 to 1.7 in blood clots, respectively. Since the fractal dimension is smaller than 2, the structure is rather open despite of the fact that it prevents the water from flowing away.

Surface fractal dimension can also be measured in materials devoid of a collapse transition, such as aerogels, as demonstrated by Devreux *et al.*.[7] An example of such a case is the use of the MAS NMR spectroscopy, which allows determination of the fractal geometry in real space on a microscopic scale and, in particular, determination of the fractal dimension. Fractal dimensions obtained in this way are in good agreement with small angle X-ray scattering (SAXS) results. The values found are close to three for dense samples as expected, while they are between 2.1 and 2.3 for fractal aerogels. This is in agreement with the SAXS result, where a fractal dimension of 2.3 has been found. The volume fractal dimension has been recently measured in hydrating cement pastes by NMR imaging.

In addition to the fractal structural information illustrated above, one can also obtain dynamic information about fractals by measuring the self-diffusion. Thus, PFG experiments have been carried out and have shown[17] that $d_\omega > 2$ in molten polyethylene (Figure 4), while paraffin melts behave classically ($d_\omega = 2$). Also, in polyethylene melts for long diffusion time Δ, when $R > \xi$, $D(\Delta)$ crossed over to a constant value ($D \neq D(\Delta)$) as expected. Dynamic information can also be obtained by measuring the frequency and temperature dependence of the NMR spin-lattice relaxation time, which is connected to the vibrational spectrum of the system.[18,19]

CONCLUSIONS

The fractal geometry of matter influences also the measured spectroscopic properties. Magnetic resonance is a convenient tool for the measurement of both the fractal geometry and the fractal dynamics. We have shown in particular that:

(i) The surface fractal dimension can be measured either by observing the non-exponential magnetization recovery in a system where the spin-lattice relaxation is caused by dipolar interactions or with the help of the collapse transition in gels;

(ii) The random walk dimension can be determined by an NMR or EPR self-diffusion experiment. Thus, independent determination of the fractal dimension reveals also the value of the fracton dimension;

(iii) The fracton dimension can be determined from the temperature and frequency dependence of the spin-lattice NMR or EPR relaxation rates;

(iv) Stretched-exponential correlation functions are consistent with the fractal structure of the potential and of the corresponding free energy;

(v) The volume fractal dimension can be measured by observing the mass-length relation $m \propto R^{\bar{d}}$ by NMR imaging with different magnifications.

The field is just being opened and many more new applications of magnetic resonance in the study of the fractal geometry of matter are being developed.

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SAŽETAK

Fraktalni efekti u magnetskoj rezonanciji

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Raspravlja se o utjecajima fraktalne strukture na fenomene magnetske rezonancije. Fraktalna teorija jest matematički alat korišten za opisivanje geometrijski kompleksnih neuređenih sustava. Mjerenjem relevantnih spektroskopskih parametara načelno se mogu dobiti karakteristične informacije o fraktalnoj strukturi i dinamici. U radu je pokazano da je s pomoću nuklearne magnetske rezonancije i elektronske paramagnetske rezonancije moguće mjeriti površinsku fraktalnu dimenziju, fraktonsku dimenziju i dimenziju slučajnog hoda. Također je pokazano da nuklearno-magnetski relaksacijski podaci omogućavaju određivanje ne-eksponencijalnih korelacijskih funkcija, koje otkrivaju fraktalnu strukturu međumolekulskih potencijala i odgovarajuće slobodne energije. Raspravljen je koncept vremensko-fraktalnih sekvencija događaja, koje rezultiraju eksponencijalnim korelacijskim funkcijama.