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Nuclear magnetic resonance dephasing effects in a spherical pore with a magnetic dipolar field

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The NMR dephasing behavior of the nuclear spins of a fluid confined in a porous material can be investigated by Hahn spin echoes. Previous experimental results on water in a magnetically doped clay have shown a nonmonoexponentially decaying magnetization, which can be understood neither by the known dephasing rate of freely diffusing spins in a uniform gradient nor by spins diffusing in a restricted geometry. For a better understanding of NMR measurements on these systems, a systematic survey was performed of the various length scales that are involved. The standard length scales for the situation of a uniform gradient are diffusing length, structure length, and dephasing length. We show that for a nonuniform gradient, a new length scale has to be introduced: the magnetic-field curvature length. When a particle diffuses less than this length scale, it experiences a local uniform gradient. In that case the spin-echo decay can be described by the so-called local gradient approximation (LGA). When a particle diffuses over a longer distance than the structure length, the spin-echo decay can be described by the motional averaging regime. For both regimes, scaling laws are derived. In this paper, a random-walk model is used to simulate the dephasing effect of diffusing spins in a spherical pore in the presence of a magnetic dipole field. By varying the dipole magnitude, situations can be created in which the dephasing behavior scales according to the motional averaging regime or according to the LGA regime, for certain ranges of echo times. Two model systems are investigated: a spherical pore in the vicinity of a magnetic point dipole and a spherical pore adjacent to a magnetic dipolar grain of the same size as the pore. The simulated magnetization decay curves of both model systems confirm the scaling laws. The LGA, characterized by a nonmonoexponential magnetization decay, is also investigated by calculating the spatially resolved magnetization in the pore. For this regime, the magnetization is found to be inhomogeneously distributed within the pore, whereas it is homogeneously distributed in the motional averaging regime. © 2003 American Institute of Physics. [DOI: 10.1063/1.1536970]

I. INTRODUCTION

Soon after the first ^1H NMR measurements, it became clear that the Hahn spin-echo decay¹ of the nuclear magnetization of water confined in a porous material differs from its bulk behavior. For a constant magnetic-field gradient, this is caused by two competing effects: relaxation at surfaces and dephasing due to diffusion in inhomogeneous magnetic fields. The decay rate of confined water will increase compared to the bulk fluid, because the water molecules hit the pore wall, where the nuclear spin has a higher probability to relax. On the other hand, the decay rate will decrease because the dephasing in a confined geometry is less. This is caused by the fact that the molecules are hindered to diffuse to regions in the material, where the magnetic field is very different from the magnetic field they experienced at the beginning of the pulse sequence.

There has been a lot of research, both experimental and theoretical, on these two magnetization decay mechanisms. Brownstein and Tarr have first described the enhancement of the NMR relaxivity of a water-saturated pore by its pore

surface in the seminal article.² This description was extended by Cohen and Mendelson³ for a system of interconnected pores. The dephasing in a porous material was first described by Wayne and Cotts.⁴ Robertson⁵ provided the necessary theory to explain the experimental data. Recently, Hürlimann⁶ gave an overview of all possible spin-echo decay mechanisms due to dephasing in a single pore in the presence of a uniform magnetic-field gradient. Relaxivity is neglected in this analysis, because it is independent of the dephasing mechanism. For short times, the “free-diffusion” decay is dominant, because the majority of the spins did not feel the influence of the pore walls yet. For longer times and small magnetic-field gradients, the “motional averaging” regime is valid, in which the spins travel a long time through the pore, hitting the pore wall often, before significant dephasing occurs. For longer times and large magnetic-field gradients, the “localization” regime is found,⁷ in which the spins dephase before reaching the pore wall. With the aid of a random-walk model, we studied the intermediate regime between the motional averaging and the localization regime.⁸

According to this model, the presence of a uniform magnetic-field gradient results in monoexponential decay curves for all regimes except for the free-diffusion regime.

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This is in contrast to the experimental data on clay and fired-clay bricks,⁹ which show pronounced nonmonoexponential decay, which of course could not be attributed to free diffusion in a uniform gradient. In the present study, we introduce a model which describes the observed spin-echo decay due to dephasing more accurately. Fired-clay bricks contain a lot of ferromagnetic impurities, which can give rise to large inhomogeneous magnetic fields. Therefore, we have incorporated a dipolar magnetic field in the model, which is probably more realistic than a uniform gradient. This will be described in Sec. II. Weisskoff *et al.*¹⁰ reported simulations and experiments on the influence of microscopic susceptibility variations on dephasing rates. This study is valuable for understanding the effect of contrast agents in medical NMR, which shows some similarities with our magnetic impurities.

We will show that for a dipolar magnetic field the spin-echo decay is more complex than the widely used simplification of a uniform gradient. By defining a magnetic-field curvature length we will quantify the validity of a so-called local gradient approximation. We will investigate how the decay rate of the magnetization scales with the magnitude of a magnetic field with arbitrary geometry and formulate scaling laws for the various regimes. This will be done in Sec. III. In Sec. IV numerical simulation results will answer the question under which conditions the various regimes appear in the presence of a magnetic dipolar field and how the dephasing rate in these regimes is related to the magnetic dipole strength. Section V concludes the paper.

II. SIMULATION MODEL

The main goal of the simulation model is to describe the magnetization decay in a porous material. As a starting point, we have studied the dephasing behavior of the spins in one single pore. The numerical model allows for an arbitrary number of dipoles in the porous matrix surrounding the pore. However, for sake of clarity only one single pore in the vicinity of one dipole is considered. Two configurations of this system are investigated: one with a magnetic point dipole and one with a magnetic dipolar grain, which has the same size as the pore itself.

In a single water-saturated pore, random walks are performed by the water molecules, and hence by the ¹H nuclei which are measured in NMR experiments. These random walks are generated on a lattice instead of in a continuum because of computational efficiency. A cubic lattice with a size of 100×100×100 lattice points is used. We introduced this random-walk model in a previous paper⁸ to which the reader is referred for a detailed description of the simulation method. The numerical program has been checked extensively for the case of free diffusion and for a single pore with a uniform magnetic-field gradient.

A. Dipolar magnetic field

Consider one ferromagnetic grain in the solid matrix of a porous material. The main magnetic field B_0 is applied along the z -axis. The magnetic field in the z -direction produced by the ferromagnetic grain, B_{dip} , can be written as

$$B_{\text{dip}} = \frac{\mu_0 \mu}{r^3} (1 - 3 \cos^2 \theta). \quad (1)$$

In this equation r is the length of the vector $\mathbf{r}$ from the center of the dipole to the position of the spin of interest, θ is the angle between $\mathbf{r}$ and the z -axis, μ_0 is the magnetic permeability, and μ is the dipole moment of a ferromagnetic grain with volume $V_{\text{Fe}_2\text{O}_3}$,

$$\mu = M_{\text{Fe}_2\text{O}_3} V_{\text{Fe}_2\text{O}_3}, \quad (2)$$

where $M_{\text{Fe}_2\text{O}_3}$ is the saturation magnetization of iron oxide (Fe_2O_3) present in, for instance, a fired-clay brick.¹¹ From SQUID magnetization measurements, it was found that at $B_0 = 0.8$ T, the field corresponding to our NMR measurements, the saturation magnetization is reached.¹² This implies that all dipoles are aligned with B_0 . In the following sections, it will become clear that B_{dip} does not necessarily have to be aligned with B_0 . The total magnetic field in the z -direction ($B_0 + B_{\text{dip}}$) will be present not only in the solid matrix of the porous material but also in the voids. Because the susceptibility mismatch between air, water, and the bulk material causes much smaller magnetic effects than this dipolar magnetic field, it will be neglected in the present study.

Although the gradients produced by a dipole can be very large, the spins will only probe the magnetic field over a very short distance, of the order of a pore size. Therefore the magnetic field variation within a pore, produced by such a dipole, will never become as large as the main magnetic field. In the random-walk model all spins are excited. In a typical NMR experiment spins are excited within a band of $10^{-3} B_0$ around B_0 .¹³ The spins in the direct vicinity of the dipole do therefore not contribute to the NMR signal in a real experiment. For the case of the largest dipolar strength used in the present study, about 10% of the spins would not be excited. However, in real materials it is not expected that all dipolar grains are in close contact with the pore, as in the model, but most will be enclosed in the solid matrix. The difference between the random-walk model and a NMR experiment therefore affects only a small fraction of the spins and will be neglected in the remainder of this paper.

B. Dephasing spin-echo decay

In a NMR experiment, the transverse nuclear magnetization M is measured. It is equal to the sum of the magnetic moments of all individual spins of the ensemble,

$$M = M_0 \langle \exp(i\varphi) \rangle \equiv \frac{M_0}{K} \sum_{k=1}^K \exp(i\varphi^k), \quad (3)$$

where the superscript k refers to one of the K spins and M_0 is the magnitude of the equilibrium nuclear magnetization. If the phase φ^k of all spins is known, also the resulting magnetization is known and can be compared with experimental data. The phase φ^k can be calculated from a random-walk simulation of the diffusive motion of the spins within the pore. In order to correctly describe this continuous process of dephasing by a random walk, the mean squared displacement resulting from the actual self diffusion D of water has to be

equal to the mean squared displacement in the simulations. This condition is satisfied by taking the following time step $\Delta\tau$ for a random walk:

$$\Delta\tau = \frac{l^2}{2dD}, \quad (4)$$

where $d=3$ is the number of dimensions and l is the distance between two neighboring lattice points.

The phase $\Delta\varphi^k$ accumulated during a time interval $\Delta\tau$ equals

$$\Delta\varphi^k = 2\pi f_L(\mathbf{r}^k)\Delta\tau. \quad (5)$$

Here $\mathbf{r}^k$ is the position of particle k and f_L is the Larmor frequency at that position, which depends on the magnetic field by $f_L = \gamma B/2\pi$, where γ is the gyromagnetic ratio ($\gamma = 2.67 \times 10^8$ rad/Ts).

We concentrate on the Hahn spin-echo intensity, because this is of most interest for the dephasing study. The 90° pulse defines the starting time and the 180° pulse, which inverts the accumulated phase, is applied at $t = J\Delta\tau$. Consequently, the phase of a particle at the spin-echo time $t_E = 2J\Delta\tau$ is given by

$$\varphi^k = \gamma\Delta\tau \left[\sum_{j=1}^J B(\mathbf{r}_j^k) - \sum_{j=J+1}^{2J} B(\mathbf{r}_j^k) \right], \quad (6)$$

where $\mathbf{r}_j^k$ is the position of particle k after j time steps and $B(\mathbf{r}_j^k)$ is the spatially dependent magnetic field.

III. THEORY

A. Uniform magnetic-field gradient

For the spin-echo decay in the presence of a uniform magnetic-field gradient, three length scales are important:⁶

- (1) The diffusion length, $l_D = \sqrt{6Dt}$;
- (2) The structural length, $l_S = V/S$, which is equal to $R/3$ for a spherical pore with volume V , surface area S , and radius R ;
- (3) The dephasing length, $l_g = \sqrt[3]{D/\gamma g}$, where g is the gradient strength.

It should be noted that the diffusion length is a function of time. The longer the molecules can diffuse, the larger the distance they can travel. The structural length determines how far the molecules can travel because of the restricted geometry. The dephasing length indicates how far a particle has to travel to dephase by 2π . Only particles with less dephasing contribute significantly to the spin-echo decay.

The spin-echo decay due to dephasing is generally given as a dephasing rate R_d ,

$$\ln \left(\frac{M(t)}{M_0} \right) \approx -R_d t + \theta(t^2). \quad (7)$$

Note, that when the magnetization decays exponentially, Eq. (7) becomes equal to $M(t) = M_0 \exp(-R_d t)$. As mentioned before, the relaxation contribution is not considered. The shortest of the length scales determines the dominant mechanism of the spin-echo decay. Free diffusion will occur when the diffusion length is the shortest length scale, which will

occur always for very small times. Motional averaging will occur when the structural length is the shortest length scale. This means that the particles can probe the complete pore space, without significant dephasing. Finally, the localization regime will occur when the dephasing length is the shortest length scale. This means that the particles dephase significantly before they reach the pore wall. It was found that in the motional averaging regime the dephasing rate scales with g^2 and in the localization regime with $g^{2/3}$ (cf. Ref. 8). It is not clear whether these scaling laws hold in the presence of a dipolar field.

B. Nonuniform magnetic-field gradient

Obviously, in the case of a dipolar field, or more generally, a nonuniform magnetic-field gradient, one can no longer use the gradient strength as a parameter, because it now depends on position. Although we are interested in dipolar fields, which vary in all spatial directions (3D), we limit our discussion in Secs. III B and III C to fields that vary only in one direction x (1D). We have done this to keep this discussion as simple as possible, because it is meant as a qualitative explanation of the dephasing behavior. Now, the important question is what will happen with the above defined length scales:

- (1) The diffusion length is independent of the magnetic field and therefore remains the same, $l_D = \sqrt{6Dt}$;
- (2) The structural length is also independent of the magnetic field and remains, $l_S = V/S$;
- (3) The dephasing length becomes a function of the position x , $l_g(x) = \sqrt[3]{D/\gamma g(x)}$, where $g(x)$ is the local gradient strength.

The dephasing spin-echo decay depends on the magnitude of the magnetic field gradient. The diffusing particle will probe an approximately uniform magnetic-field gradient during the very first period of the spin-echo measurement. However, after a certain amount of time, the particle starts to experience deviations from this uniform gradient. This can be quantified using a Taylor expansion of the magnetic field around x_0 ,

$$B(x) = B_0 + \left. \frac{\partial B}{\partial x} \right|_{x_0} (x - x_0) + \frac{1}{2!} \left. \frac{\partial^2 B}{\partial x^2} \right|_{x_0} (x - x_0)^2 + \Theta((x - x_0)^3), \quad (8)$$

where the first derivative is the local gradient,

$$g(x_0) \equiv \left. \frac{\partial B}{\partial x} \right|_{x_0}, \quad (9)$$

and the second derivative is the curvature,

$$C(x_0) \equiv \left. \frac{\partial^2 B}{\partial x^2} \right|_{x_0}. \quad (10)$$

Now we introduce a magnetic-field curvature length scale l_B , which is defined as the ratio of the first and the second derivative,

FIG. 1. Schematic picture of spatially (1D) varying length scales in a pore. On the horizontal axis, the position x in the pore is depicted. On the vertical axis the length scales are plotted. The diffusion length l_D is independent of x , but a function of time. The structure length l_S is independent of x and is shown as a dashed line. Both the dephasing length $l_g(x)$ and the magnetic-field curvature length $l_B(x)$ are a function of the position in the pore. For a known magnetic field, these length scales can be calculated. In this example, they are drawn with an arbitrary shape. In the dark gray area, no magnetization is left. The spin-echo decay in the light gray area can be described by the LGA. In the white area, some magnetization will be present, but the spin-echo decay rate is unknown. The transitions from one regime into another regime occur at times t_I , t_{II} , and t_{III} , which are explained in the text.

$$l_B(x) \equiv \left| \frac{g(x)}{C(x)} \right|. \quad (11)$$

As long as the particles have diffused a distance small compared to this magnetic-field curvature length, they experience a uniform gradient and the higher order terms of the magnetic field are negligible. Often this is called the local gradient approximation (LGA).^{6,14,15} When the particles travel over longer distances, the effect of the higher order terms becomes significant and the LGA is no longer applicable. There is no general analytical formula describing this situation. Only the magnetization decay in a perfectly parabolic magnetic field has been solved exactly by Doussal and Sen.¹⁶ We find it useful to put all relevant length scales in one schematic graph, Fig. 1. One should note that this situation is just one example of all the possible situations which can occur. (In Sec. III C more situations will be shown.) On the horizontal axis the position x in the pore is depicted. On the vertical axis the length scales are plotted. The structural length l_S is a constant for all particles and therefore a horizontal line. The diffusion length l_D is also equal for all particles in the porous material. However, it is a function of time. This is visualized in Fig. 1 by the analytical expression for the diffusion length on the vertical axis below the arrow. Both the dephasing length $l_g(x)$ and the magnetic-field curvature length $l_B(x)$ are a function of position.

The graph can be used to determine the regime of the spin-echo decay. For very short times the diffusion length is the shortest length scale for all particles at all positions. The local gradient approximation gives the spin-echo decay. At a

FIG. 2. Overview of the situations which can occur with respect to the length scales, l_D , l_S , $l_g(x)$, $l_B(x)$. On the horizontal axis the position x in the pore is depicted and on the vertical axis the length scales are plotted. In (a) the smallest length scale is l_B , which implies that the LGA will only hold for a certain time interval. Thereafter unknown spin-echo decay will occur. The situation of (b) is similar to Fig. 1. When $l_g(x)$ is the shortest length scale, as shown in (c), the LGA can be used for the complete spin-echo decay curve. When l_S is smaller than both $l_g(x)$ and $l_B(x)$, the motional averaging regime is applicable, as shown in (d).

certain time, t_I , some particles have diffused further than the dephasing length. These particles have accumulated such a large phase difference, that they do not contribute significantly to the signal anymore. This regime is dark gray in Fig. 1. Some time later, t_{II} , some particles have diffused further than the magnetic-field curvature length l_B . Therefore, the LGA is not valid anymore for these particles. However, they have not moved further than the dephasing length l_g and therefore they still contribute to the spin-echo signal. At this time, the LGA breaks down and will no longer describe the spin-echo decay correctly. The regime of the spin-echo decay where the LGA holds is shaded light gray in Fig. 1. As said before, it is not clear how to describe the spin-echo decay at larger times. At very large times, t_{III} , when there is still some signal left because for some particles $l_D < l_g$, a fraction of these particles feel the structure length l_S as the shortest length scale. However, the rest of these particles feel the magnetic-field curvature length l_B as the shortest length scale. Also in this case, the resulting spin-echo decay is unknown.

C. Regimes

In the previous section we have discussed a specific situation (cf. Fig. 1). Now, in Fig. 2, a comprehensive overview is given. The horizontal axis again reflects the position x in the restricted geometry and the vertical axis denotes the various length scales. The situation of Fig. 2(b) is described in the previous subsection. Figure 2(a) differs from Fig. 2(b) in the sense that the LGA breaks down before any particle has

travelled over a distance longer than l_g . In Fig. 2(c) the complete spin-echo experiment is described by the LGA. To get a motional averaging regime after $l_D > l_S$, it is needed that $l_S < l_g$ for the complete pore. For this case, the magnetic-field curvature length is not important. An example of this situation is shown in Fig. 2(d).

To distinguish between the various situations, scaling laws can be helpful. The scaling for the motional averaging regime will be given in the next subsection. Thereafter, the scaling for the LGA (situation c) will be derived. The remaining situations (a) and (b) are described by the LGA with respect to the first part of the spin-echo decay. One can calculate the time at which deviations are expected and the unknown spin-echo decay starts. These deviations become visible in the numerical results which will be discussed in Sec. IV.

D. Motional averaging scaling

Wayne and Cotts have analyzed their experiment on a confined gas as a motional-narrowing problem.⁴ This approach gives a good idea about the phase accumulation of a diffusing spin in the motional averaging regime. Although the applied magnetic field is static, a diffusing spin experiences a time-dependent magnetic field. The resulting dephasing rate is given by the autocorrelation function of the randomly varying part of the magnetic field, $B(x(t))$, seen by the diffusing spin,¹⁷

$$R_d = \gamma^2 \int_0^\infty \langle B(x(0))B(x(t)) \rangle dt. \quad (12)$$

This equation is valid for times $t \gg \tau_c$, the correlation time of the motion. The scaling of Eq. (12) for different pore sizes and magnetic fields is of great interest, because it will give us a tool to identify the motional averaging regime. The magnetic field can be written as

$$B(x(t)) = \mu h(x(t)), \quad (13)$$

where μ is a factor reflecting the magnitude of the magnetic field and $h(x)$ is the spatial geometry of the field. Note that for the situation of a dipolar field, μ can be taken equal to the dipole strength. However, we like to derive a scaling law for an arbitrary magnetic field. Substitution of such a field (13) into Eq. (12) yields

$$R_d = \gamma^2 \mu^2 \int_0^\infty \langle h(x(0))h(x(t)) \rangle dt. \quad (14)$$

If only the magnetic field strength is varied, it is clear that R_d scales with μ^2 . We like to stress that Eq. (14) also holds for 3D systems. For such a system $x(t)$ should be replaced by the position vector $\mathbf{r}(t)$.

E. Local gradient scaling

The spin-echo decay for a freely diffusing particle in a uniform magnetic-field gradient g is given by¹

$$M = M_0 \exp\left(-\frac{D\gamma^2}{12} g^2 t^3\right), \quad (15)$$

where t is the spin-echo time. If g depends on the position $\mathbf{r}$, it is shown in Sec. III B that this description of the spin-echo decay remains valid as long as $l_D < l_B$,

$$M = \frac{M_0}{V} \int \exp\left(-\frac{D\gamma^2}{12} g^2(\mathbf{r}) t^3\right) d^3\mathbf{r}. \quad (16)$$

To find the scaling of the dephasing with magnetic field strength, the magnetic field will again be written as $B(\mathbf{r}) = \mu h(\mathbf{r})$. Hence the magnetic-field gradient can be written as $g(\mathbf{r}) = \mu f(\mathbf{r})$. Substitution of this gradient into Eq. (16) yields

$$M = \frac{M_0}{V} \int \exp\left(-\frac{D\gamma^2}{12} f^2(\mathbf{r}) (\mu^{2/3} t)^3\right) d^3\mathbf{r}. \quad (17)$$

By putting the magnetic field strength μ and spin-echo time t together, it becomes clear that the magnetization is a function of the combination of these two quantities,

$$M = M(\mu^{2/3} t). \quad (18)$$

This implies that the dephasing rate scales with the magnitude of the magnetic field to the power 2/3 ($R_d \sim \mu^{2/3}$) when the field geometry is taken constant. One should remember that this only holds if the particle diffuses freely and experiences a uniform local gradient (the LGA condition). Finally, we want to stress that Eq. (17) is applicable to both 1D and 3D systems as long as the spins experience variations in the magnetic field that vary linearly with position. In this case the reference frame can always be oriented such that the gradient in the field is oriented along one of the axes.

IV. RESULTS AND DISCUSSION

For two model systems, the dephasing of the magnetization is simulated. In the first system, a magnetic point dipole is located at the wall of a pore of constant size. Simulations are performed for various dipole strengths. The upper and lower bound of the dipole strength are chosen in such a way that the simulated dephasing rate is of the same order as the dephasing rates that can be measured in a NMR experiment. In the second system, a dipolar grain of varying size is put adjacent to a pore of varying size, but for every simulation the dipole size is equal to the pore size. Again scaling laws will give insight into the dephasing process for dephasing rates in the experimentally accessible range.

A. Varying magnetic dipole strength

First, two simulations are presented of the same model with a different magnetic dipole strength to show the difference in spin-echo decay. These two simulations correspond to the lower and upper bounds of the dipole strength variation in the more systematic survey, presented at the end of this section. These bounds are chosen in such a way, that the dephasing rates are within the range of experimental verification.

Consider one dipole with a dipole strength μ , located at the pore wall, just inside the porous material (cf. Fig. 3). The pore size is taken such that $l_S = 0.33 \mu\text{m}$ and the dipole po-

FIG. 3. Schematic picture of the simulated situation. A magnetic dipole with strength μ is located just outside the pore with radius $R = 3l_s$. The position of the dipole is specified by the angle ϕ .

sition is taken arbitrarily at $\phi = \pi/2$. The magnetic dipole strength equals 10^{-14} A m^2 and the dipole is assumed to be a point dipole.

Figure 4(a) shows the simulated spin-echo decay for 50 Hahn spin echoes. The number of simulated particles is 3×10^6 , which appears to give a noise level of about 2×10^{-3} . It is clearly visible that the spin-echo decay is not monoexponential, in contrast to all previous simulation results with a uniform magnetic-field gradient.⁸ This nonmonoexponential behavior is also observed in NMR Hahn spin-echo measurements on heavily (wt. % $\text{Fe}_2\text{O}_3 \geq 5\%$) magnetically doped materials.⁹ It is expected that these simulations are characterized by the situation of Figs. 2(a) or 2(b), in which the LGA breaks down. In this case, for a significant number of particles the diffusion length becomes equal to the magnetic-field curvature length before it becomes equal to the dephasing length. It is not clear yet, how the dephasing rate can be described after this transition time [time of the kink in Fig. 4(a)]. However, before the transition time, we expect that the slope of the spin-echo decay scales according to the LGA, which will be shown below.

Next, the magnetic dipole strength μ is decreased to 10^{-19} A m^2 , without changing the configuration, to observe the effect on the spin-echo decay. Figure 4(b) shows the result of this simulation. The spin-echo decay is monoexponential

FIG. 4. Simulated Hahn spin-echo intensity as a function of spin-echo time for a pore size corresponding to $l_s = 0.33 \mu\text{m}$ and a dipole position $\phi = \pi/2$. The solid line represents the initial slope of the data. (a) Dipole strength $\mu = 10^{-14} \text{ A m}^2$; (b) $\mu = 10^{-19} \text{ A m}^2$.

FIG. 5. Dephasing rate R_d as a function of the magnetic dipole strength μ for three pore sizes. The solid lines represent the scaling laws for the motional averaging regime (slope=2) and the LGA situation (slope=2/3).

nential for all times. The number of simulated particles is 4×10^4 , which appears to give a noise level of about 5×10^{-3} . Because the relaxivity of bulk water without dephasing is of the order of 1 s^{-1} and the relaxivity of restricted water easily gets one order of magnitude larger, only a very small spin-echo signal will be left at $t = 0.5 \text{ s}$. Therefore it might be difficult to measure such a small dephasing rate in an actual NMR measurement.

To get a better understanding of the relaxivity of this model system, the dipolar strength is varied systematically between $\mu = 10^{-19} \text{ A m}^2$ and 10^{-14} A m^2 . The dephasing rate R_d is taken equal to the initial slope of the spin-echo decay curve, because the LGA describes the initial magnetization decay. The scaling laws for the motional averaging regime hold for all times. The observed spin-echo decays in this regime are monoexponential.

Figure 5 shows the dephasing rate as a function of dipole strength μ for three structural lengths $l_s = 0.1, 0.33$, and $1 \mu\text{m}$ (the pore radius $R = 3l_s$, and the total lattice size $l = 3R$). For every pore size a transition can be seen from a

FIG. 6. Isomagnetization surface of $\frac{1}{2}M_0$ for four successive spin-echo times. The magnetic dipole ($\mu = 10^{-14} \text{ A m}^2$) is situated at the top of the pore with a radius of $3 \mu\text{m}$.

behavior of $R_d \sim \mu^2$ to a behavior of $R_d \sim \mu^{2/3}$. This transition shows some similarity with simulations based on a varying uniform gradient strength (cf. Fig. 5 from Ref. 8). For that situation it was found that the motional averaging regime scales with g^2 and the localization regime with $g^{2/3}$. The scaling of the simulated dephasing rate for the present situation of a dipolar field with a varying strength can be understood from the scaling laws presented in Sec. III. We already showed that the dephasing rate scales with μ^2 [cf. Eq. (14)] in the motional averaging regime. This behavior is most clear for the smallest ($l_s = 0.1 \mu\text{m}$) pores (cf. Fig. 5), which can be understood from the fact that for motional averaging, the diffusion length has to be larger than the pore size. For the LGA, we derived that the dephasing rate scales with $\mu^{2/3}$ [cf. Eq. (18)], if the field geometry is not changed. This behavior is indeed observed in Fig. 5.

The difference in dephasing behavior between the motional averaging regime and the LGA regime can be clarified by observing the spatially resolved transverse magnetization. For this purpose, the magnetization needs to be simulated at every lattice point (10^6 in total). It was found that a simulation of 10^8 particles is required to get a good signal to noise ratio. For the motional averaging regime [simulation of Fig. 4(b)] the magnetization was found to be homogeneously distributed for every spin-echo time. In case of a large dipole strength $\mu = 10^{-14} \text{ A m}^2$ [simulation of Fig. 4(a)] the magnetization was found to be inhomogeneously distributed. To visualize the spatial distribution of the magnetization, isomagnetization surfaces were plotted. Figure 6 shows the regions with a transverse magnetization larger than $\frac{1}{2}M_0$ for four successive spin-echo times, in a simulation with a pore radius of $3 \mu\text{m}$, corresponding to $l_s = 1 \mu\text{m}$, and a dipole strength $\mu = 10^{-14} \text{ A m}^2$. It is clearly visible that the magnetization is destroyed by dephasing in the neighborhood of the dipole. The volume of zero magnetization increases faster

FIG. 7. Schematic picture of the simulation with equally sized pore and dipole. In the actual calculations the effect of the dipole is represented by a point dipole with a strength $\mu \sim R^3$ placed in the center of the finite-sized dipolar grain.

than the diffusion process. For example, consider the last spin-echo time $t = 7.6 \mu\text{s}$ in Fig. 6. At that time, the diffusion length is only $0.3 \mu\text{m}$, whereas the volume of zero magnetization is nearly equal to the pore radius of $3 \mu\text{m}$.

B. Dipole size equals pore size

In the above simulations, the dipole was considered as a point dipole with a certain strength. In a real material, however, a varying dipole strength can only be achieved by a varying dipole size [cf. Eq. (2)]. Therefore we have performed simulations in which the effect of the dipole size is included. To keep the amount of simulations manageable, we focus on the configuration of a dipole with a size equal to the pore size (cf. Fig. 7). The dipole strength is calculated for a sphere of Fe_2O_3 with radius R . Next, this strength is associated with a point dipole at a distance R from the pore wall.

The radius R of both the pore and the dipole was varied between $0.1 \mu\text{m}$ and $100 \mu\text{m}$. Simulating pores and magnetic grains smaller than $0.1 \mu\text{m}$ is very time consuming, because the lattice dimension scales with the pore size (cf. Ref. 8 for details). Pores and magnetic dipoles larger than $100 \mu\text{m}$ were found to give a deviation from the monoexponential decay for very short times. In that case, the initial decay rate is only valid for a small part of the spin-echo decay. Figure 8 shows the resulting dephasing rate as a function of radius R . This figure illustrates that the dephasing rate for this configuration also gives two scaling regimes, one in which $R_d \sim R^2$ and one in which $R_d \sim R^{2/3}$.

To understand these two scaling properties, a dimensionless space coordinate $\mathbf{r}' = \mathbf{r}/R$ is introduced. Next, we consider the magnetic dipole field [cf. Eq. (1)], in which the dipole strength can be made dimensionless with

$$\mu' \equiv \frac{\mu}{R^3}, \quad (19)$$

because it depends linearly on the volume of the dipole [cf. Eq. (2)]. It follows from Eqs. (1), (13), and (19) that the field geometry $h(r, \cos \theta)$ and the scaled field geometry $h'(r', \cos \theta)$ are related by the following equation:

$$h'(r') \equiv h(r) R^3 \sim \frac{R^3}{r^3} = \frac{1}{(r')^3}. \quad (20)$$

FIG. 8. Dephasing rate as a function of dipole size and pore size for two different dipole strengths. The solid lines are guides to the eye to show the scaling behavior of the dephasing rate in the motional averaging regime (slope=2) and the LGA situation (slope=−2/3).

When the pore size and the lattice size scale with R ($l' = l/R$), the time step, $\Delta\tau$, scales according to [cf. Eq. (4)].

$$\Delta\tau' = \frac{l'^2}{2dD}. \quad (21)$$

As a consequence, the time in this simulation, which is always a multiple of $\Delta\tau$, scales with

$$t' = \frac{t}{R^2}. \quad (22)$$

For the motional averaging regime, all these scaling properties [Eqs. (19), (20), (22)] are substituted in the general equation for the dephasing rate [cf. Eq. (14)], resulting in

$$R_d \sim \mu^2 \int_0^\infty \langle h(0)h(r) \rangle dt \sim \mu'^2 R^6 \int_0^\infty \langle h'(0)h'(r')R^{-6} \rangle dt' R^2 \sim R^2. \quad (23)$$

Therefore the dephasing rate scales with R^2 in the motional averaging regime, as is also observed in Fig. 8. Hence we can conclude that for small dipolar magnetic grains, the system is in the motional averaging regime.

To understand the scaling in the LGA, the spatial derivative of the field is also needed. Using Eqs. (1), (13), (19), (20) and $\nabla = (1/R)\nabla'$ yields

$$|\nabla B| = \frac{\mu'}{R} |\nabla' h'|. \quad (24)$$

Substitution of this dimensionless magnetic-field gradient into the general LGA equation [Eq. (16)] yields

$$M = \frac{M_0}{V'} \int \exp\left(-\frac{D\gamma^2}{12} |\nabla' h'|^2 \left(\frac{\mu'}{R}\right)^{2/3} t\right) d^3 \mathbf{r}'. \quad (25)$$

This equation shows that the dephasing rate in the LGA scales with the dipole size and pore size $R^{-2/3}$, as is observed for large dipolar magnetic grains in Fig. 8.

However, large dipolar magnetic grains result in very curved exponential decay. Therefore we decided to decrease the dimensionless dipole strength μ' by a factor of 10. This corresponds to a ferromagnetic material with a 10 times smaller saturation magnetization. A nice advantage of this smaller dipole strength is that the crossover point from the motional averaging regime into the LGA regime occurs at a dephasing rates which is accessible with experimental NMR. It can also be understood why the transition from the motional averaging regime into the LGA regime occurs now at a larger dipole size, because the 2π phase accumulation limit is reached for larger pores. The absolute value of the dephasing rate in the motional averaging regime decreases by a factor of 10^2 for the same value of R , which is consistent with Eq. (23). From Eq. (25) we expect a factor of $10^{2/3}$ decrease for the part of the curve corresponding to large pore sizes and dipole sizes (after the transition), which tendency can also be deduced from Fig. 8. Therefore not only the scaling of the decay rate with dipole size, but also the scaling with dipole strength is understood.

V. CONCLUSIONS

A random-walk model is used to investigate the NMR dephasing behavior of hydrogen spins of water in a pore subject to a dipolar magnetic field. It is found that in such a magnetic field a motional averaging regime can occur, as also observed for a uniform magnetic-field gradient. Because a dipolar magnetic field gives rise to a distribution of magnetic-field gradients, the localization regime no longer appears. Instead of this, the spin-echo decay is more complex. To clarify this situation, a spatially varying magnetic-field curvature length is defined. If the diffusion length is small compared to this magnetic-field curvature length, particles experience a local uniform gradient. In this situation, the spin-echo decay can be described by a so-called LGA.

If the dephasing length is larger than the structural length for all particles in the pore, the motional averaging regime will occur at large echo times. In this regime the dephasing rate scales with the strength of the dipolar field squared. If the dephasing length is smaller than the structural length for a significant fraction of the particles in the pore, the situation is more complicated. The LGA will hold as long as the diffusion length is smaller than the magnetic-field curvature length for all particles in the pore. For this situation, we have derived that the dephasing rate scales with the strength of the dipolar field to the power 2/3. This scaling is not only valid for a dipolar magnetic field, but holds for an arbitrary magnetic field with a fixed spatial geometry and a varying magnitude.

The random-walk simulations have proven that the general scaling laws derived for the dephasing rate in the motional averaging regime and for the LGA are correct. The simulations with large dipole strengths also showed a transition time at which the spin-echo decay starts to deviate significantly from the LGA regime. To investigate the effect of the size of the dipole, simulations are performed in which the

dipole size is taken equal to the pore size. For this situation, again the dephasing rate scales differently in the LGA regime and the motional averaging regime. Scaling laws specific for this configuration are derived and are found to agree quantitatively with the simulation results.

Direct proof of the presence of two distinct regimes can also be found in the 3D spatially resolved magnetization plots. These demonstrate that the magnetization is homogeneous for the motional averaging regime and inhomogeneous for the LGA regime.

In conclusion, the random-walk model reveals new fundamental insight into the dephasing behavior of diffusing spins in inhomogeneous magnetic fields. The model is currently used to interpret NMR spin-echo measurements on materials containing large amounts of ferromagnetic impurities.

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