Spin echo diffraction in disordered media with single length scales

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The spin echo diffraction observed in a pulsed field gradient NMR experiment is studied by simulation in computer generated two-dimensional disordered porous media characterized by a single length scale such as their mean pore diameter. In the propagator formulation of the pulsed field gradient experiments carried out in fluids confined inside porous media one expects to see a diffraction pattern characterizing the above length scale. We have explored the possibility of using this *echo diffraction* technique as a practical noninvasive tool to extract information about the pore geometries. It turns out that even for a disordered medium, the echo-diffraction pattern picks up the dominant length scale. [S0163-1829(97)12417-1]

I. INTRODUCTION

Thermodynamic and transport properties of fluids in porous media depend sensitively on the structure of their cavities and their interconnections.[1] Examples of porous media are naturally occurring rocks, biological cells, Vycors, zeolites, intercalated layered systems such as pillared Lamellar oxides and more recently discovered nano and meso tubes like MCM-41. The physical phenomena occurring in these porous systems are very diverse starting from heterogeneous catalysis, biological perfusion, percolation, permeation and shifting, and even a drastic change of the phase diagram of physical systems confined in such media.[2]

Nuclear magnetic resonance[3] has been traditionally used as a successful noninvasive tool to explore the geometrical structure of porous media.[4] Diffusion rates of confined particles (or fluids) are routinely obtained from measurements of attenuation of the spin echo amplitude.[5] Recently pulsed magnetic-field gradient echo experiments have revealed *diffraction*-like properties[6] which then fall into the same category as that of probing solids using x-ray or neutron scattering. This observation has lead to a different way of extracting information about pore geometries. The rightly tuned wave vector, as done in a scattering experiment, can pick up the relevant length scale of the pore.

Theoretical justifications of looking at the spin echo amplitude in the light of scattering theory assumes a δ-function pulse; in other words the strength of the pulse is very large and its duration is extremely short; even under this so-called ''narrow pulse'' approximation exact analytic treatment are only limited to certain regular geometries.[7–12] On the other hand, computer simulations with a view towards (i) designing the media with tunable parameters and (ii) carrying out simulations in computer generated porous media can embellish the field with interesting results. Previous numerical simulations on models of fused glass beads have revealed interesting features consistent with theoretical predictions using the propagator approach.[8–13] In this paper we report observation of an *echo diffraction* pattern in another class of disordered media by simulating a pulsed field gradient spin echo (PFGSE) experiment. We have deviated away from the well-studied cases of periodic geometries and have instead focused on a class of systems which are characterized by a single length scale but otherwise disordered. Moreover these two-dimensional (2D) media with right porosity and pore radii are analogs of commercially prepared Vycors which gives further motivation to simulate echo experiments in these systems.

II. THEORY

In PFGSE, the attenuation of the spin echo signal $M(\vec{k},\Delta)$ results from the displacement (via diffusion) of a nuclear spin originating at $\vec{r}$ at the time of the first pulse and reaching at $\vec{r}\,'$ at the time Δ when the second pulse is applied and the accumulated phase shift $\Delta\phi=\gamma\delta\vec{g}\cdot(\vec{r}-\vec{r}\,')=\vec{k}\cdot(\vec{r}-\vec{r}\,')$. Here $\vec{k}=\delta\gamma\vec{g}$, where δ is the pulse width, $\vec{g}$ is the field gradient, and γ refers to the nuclear gyromagnetic ratio. In the limit of narrow pulse width (i.e., $\delta\rightarrow 0$, $|\vec{g}|\rightarrow\infty$ such that $g\delta=\text{const}$), the echo amplitude $M(\vec{k},\Delta)$ then satisfies a very simple Fourier relationship with $P_s(\vec{r}|\vec{r}\,',\Delta)$, the conditional probability that a particle (nuclear spin) starting from a position $\vec{r}$ diffuses to $\vec{r}\,'$ in a time interval Δ:

$$M(\vec{k},\Delta)=\int p(\vec{r})\int P_s(\vec{r}|\vec{r}\,',\Delta)e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')}d\vec{r}d\vec{r}\,', \qquad (1)$$

where $p(\vec{r})$ is the probability of finding the particle at $\vec{r}$ and $P_s(\vec{r}|\vec{r}\,',t)$ can be looked at as the diffusion propagator. The above equation looks at the echo amplitude as a Fourier transform of the diffusion propagator and has been the starting point of many analyses in the work in Refs. 8–13. A useful definition introduced by Kärger *et al.*[14] is that of an average propagator $\overline{P_s}$ written as

$$\overline{P_s}(\vec{R},\Delta)=\int p(\vec{r})P_s(\vec{r}|\vec{r}+\vec{R},\Delta)d\vec{r}. \qquad (2)$$

With this definition Eq. (1) can be written as

$$M(\vec{k},\Delta)=\int \overline{P_s}(\vec{R},\Delta)\exp(-i\vec{k}\cdot\vec{R})d\vec{R}. \qquad (3)$$

This way of writing the echo amplitude has a distinct computational advantage as we will see later. We will only calculate spherical averages of the above two quantities which we will denote as $\overline{P_s}(R,\Delta)$, and $M(k,\Delta)$, respectively. For a free particle diffusion the echo amplitude is given by $M(\vec{k},\Delta)=\exp(-k^2D\Delta)$, which is the same as the one obtained by Stesjkal and Tanner[7] in the ''narrow pulse approximation.'' For diffusion in restricted geometries if one waits for a sufficiently long time, the propagator $P_s(\vec{r}|\vec{r}',\infty)$ becomes independent of the starting position and approaches $p(\vec{r}')$. Therefore at sufficiently long times

$$\overline{P_s}(\vec{R},\infty)=\int p(\vec{r}+\vec{R})p(\vec{r})d\vec{r}, \tag{4}$$

$$M(\vec{k},\infty)=\int p(\vec{r})\int p(\vec{r}')e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}d\vec{r}d\vec{r}'=S(\vec{k}), \tag{5}$$

where $S(\vec{k})=|\Psi(\vec{k})|^2$ is the structure factor and

$$\Psi(\vec{k})=\frac{1}{V_p}\int p(\vec{r})e^{-i\vec{k}\cdot\vec{r}}d\vec{r}; \tag{6}$$

V_p is the pore volume. We will denote the spherical averages of these quantities by omitting the vector sign. Equation (5) is identical to the one which gives the amplitude of a wave scattered from a medium with a distribution function $p(\vec{r})$ of scattering centers with the scattering wave vector $\vec{k}$. It forms the basis of interpreting the spin echo attenuation as the scattering intensity at wave vector $\vec{k}$. Naturally the resolution becomes $\vec{k}$ limited; in order to probe smaller pore space one needs larger values of k. The *diffraction* in spin echo has been observed in yeast cells containing water,[6,12,13] and in tetrafluoromethane confined in zeolite crystallites.[14]

III. NUMERICAL SIMULATION

The purpose of this paper is to predict results of possible future experiments in certain classes of disordered media. As a prototype and for a systematic study we have chosen a class where the medium is otherwise disordered but can be characterized with a single length scale. A typical pattern is shown in Fig. 1(a). The porous media is prepared by quenching (and subsequent etching one of the components) a critical binary liquid mixture below its miscibility temperature (T_c) and arresting the coarsening procedure after a certain time. Further fine tuning to adjust the porosity is achieved by suitable computer etching of one or the other component.[15] It is known that a binary liquid mixture below T_c orders through small amplitude long-wavelength fluctuations knows as spinodal decomposition. Its late time phase ordering dynamics[16,17] is characterized by a single length scale specifying a measure of the domain size of each component. The main result of this paper is the observation of an *echo diffraction* pattern in these media which corresponds to the dominant length scale alluded to above. The results also show how the echo intensity develops in time giving some idea of designing such an experiment to extract informations in Vycor-like materials.

In the simulation, just like a proton in a real NMR experiment, a random walker probes the pore space.[18] The average propagator and its Fourier transform are obtained by keeping track of the location of the random walkers. The random walkers move around one at a time starting from different initial positions inside the pore space. For any attempted move by the walker towards a grain boundary it stays at the same point but the clock advances one unit. In order to calculate the echo amplitude $M(k,\Delta)$ using random walkers we have used Eqs. (2) and (3), respectively. We first determine the spherically averaged $\overline{P_s}(\vec{r},\Delta)$ for all possible directions of $\vec{r}$ and then get the echo amplitude from Eq. (3).[19] At this point we want to clarify the role of random walkers in the simulation. In order to obtain the structure factor of the medium one might as well use the Fourier transform of $\overline{P_s}(\vec{R},\infty)$ obtained from Eq. (5) which gives $S(\vec{k})$, or use Eq. (6). For any porous medium constructed out of a square mesh this can be exactly calculated numerically by binning the distance for every point from an arbitrary origin. Neither of these two schemes require a random walker to explore the pore space. The role of random walkers in sampling the pore space becomes important when one wants to monitor the echo amplitude as a function of time which in the very long-time limit gives information about the static structure factor so that one can relate this time scale to an experimental situation, provided one knows the diffusion rate. This issue will be discussed after we present our results.

IV. RESULTS OF NUMERICAL SIMULATION

A. A square pore

First as a test case we have compared our simulation results with known exact results for a square pore of side 100, which is roughly the average diameter of the porous medium considered here. We define a quantity, density of states $\rho(r)$, which is related to the quantity $p(\vec{r})$ in a simple way, $\rho(r)=\int p(\vec{r})d\Omega$. Choosing the origin at the center and noting that $p(\vec{r})=1$ inside the pore space and zero otherwise, the density of states $\rho(r)$ for a square pore of side a is given by

$$\begin{aligned}\rho(r)&=1, \quad 0<r<a/2\\ &=1-\frac{4}{\pi}\cos^{-1}\left(\frac{a}{2r}\right), \quad \frac{a}{2}<r<\frac{a}{\sqrt{2}}\\ &=0, \quad r>\frac{a}{\sqrt{2}}.\end{aligned} \tag{7}$$

The structure factor $S(k)$ is then obtained by taking the square of $\Psi(k)$ which is given by

$$\Psi(k)=\frac{1}{V_p}\int \rho(r)J_0(kr)2\pi r dr, \tag{8}$$

where a spherical average over all possible directions for a given value of k has been carried out. The propagator $P(\vec{r},\vec{r}',t)$ for the square pore is also known exactly and is given by

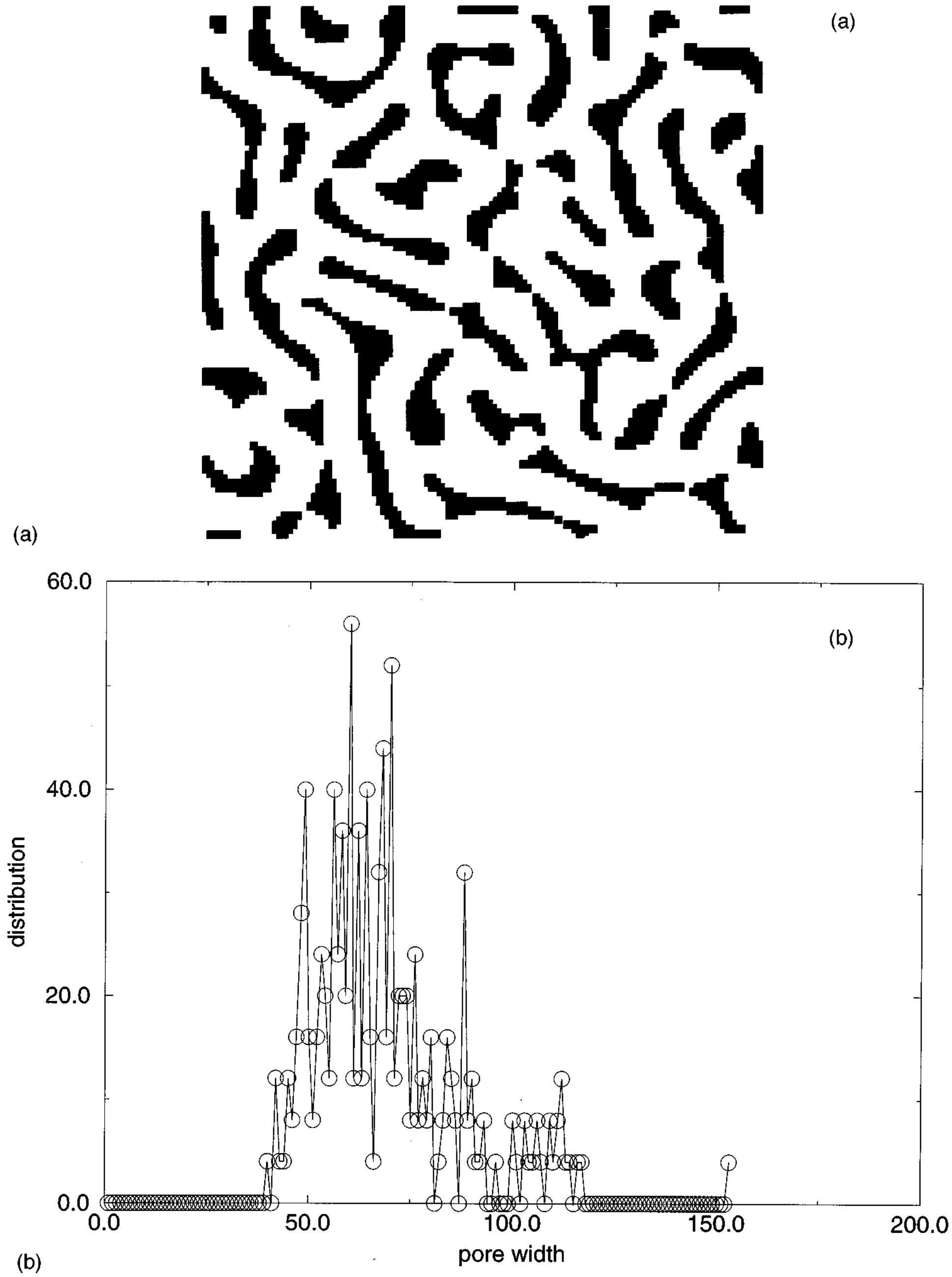

FIG. 1. (a) Picture of a typical porous media used in the simulation. The porosity is 80% and the average pore width is 68 units. The media is constructed from a square mesh of 512×512 lattice; (b) distribution of pore sizes in the above medium.

$$P(x,x',y,y',t)=\frac{1}{a^2}+\frac{4}{a^2}\sum_{m,n}\cos\left(\frac{m\pi x}{a}\right)\cos\left(\frac{m\pi x'}{a}\right)\times\cos\left(\frac{n\pi y}{a}\right)\cos\left(\frac{n\pi y'}{a}\right)\times\exp\left(\frac{-(m^2+n^2)Dt}{a^2}\right). \tag{9}$$

Figure 2 shows $\overline{P_s}(r,t)$ and the inset shows the corresponding $M(k,t)$ for $t=40\,960$ which is a sufficiently long time for the walkers to sample the pore space. We have checked that the diffraction pattern starts to develop at a time $\sim a^2/D$. For comparison we have also shown $S(k)$ in the inset calculated using Eq. (7). Evidently the random walkers sample the geometry of the square very efficiently at sufficiently long time.

B. 2D porous media

We now present results for the porous medium shown in Fig. 1(a). The average pore radius is about 34 lattice units and its porosity is 80%. The distribution of pore sizes is shown in Fig. 1(b). It has a fairly broad width of ~ 20 units around the main peak. One notices it is dominated by a single peak characterizing the average pore width. In this paper we are concerned with the length scale characterizing this peak. The other relevant issues, e.g., how the distribution affects the echo signal will be discussed in a separate paper. The porosity has been chosen intentionally higher than the porosity of an actual 3D Vycor for convenience to generate a single connected percolating pore space. In our future work on 3D porous media we will choose the right porosity range of a Vycor. However, as we will see later our general conclusions will remain the same. The 2D porous media has been generated originally on a 128×128 lattice by a cell-

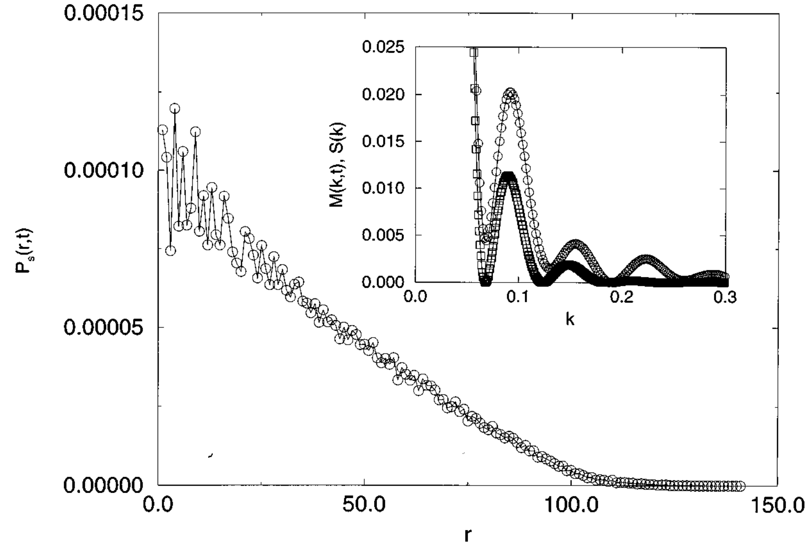

FIG. 2. $\overline{P_s}(r,t)$ as a function of r for $t=40\,960$ for the square pore. The inset shows $M(k,t)$ (circles) as a function of k. On the same graph is plotted $S(k)$ (squares) obtained from $\Psi(k)$ using Eq. (7).

dynamics approach,[20] the details of which can be found in Ref. 15. It was then blown up by a scale factor 4. This enhances the resolution in the coordinate space. Since the entire system is embedded on a lattice, its pair-correlation function $g(|i-j|)=\langle\sigma_i\sigma_j\rangle$ (where σ_i takes the values 0 or 1 at the lattice site i, and $\sigma=1$ characterizes the pore region) and the corresponding Fourier transform, namely the structure factor $S(k)$, can be calculated numerically but otherwise exactly. Obviously $g(r)$ is the $t\to\infty$ limit of $\overline{P_s}(r,t)$. Before we present our results we introduce a scaled pair-correlation function

$$\overline{g(r)}=\frac{g(0)-g(r)}{g(0)-g(\infty)}. \tag{10}$$

This function retains all the structural features of $g(r)$ but goes over to zero at large distances. In order to calculate the structure factor it is better to take the Fourier transform of $\overline{g}$; the numerical integration then does not contain the dominating $k=0$ component and serves better to extract any $k\neq0$ structure. For the tortuous geometry of the Vycor-like disordered media considered here the average propagator is calculated in the following manner. Starting from arbitrary positions of the walkers the quantity $\langle h(|\vec{r}-\vec{r}\,'|,t)\rangle=\langle\langle|\vec{r}(t_0)-\vec{r}\,'(t+t_0)|\rangle\rangle$ is calculated where $\langle\langle\,\rangle\rangle$ denotes average over all possible values of t_0, and for all walkers, respectively. The histogram of this quantity then gives $\overline{P_s}(r,t)$. In principle, if one waits for a sufficiently long time, a single walker will eventually sample the whole pore space and $h(r,t)$ will produce $\overline{P_s}(r,t)$. However that will require storing a very large number of position coordinates. Therefore an ensemble average over many possible walkers, each walking for shorter intervals of time, is performed which easily gives a better statistics.

Figure 3 shows the development of $\overline{P_s}(r,t)$ as a function of time. This gives a picture of how echo amplitude builds up as a function of time. As discussed earlier, initial decay of the amplitude at early time is given by a Gaussain free particle propagator. Once the walkers feel the presence of the walls in the pore space $P_s(r,t)$ gradually picks up the length scales. In this particular case the medium has a single dominant length scale. The walkers eventually extract this scale. Figure 4 shows the corresponding $M(k,t)$ for the same set of times shown in Fig. 3. If one waits long enough eventually $\overline{P_s}(r,t)$ and $M(k,t)$ become stationary and independent of time.

Figure 5 shows $\overline{P_s}(r,t)$ and its scaled counterpart[21] for a very long time ($t=5\times10^5$). In the same figure shown are $g(r)$ and $\overline{g(r)}$ given by dashed and dot-dashed curves, respectively. As expected $\overline{P_s}(r,t)$ eventually gives the pair-correlation function. The first minimum corresponds to the average pore radius. The inset shows the echo amplitude $M(k,t)$. For comparison we have also included the structure factor calculated directly from the pore coordinates. The peak at the structure factor corresponds to the same length scale.

Let us make some remarks about the tail of the structure factor. Since our two-dimensional porous media is prepared using a spinodal decomposition scheme it is expected that $S(k)\sim k^{-(d+n)}$, for $kR\gg1$, where d is the physical dimensionality of the system (in our case $d=2$), n is the dimension

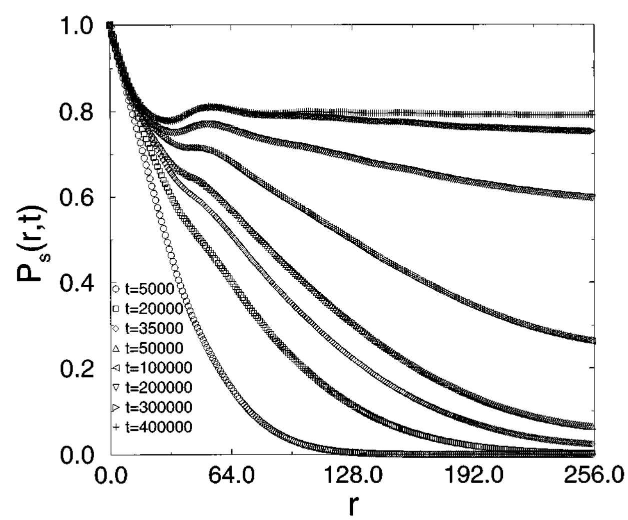

FIG. 3. Development of $\overline{P_s}(r,t)$ as a function of time.

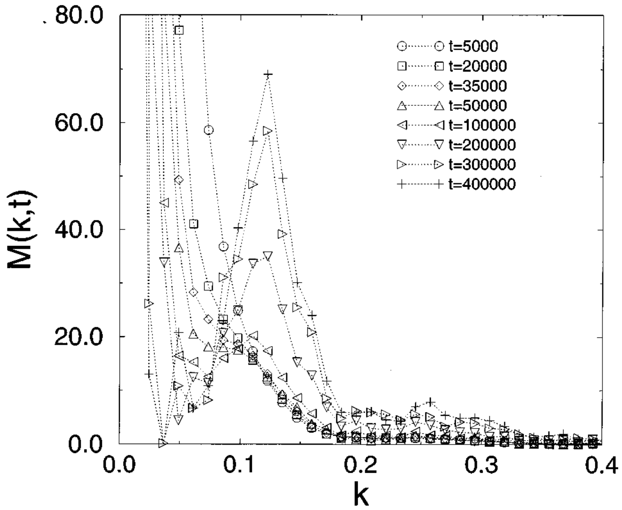

FIG. 4. The corresponding $M(k,t)$ for same set of times.

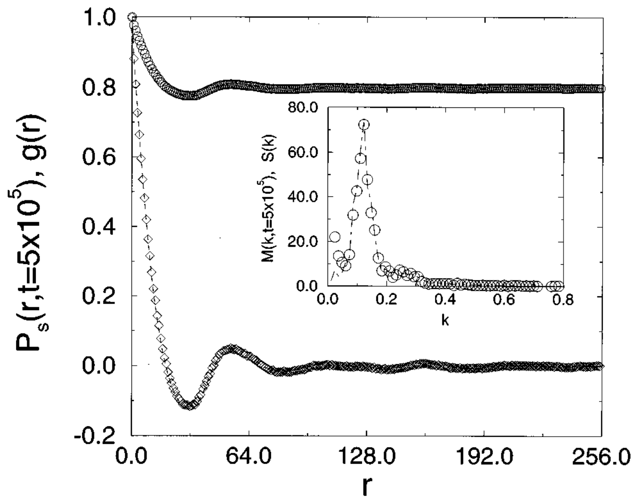

FIG. 5. $\overline{P_s}(r,t)$ as a function of r (circles) for $t=5\times10^5$. The diamonds correspond to the scaled $P_s(r,t)$ as explained in the text. The dashed and the wide dashed line correspond to $g(r)$ and $\overline{g(r)}$, respectively. Inset shows the corresponding $M(k,t)$ (circles) The dashed-dotted line (inset) represents the structure factor calculated directly from the pore coordinates.

of the order parameter (in our case it is a scalar, so $n=1$), and R is a characteristic domain size (in our case it is the pore width). That the tail of the structure factor $\sim k^{-(d+n)}$ has some universal features which are independent of microscopic details has been discussed in detail by Bray.[17] We have checked that for the two-dimensional porous media considered here, for $kR \gg 1$, $S(k) \sim k^{-3}$. Sen *et al.* also found the same result in three-dimensional porous media (constructed out of spherical beads), where $s(k) \sim k^{-4}$.[13]

Finally we would like to comment on the real time scale and feasibility to observe diffraction in spin echo experiments in the porous media considered here. The time ($t_{\rm min}$) after which the diffraction pattern begins to develop $t_{\rm min} \sim l_p^2/D$, where l_p is the average pore width. Kärger *et al.*[14] have done similar experiments in a zeolitic bed using CF_4 as diffusants at room temperature. A typical value for $D \sim 5\times10^{-10}$ m^2/s. For the porous media considered here $l_p \sim 70$ Å which gives $t_{\rm min} \sim 0.1$ ms. Evidently the time scale for these are much shorter than the experiments mentioned above where the observation time goes up to several hundred milliseconds. Therefore the nuclear-spin-relaxation time T_1 should not cause any problem here. On the contrary the wave vector $k=\delta\gamma g$ needed is much larger than used in the experiment of Kärger *et al.* The typical magnetic-field gradient ~ 20 T/m. It is worth wondering how to increase the k resolution. One can try to increase the value of the field gradient as much as possible. The other possibility is to increase the value of the pulse duration δ. In that case the effects of deviation from the ''narrow pulse approximation'' will begin to be important. Naturally, one then has to check how the finite pulse width deteriorates the echo-diffraction pattern which we plan to investigate in a separate paper. We would also like to make a remark about *static* field gradient experiments. It has been reported that using an anti-Helmholtz arrangement of split superconducting coils it is possible to obtain a field gradient of up to 180 T/m, whereas for pulsed field gradient experiments the technical limitations prohibit going beyond 50 T/m.[22] So one has to compare the relative merits of these two methods under special circumstances.

In summary, we have predicted observation of *echo diffraction* in two-dimensional disordered media which could be characterized with a single length scale. Our simulation results show that the echo diffraction pattern picks up the dominant mean length scale despite the fact there is a distribution of pores around the mean. We are extending the calculations for 3D image-based porous media[23] whose resemblance to the commercially prepared Vycors is very close. Experimental results will certainly make these efforts more interesting.

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