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Percolation diffusion of guest molecules in NaCaA zeolites: field gradient NMR studies and Monte Carlo simulations

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Abstract

Percolation diffusion of guest molecules in NaCaA zeolite is simulated by the Monte Carlo method and monitored by the pulsed field gradient (PFG) nuclear magnetic resonance (NMR) technique. The simulations are performed to evaluate possible manifestations of anomalous percolation diffusion in NaCaA zeolite observable by PFG NMR. The observation of normal diffusion of ethane in NaCaA by PFG NMR was found to be in agreement with the results of Monte Carlo simulations. The conditions of the observation of anomalous percolation diffusion by PFG NMR are discussed.

Keywords: Percolation diffusion; NaCaA zeolite; Monte Carlo

1. Introduction

The framework of zeolite A consists of relatively large (1.1 nm in diameter) interconnected cavities which form a simple cubic lattice. The framework elementary charge of -12/cavity is compensated by the exchangeable cations. In A-type zeolites, the exchangeable cations play a particular role due to their ability to block the windows between adjacent cavities [1,2]. The fraction of ''open'' windows in the zeolite depends on the total number of the cations per cavity. Thus, replacement of two Na^+ cations by one Ca^{2+} in NaCaA zeolite may change this fraction from 0 to 1. The framework of NaCaA zeolites with different Ca contents, therefore, can be considered as a percolation lattice with a variable fraction of open windows (p).

Diffusion in NaCaA zeolites with different Ca contents was previously investigated by the macroscopic sorption techniques [2]. The dependence of the diffusion coefficients of guest molecules on the fraction of open windows studied by these methods was found to be in agreement with the predictions of the percolation theory. In this work, we report the results of the investigation of the propagator, i.e. of the probability density of diffusion-initiated displacements of guest molecules in NaCaA zeolites with different fractions of 'open' windows between zeolite cages. This approach, in contrast to the earlier reported measurements of the diffusion coefficients in NaCaA zeolites, allows to monitor directly the deviations of percolation diffusion from normal diffusion. The diffusion

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in NaCaA was modeled by Monte Carlo simulations and monitored by the pulsed field gradient (PFG) nuclear magnetic resonance (NMR) technique [2].

2. Results and discussion

The propagator $P(r,t)$ represents the probability density that during a time interval t, the molecules under study are displaced over a distance r. In quasi-homogeneous systems, including A zeolite with a zero fraction of 'closed' windows, the propagator is Gaussian:

$$P(r,t) = (4\pi Dt)^{-3/2}\exp\left(-r^2/(4Dt)\right), \quad (1)$$

where D is the diffusion coefficient. In a lattice with the fraction of 'open' windows (p) between 1 and that of the percolation threshold ($p_c = 0.2488$ for three-dimensional lattices), the propagator is no longer Gaussian for displacements smaller than the correlation length of the lattice [3].

In the present work, we have carried out Monte Carlo investigations of how well the Gaussian function describes the propagator for A zeolites at the vicinity of the percolation threshold in the long time (large displacement) limit relevant for PFG NMR experiments. Following the approach used in Refs. [4,5], the displacements (r) of random walkers were registered as a function of the number of steps (and hence, of time) and the mean values $\langle |r|^n \rangle$ for different large numbers of steps and $n = 1, 2, 3, 4$ were calculated. These mean values represent the first four moments of the propagator $P(r,t)$:

$$\langle |r|^n \rangle = \int |r|^n P(r,t)\mathrm{d}r, \quad (2)$$

where $n = 1, 2, 3, 4$. The applicability of the Gaussian propagator was tested by comparison of the values of D derived from the different moments according to Eq. 2 under the condition that $P(r,t)$ in Eq. 2 is a Gaussian function (Eq. 1). The agreement between the values of D obtained for different $n(D_n)$ is a direct indication that the propagator is, in fact, Gaussian [4,5].

Monte Carlo simulations were carried out on a cubic percolation lattice of a size of L^3 ($L = 300$) with periodic boundary conditions. The windows (bonds) between adjacent sites were randomly blocked with a probability $(1-p)$. For each lattice with a certain p and a certain configuration of blocked windows, 500–10,000 starting points were randomly selected. Then N step random walks ($N \leq 2 \times 10^7$) originating in these starting points were generated. Correlations between different random walkers were neglected. For each p, the final results represent the averages of over 20 lattices with different configurations of blocked windows.

Fig. 1a shows the values of D_n determined from the moments $n = 1, 2, 3, 4$ for the whole percolation lattice (all finite and infinite clus-

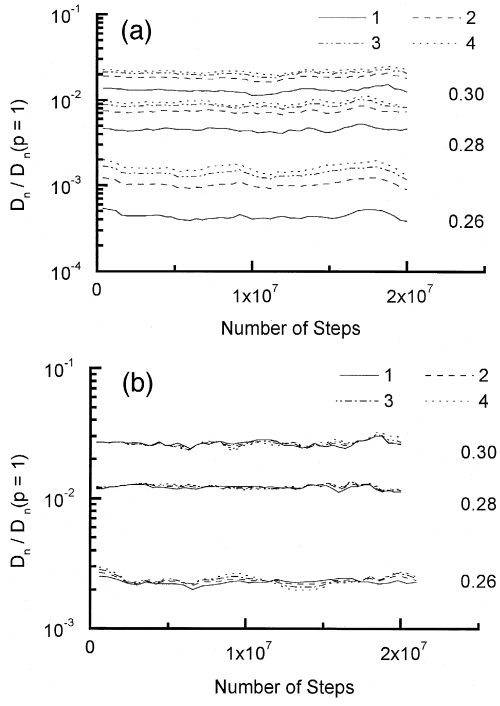

Fig. 1. The normalized values of $D_{1,2,3,4}$ in dependence on the number of steps for $p = 0.30$; 0.28; 0.26: (a) the random walk simulations are carried out on all (finite and infinite) clusters; (b) the random walk simulations are carried out only on the infinite cluster.

ters) in dependence on the number of steps. It can be seen that, on the time scale of Fig. 1, the values of D_n are already time-independent. However, the $D_{1,\ldots,4}$ do not coincide ($D_1 < D_2 < D_3 < D_4$) and the relative difference between different D_n increases as p approaches p_c. This indicates that the shape of the propagator is not Gaussian and that the deviation from the Gaussian propagator increases as p approaches p_c. At the same time, the $D_{1,\ldots,4}$ were found to be identical when only random walks on the cluster spanning the whole lattice were taken into account (Fig. 1b). We assumed that this cluster is an infinite cluster. The coincidence of the D_n in Fig. 1b indicates that in this case, the propagator is Gaussian. Hence, we conclude that the reason of the non-Gaussian shape of the propagator of the diffusion on the whole lattice is the existence of the essentially immobile random walkers trapped in the finite clusters. The mean square displacements of these walkers were found to be orders of magnitude smaller than those on the infinite cluster.

The abovediscussed results have a very simple implication to the PFG NMR diffusion measurements in percolation systems. The quantity accessible by PFG NMR is the attenuation of the NMR signal (the 'spin echo'), which is the Fourier transform of the propagator $P(r,t)$:

$$\psi(\gamma\delta g,t) = \int P(r,t)\exp(i\gamma\delta gr)\mathrm{d}r, \qquad (3)$$

where γ denotes the gyromagnetic ratio and δ, g and t stand for the duration, amplitude and separation of the field gradient pulses [2]. In the percolation systems considered in this work, the molecules on finite and infinite clusters represent two non-overlapping ensembles which can be assigned two different propagators. Since the molecules on the finite clusters are essentially immobile, the propagator of these molecules may be well approximated by the delta function $\delta(r)$. Hence, the spin echo signal of the molecules on the finite clusters Ψ_{im} is a constant, independent of the amplitude and the duration of the magnetic field gradient pulses. The spin echo amplitude of all molecules on the percolation lattice can then be written as:

$$\Psi(\gamma\delta g,t) = \Psi_{\mathrm{im}} + \Psi_{\mathrm{m}}\int P(r,t)\exp(i\gamma\delta gr)\mathrm{d}r, \qquad (4)$$

where Ψ_{m} is the spin echo amplitude of the molecules on the infinite cluster in the absence of the magnetic field gradients and $P(r,t)$ is the Gaussian propagator of these molecules.

Let us now consider the case when the random walkers can penetrate through closed windows with a certain low probability ω. It is intuitively clear that for $\omega \gg 1/N$, where N is the number of steps, random walks with starting points on the infinite and finite clusters are equivalent. Hence, taking into account the abovereported results, it can be expected that also in this case, the propagator is Gaussian. Our results of the Monte Carlo simulations were found to be in agreement with this expectation.

Using the results reported in Ref. [6], we estimate that under the experimental conditions of our PFG NMR measurements of ethane in NaCaA, the condition $\omega \gg 1/N$ is fulfilled. This, according to our results of the Monte Carlo simulations, should lead to a Gaussian

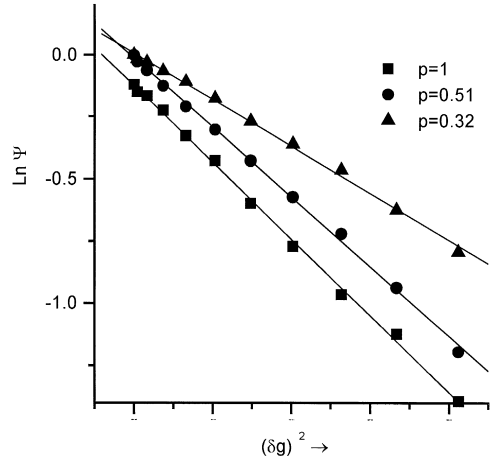

Fig. 2. NMR spin echo amplitude in dependence on the PFG intensity (g) for ethane in NaCaA with different fractions of open windows (p). The PFG NMR measurements were carried out under conditions similar to those described in Ref. [7].

propagator and hence, according to Eq. 3, to an exponential dependence:

$$\psi(\gamma\delta g, t) = \exp(-\gamma^2\delta^2 g^2 tD), \quad (5)$$

of the spin-echo attenuation. The experimentally observed linear dependencies of $\ln\psi$ on g^2 for different values of p (Fig. 2) show that, in agreement with the simulations, the propagator of ethane diffusion in NaCaA zeolite is Gaussian.

3. Conclusions

The results of the Monte Carlo simulations reported in the present communication show under which conditions, anomalous diffusion in NaCaA zeolites can become observable by the PFG NMR technique. The reported PFG NMR diffusion data for ethane in NaCaA give an example of normal diffusion in the percolation system, in agreement with the results of the Monte Carlo simulations.

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