

Diffusion and spin correlation in fractal percolation clusters

J.-P. Korb and J.-F. Gouyet

Laboratoire de Physique de la Matière Condensée, Ecole Polytechnique, 91128 Palaiseau, France

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We have performed Monte Carlo simulations and theoretical calculations of the time decay behavior of the dipolar and spin exchange autocorrelation functions $G_N(\tau)$ over a range of concentrations p ($0 < p < 1$) of randomly diluted magnetic species diffusing in a lattice. For p below the percolation threshold p_c , $G_N(\tau)$ decays exponentially, at long time, with an effective time constant $\tau(p)$ increasing with the concentration. We show that this result is characteristic of a bounded diffusion in a single average cluster explored in the average time $\langle \tau(p) \rangle$. At the percolation threshold $p = p_c$, $G_N(\tau)$ tends asymptotically towards the same power law $\tau^{-d_{\text{eff}}(p_c)/2}$ either for a dipolar or a spin exchange interaction. Here $d_{\text{eff}}(p_c)$ is an effective dimensionality, which appears to be lower than the Euclidean dimensionality d . A theoretical calculation of the kinetics of reencounters of two spins diffusing in a distribution of clusters leads to the relation $d_{\text{eff}}(p_c) = 2 - d_s(3 - \tau_a)$ in terms of the spectral density d_s and the critical exponent τ_a for the distribution of clusters in the theory of percolation. This relation gives $d_{\text{eff}}(p_c) = 0.76, 0.95,$ and $\frac{4}{3}$ for $d = 2, d = 3,$ and $d = 6,$ respectively. The asymptotic expression found for $G_N(\tau)$ is then coherent with a process of anomalous diffusion in a reduced spatial dimensionality. Finally for p above p_c , one finds for each value of p , a power law $G(\tau) \propto \tau^{-d_{\text{eff}}(p)/2}$. There exists a crossover for $d_{\text{eff}}(p)$ between $d_{\text{eff}}(p_c)$ and d for times sufficiently long that the temperature-dependent diffusion length exceeds the concentration dependent correlation length. This solves the seeming contradiction appearing in recent interpretation of nuclear-magnetic-resonance (NMR) results in mixed paramagnetic compounds.

I. INTRODUCTION

Nuclear magnetic resonance (NMR) has been widely used in the study of randomly disordered magnetic systems. Systems of interest include mixed paramagnetic compounds,^{1,2} hydrogen tungstene bronzes,³ polymer gels,⁴ conducting polymers,⁵ porous media,⁶ and heterogeneous systems.⁷ However, the interpretation of the measured data (linewidths, and spin relaxation rates) is difficult. The origin of difficulty often comes from the theoretical model that is used to follow the relaxation process induced by the collective spin dynamics. In the general case of spin motion, the persistence of the fluctuations of the spin interaction can be represented by the many-body spin-correlation function

$$G(\tau) \equiv \sum_{\substack{i,j \\ i < j}} E(\mathbf{r}_{ij}(0)) \sum_{\substack{k,l \\ k < l}} E(\mathbf{r}_{kl}(\tau)).$$

Here $E(\mathbf{r}_{kl}(\tau))$ describes the spin interaction, including the spin operators and the spatial dependences, for instance, in dipolar or exchange interaction between a pair of spins k and l separated by $\mathbf{r}_{kl}(\tau)$ at time τ and $\mathbf{r}_{kl}(0)$ at time $\tau = 0$. Actually, simplifications occur in this expression of $G(\tau)$, namely by separating the autocorrelation and intercorrelation functions,⁷ but also replacing the summations over spins by an ensemble average, noted $\langle \rangle$, taken as an integral over a pair conditional probability, assuming that the interspin distance \mathbf{r} is a random variable. This gives the following spin-correlation function

$$G(\tau) = n [\langle E(\mathbf{r}_0)E(\mathbf{r}) \rangle - |\langle E(\mathbf{r}) \rangle|^2],$$

where n is the spin density.⁷ In the case of translational diffusion of the spins in a homogeneous medium with an Euclidean dimensionality d , the time decay of $G(\tau)$ leads, at long times, to the form $G(\tau) \propto \tau^{-d/2}$. However, this latter form is not valid anymore, for a random medium, because of the inhomogeneities of the spin distribution and anisotropies in the diffusion properties.

The purpose of this paper is precisely to propose a generalization of such statistical description to the randomly disordered systems which have the fractal geometry of percolation clusters. We propose computer simulations and theoretical calculations of the time decay behavior of the dipolar and spin-exchange autocorrelation functions over a range of concentrations p ($0 < p < 1$) of magnetic species diffusing in a lattice. A previous simulation has been done by Klenin and Blume for a dilute Heisenberg magnet at infinite temperature.⁸ However, their calculations were limited to very short times so that no quantitative statement has been made about a possible asymptotic behavior of $G(\tau)$ of the form $G(\tau) \propto \tau^{-d_{\text{eff}}(p)/2}$, where $d_{\text{eff}}(p)$ is an effective dimensionality varying smoothly with p . Different interpretations exist about the use of such asymptotic behavior in the NMR data. For instance, in mixed paramagnetic compounds, d'Ariano *et al.*¹ confirm this asymptotic behavior for concentration p above the percolation concentration p_c , while Engelsberg *et al.*² disagree with such interpretation, at least for $(p - p_c) \geq 0.1$, and fit their data with $d_{\text{eff}}(p) = d$. It is then interesting to provide computer simulation to

solve this seeming contradiction for p above p_c , but also to clearly find out the asymptotic behavior of $G(\tau)$, at long times, for p below and precisely at this percolation threshold p_c .

In Sec. II, we present the Monte Carlo simulation used to calculate the time decay of $G(\tau)$ for spins diffusing on randomly diluted square lattices.

In Sec. III, we present and discuss the asymptotic behaviors of $G(\tau)$, at long times, for $p < p_c$, $p = p_c$, and $p > p_c$, respectively. For $p < p_c$ we show that $G(\tau)$ decays exponentially, at long times, with an effective time constant $\tau(p)$ increasing with the concentration p . This behavior is shown to be characteristic of a bounded diffusion on finite clusters. At the percolation threshold ($p = p_c$) our results, either for a dipolar or a spin-exchange interaction, tend asymptotically towards the same analytical result

$$G_N(\tau) \propto \tau^{-d_{\text{eff}}(p_c)/2},$$

with

$$d_{\text{eff}}(p_c) = 2 - d_s(3 - \tau_a),$$

where $d_{\text{eff}}(p)$ is an effective dimensionality lower than d , d_s is the spectral density,⁹ and τ_a is the critical exponent which describes the distribution of clusters in the percolation theory.¹⁰ This asymptotical form has been obtained by a calculation of the kinetics of collision of the two spins diffusing in a large cluster and averaged over the distribution of clusters. In two-dimensional systems, this result becomes $G(\tau) \propto \tau^{-0.38}$ [here $d_{\text{eff}}(p_c) = 0.76$]. This is quite similar to the observed time dependence of the delayed fluorescence, due to the annihilation of two migrating triplet excitations in a doped naphthalene crystal.¹¹ This proves, at least for a short range interaction, that the time decay of the spin correlations is mainly controlled by the probability of reencounters. Such reencounters increase the effective duration of interaction and make the spin correlations more persistent. Moreover, it is known that the lower the dimensionality, the greater the probability of reencounters.¹² The very slow time decay, that we observe at p_c , is then coherent with a diminution of the spatial dimensionality [$d_{\text{eff}}(p_c) < d$]. An analytical result for $G(\tau)$, at p_c , thus allows an explicit calculation of its Fourier transform and then gives information about the low-frequency behavior of spectral density $J(\omega)$ and spin relaxation rates. Finally, for $p > p_c$ one finds, for each value of p , a power law $G(\tau) \propto \tau^{-d_{\text{eff}}(p)/2}$ with $d_{\text{eff}}(p) < d$ and, for times sufficiently long that the diffusion length exceeds the correlation length ξ ,¹⁰ the asymptotic law $G(\tau) \propto \tau^{-d/2}$, characteristic of a Brownian diffusion on homogeneous medium. One shows that there exists a crossover for $d_{\text{eff}}(p)$ between $d_{\text{eff}}(p_c)$ and d , which depends on the ratio of the length of diffusion $\langle r^2(\tau) \rangle^{1/2}$ (temperature dependent) over the correlation length ξ (concentration dependent). This result is coherent with the evidence by proton magnetic resonance and relaxation of a surprising one-dimensional behavior of the microscopic diffusion of ammonium ions in β alumina.¹³

II. MONTE CARLO SIMULATION

To set up our simulation procedure, we first create a randomly diluted square lattice of size N with pN ($0 < p < 1$) accessible sites for the spins. Then we generate random walks for two interacting spins, with an interaction $E(\mathbf{r})$ (dipolar or spin exchange), at each unit step τ , which depends on the interspin vector \mathbf{r} chosen as a random variable. For a given value of p , we calculate the normalized [$G_N(0) = 1$] spin-autocorrelation function $G_N(\tau)$ defined as

$$G_N(\tau) = \frac{\langle E(\mathbf{r}_0)E(\mathbf{r}) \rangle}{\langle E(\mathbf{r}_0)^2 \rangle}, \quad (1)$$

where the notation $\langle \rangle$ stands for a statistical average over a large enough number of different trajectories N_α and lattices N_l in order to ensure an ergodic system. Basically this gives the following time array:

$$\{G_N(\tau_i)\} = \left[\frac{\sum_{l=1}^{N_l} \sum_{\alpha=1}^{N_\alpha} E(\mathbf{r}_{0al})E(\mathbf{r}_{ial})}{\sum_{l=1}^{N_l} \sum_{\alpha=1}^{N_\alpha} E(\mathbf{r}_{0al})^2} \right], \quad i \in \{0, \dots, N_s\}, \quad (2)$$

where the following indices $i \in \{0, \dots, N_s\}$, $\alpha \in \{1, \dots, N_\alpha\}$, $l \in \{1, \dots, N_l\}$ denote the number of unit steps, trajectories, and lattices, respectively.

The random walk of the pair of spins over the pN accessible sites obeys the following conditions. (i) The initial placement is chosen at random, either in the same or different clusters, (ii) At each unit step, the moving spin is chosen at random and does an independent random walk on the next neighbor accessible sites. The possibility exists, for the spins, to stay fixed at its position during a unit step. This latter possibility ends up to increase the rapidity of convergence to the asymptotic regime, possibly because of a lower probability of entering the dead ends of the clusters.¹⁴ (iii) There are reflexive boundary conditions at the limits of the clusters. (iv) There are the usual toroidal boundary conditions in order to eliminate the surface effect due to the finite size of the lattice. (v) Our data are limited by noise due to statistical fluctuations. This induces absolute errors in the spin-correlation functions of the order of several times 10^{-3} . Obviously, the spin-correlation functions must be much greater than this noise level. The possibility occurs to decrease these errors by performing runs over more trajectories, increasing N_α from 5×10^4 up to 10^5 , and averaging over more lattices, increasing N_l from 20 up to 40. Increasing the size of the lattices from 50×50 up to 150×150 also decreases the surface effects. However, an optimum between all these constraints must be chosen in order to access, in a reasonable computer time, to the asymptotic regime, at long times ($N_s = 10^3$).

III. RESULTS AND DISCUSSION

Examples of the time decays of $G_N(\tau_i)$ with $i \in \{0, \dots, N_s = 10^3\}$, for a dipolar interaction $E(r) \propto 1/r^3$, are displayed in Fig. 1 for different values of p on both sides of the percolation threshold p_c . When p decreases, one observes that the dipolar correlations are more persistent at long times. This is naturally due to the enhancement of the reencounter probabilities which drastically increases the effective duration of interaction. In the following we present and discuss the time decays of $G_N(\tau)$ at p_c and on both side of p_c .

A. Spin correlation below the percolation threshold

For $p < p_c$, the dipolar correlations tend to a constant asymptotic value $G_N(\infty)$, given by

$$G_N(\infty) = \frac{|\langle E(\mathbf{r}) \rangle|^2}{\langle E(\mathbf{r}_0)^2 \rangle}. \quad (3)$$

This asymptotic value is different from zero because the two spin distributions are not completely averaged out over the finite sizes of clusters below p_c . It results in a residual dipolar interaction whose value depends on p as shown in Fig. 2. The NMR measurement of such residual dipolar energy has proven useful to study the molecular dynamics of molten polymers.⁴ Anisotropic motions can also induce such noncompletely averaged residual interaction. For instance, it has been recently shown that the anisotropic motions of quadrupolar nuclei in superionic conductors can also induce a quadrupolar residual energy which affects particularly the lineshape and relaxation rates.¹⁵ Of course, $G_N(\infty) = 0$ at the limit of $p = p_c$ (Fig. 2), where it becomes possible to average out completely the dipolar interaction over the infinite size of the percolation cluster. Then, for $p < p_c$, it becomes necessary to renormalize Eq. (1) in order to cancel out the spin correlations at long times

$$G_N^{\text{renorm}}(\tau) = \frac{\langle E(\mathbf{r}_0)E(\mathbf{r}) \rangle - |\langle E(\mathbf{r}) \rangle|^2}{\langle E(\mathbf{r}_0)^2 \rangle - |\langle E(\mathbf{r}) \rangle|^2} = \frac{G_N(\tau) - G_N(\infty)}{1 - G_N(\infty)}. \quad (4)$$

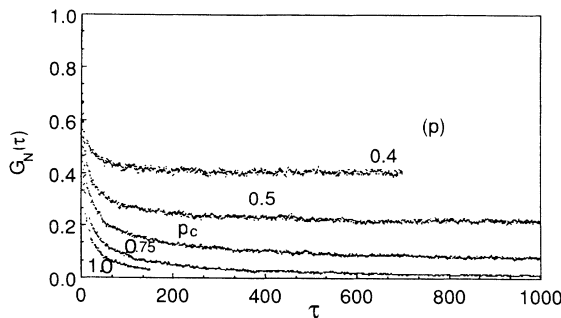


FIG. 1. Time decays of the dipolar correlation functions $G_N(\tau)$ for different concentrations p on both sides of the percolation threshold p_c . The time τ is expressed in number of unit steps.

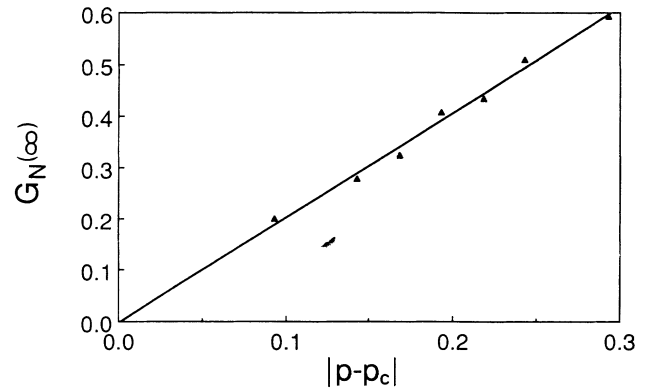


FIG. 2. Variation of the asymptotic value of the dipolar correlation function $G_N(\infty)$ with $|p - p_c|$.

In Fig. 3, we have displayed the time decays of such a function on a semilogarithmic plot for two values of $p < p_c$. In spite of the additional noise, due to the definition of $G_N^{\text{renorm}}(\tau)$, one finds, at long times, a straight line in both cases. This is characteristic of an exponential time decay

$$G_N^{\text{renorm}}(\tau) \propto \exp\left[-\frac{\tau}{\tau(p)}\right], \quad (5)$$

where $\tau(p)$ is an effective time constant increasing with the concentration p . However, a nonexponential behavior appears at the beginning of the diffusion process. This behavior is emphasized when p is very close to p_c . In previous papers,¹⁶ one of the authors has shown that such behavior is characteristic of a bounded diffusion on a finite homogeneous system. Here there is a distribution of clusters below p_c , but the exponential asymptotic regime shown in Fig. 3 is consistent with an interpretation in term of a single effective cluster, the average size of which is taken over the whole distribution. Below we present the calculation of the concentration dependence of the average time $\langle \tau(p) \rangle$ necessary for a complete exploration of a cluster of size $s \in \{1, \dots, S_{\text{max}}\}$. It is known that below p_c , we have a distribution of sizes characterized by the relation

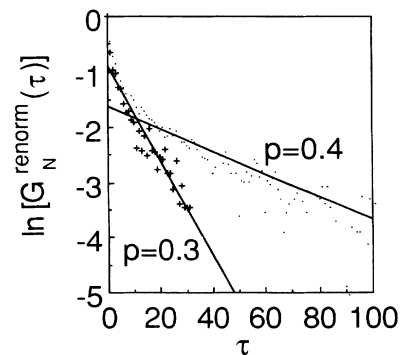


FIG. 3. Semilogarithmic variation of the time decays, of the renormalized dipolar correlation functions [Eq. (4)], for two values of the concentration below the percolation threshold p_c .

$$n_s \propto s^{-\tau_a} f[(p-p_c)s^\sigma], \quad (6)$$

where τ_a and σ are critical exponents describing the distribution and finite size of clusters in the percolation theory.¹⁰ The scaling function f describes a cutoff in this distribution, due to the finite size of the clusters. For a given cluster of s ($\in \{1, \dots, S_{\max}\}$) accessible sites, the number of visited sites $S(\tau(p))$ in the time $\tau(p)$ is given by

$$S(\tau(p)) = s \propto \tau(p)^{d_s/2}.$$

Then one has $\tau(p) \propto s^{2/d_s}$ and the average of $\tau(p)$ over n_s gives

$$\begin{aligned} \langle \tau(p) \rangle &\propto \sum_{s=1}^{S_{\max}} s n_s s^{2/d_s} \\ &\propto \int_1^{S_{\max}} ds s^{2/d_s} s^{1-\tau_a} f[(p-p_c)s^\sigma] \\ &\sim |p-p_c|^{[\tau_a-2-2/d_s]/\sigma}. \end{aligned} \quad (7)$$

Actually, instead of the exponential form given in Eq. (5), the average of $\tau(p)$ corresponds to consider only the first cumulant $\exp(-\tau/\langle \tau(p) \rangle)$. This is generally a very good approximation. In the concentration law given in Eq. (7), the exponent takes the value -3.72 for $d=2$ and -2.95 for $d=3$. For $d=2$, the concentration dependence found from the slopes of Fig. 3 agrees quite well with the theoretical relation given in Eq. (7).

Assuming that during $\tau(p)$ the average cluster explored by the diffusion corresponds to the one of size $s_\xi \sim \xi^{d_f}$, where ξ is the usual correlation length and d_f is the fractal dimension.¹⁰ For the area of such a cluster one has $A_\xi \sim \xi^d \sim s_\xi^{d/d_f}$. The use of the relation $s_\xi \propto \tau(p)^{d_s/2}$, previously defined, leads immediately to $\tau_\xi(p) \sim s_\xi^{2/d_s} \sim (A_\xi)^{2d_f/d_s d}$. Introducing the dimensionality $d_w = 2d_f/d_s$ (Ref. 17) associated to the random walk in fractals gives finally

$$A_\xi(p) \propto \tau_\xi(p)^{d/d_w}. \quad (8)$$

The homogeneous lineshape associated with an exponential dipolar correlation function is known to be close to a Lorentzian in the fast motion regime. According to Eqs. (5) and (8), we predict that the measurement of the concentration dependence of the NMR linewidth will give information about the average area of the clusters explored by the diffusion.

B. Spin correlation at the percolation threshold

For $p=p_c$, the dipolar correlations tend asymptotically to zero according to a power law $G_N(\tau) \propto \tau^{-0.38}$ (for $d=2$) shown in Fig. 4(a). One sees in Fig. 4(b) that the spin correlations, for a spin-exchange interaction $E(r) \propto \exp[-\kappa(r-r_0)]$ with $\kappa=1$ and $r_0=1$ (first neighbor separation), tends asymptotically to zero along the same power law. Basically this proves, at least for a short-range interaction [$G_N(0)$ varies as $1/r_0^6$ or

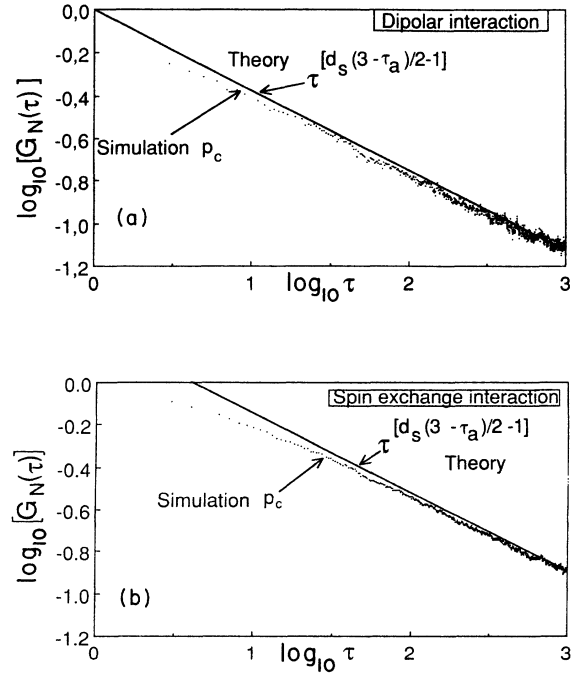


FIG. 4. (a) Logarithmic variation of the time decay of the dipolar correlation function $G_N(\tau)$ at p_c (points) and comparison with the theoretical result of Eq. (11) (solid line). (b) Logarithmic variation of the time decay of the spin-correlation function $G_N(\tau)$ for a spin-exchange interaction at p_c (points) and comparison with the theoretical result of Eq. (11) (solid line).

$\exp(-2r_0)$], that the time decay of the spin correlations is mainly controlled by the probability of reencounters rather than the static range of interaction. Once again, such reencounters increase the duration of interaction significantly, and make the spin correlations more persistent. The power law $\tau^{-0.38}$ (for $d=2$) found in Figs. 4(a) and 4(b) is quite similar to the observed time dependence of the delayed fluorescence due to the annihilation of migrating triplet excitations in a doped bidimensional naphthalene crystal.¹¹ In this latter work, this time dependence has been explained using a percolation model by a calculation of the kinetics of collision of two excitations migrating randomly on a large cluster. Here one can apply the same treatment adapted to the spin correlation. Let us consider a distribution of finite clusters, each characterized by the number s ($\in \{1, \dots, S_{\max}\}$) of accessible sites. One notices that only two spins on the same cluster have a non-negligible probability of reencounters. So we restrict our theoretical calculation on this assumption. The number of visited sites after τ step units is $N(\tau)$. The clusters for which $s < N(\tau)$ have been entirely explored by the diffusion of the two spins. The spatial distributions of such spins are then completely uniformized over these clusters. This will give no time dependence of the spin-correlation function. On the contrary, the clusters for which $N(\tau) < s < S_{\max}$ will participate to the time decay of the spin-correlation function. For a given cluster, the probability (per unit of volume) of finding two spins in a domain of $N(\tau)$ visited sites is pro-

portional to $N(\tau)$. The probability of reencounters (per unit of volume) between τ and $\tau+d\tau$ is then proportional to the difference between the probability of finding the two spins in the domain $N(\tau)$ and that of finding them in the domain $N(\tau+d\tau)$. The total probability of reencounters (per unit of volume) $P_r(\tau)$ must now be averaged over the distribution of clusters n_s

$$P_r(\tau) \propto \sum_{\substack{S_{\max} \\ s > N(\tau)}} n_s N(\tau) - \sum_{\substack{S_{\max} \\ s > N(\tau+d\tau)}} n_s N(\tau+d\tau). \quad (9)$$

Owing to Eq. (6), when $p = p_c$, the distribution of clusters is given by the relation $n_s \propto s^{-\tau_a}$. Substituting Eq. (6) into Eq. (9) and replacing the summations by integrals gives

$$P_r(\tau) \propto [N(\tau+d\tau)^{3-\tau_a} - N(\tau)^{3-\tau_a}] - S_{\max}^{2-\tau_a} [N(\tau+d\tau) - N(\tau)]. \quad (10)$$

For $N(\tau) < S_{\max}$, it is known that $N(\tau) \propto \tau^{-d_s/2}$, where d_s is the spectral dimension.⁹ Substituting this value of $N(\tau)$ gives after some elementary calculations the following expression for the time dependence of $G_N(\tau)$

$$G_N(\tau) \propto P_r(\tau) \propto \tau^{[d_s(3-\tau_a)/2-1]}. \quad (11)$$

This expression is then reducible to the form

$$G_N(\tau) \propto \tau^{-d_{\text{eff}}(p_c)/2}, \quad (12a)$$

introducing here, an effective dimensionality $d_{\text{eff}}(p_c)$ at p_c , given by

$$d_{\text{eff}}(p_c) = 2 - d_s(3 - \tau_a). \quad (12b)$$

Calculation of Eq. (12b), with $d_s = 1, 309$,^{17,18} $\tau_a = \frac{187}{91}$ (for $d = 2$), and $\tau_a = 2.2$ (for $d = 3$), gives $d_{\text{eff}}(p_c) = 0.76$ for $d = 2$ and $d_{\text{eff}}(p_c) = 0.95$ for $d = 3$. In both cases the very slow time decay, that we observe at p_c , is then coherent with a drastic diminution of the spatial dimensionality. One notes that the relation given in Eq. (12b) remains valid when $d = 1$, where it becomes $d_{\text{eff}}(p_c) = 1$, and consequently, $G_N(\tau) = \tau^{-1/2}$ as expected when $p_c = 1$. An ex-

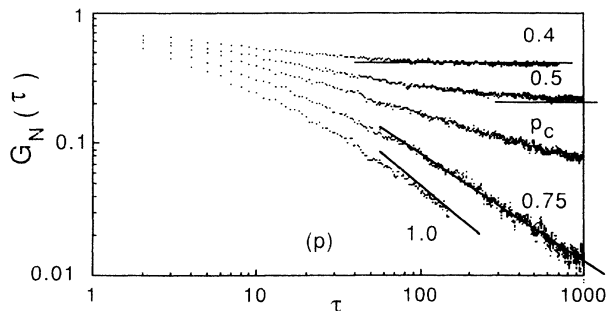


FIG. 5. Logarithmic variation of the time decays of the dipolar correlation functions $G_N(\tau)$ for different values of the concentration p on both sides of p_c . We have materialized the asymptotic behavior as solid lines. For instance, one has a slope of -1 for $p = 1$.

trapolation of Eq. (12b) to $d = 6$ is also interesting because one has, in this case, the exact relations: $d_s = \frac{4}{3}$ and $\tau_a = \frac{5}{2}$ which give $d_{\text{eff}}(p_c) = \frac{4}{3}$. The asymptotical result for $G_N(\tau)$, given in Eqs. (12a) and (12b) thus allows an explicit calculation of its Fourier transform and then gives information about the low-frequency behavior of the spectral density $J(\omega)$ and spin relaxation rates. In the case of a d -dimensional system, one finds at p_c

$$J(\omega) \propto |\omega|^{d_{\text{eff}}(p_c)/2-1}. \quad (13)$$

For $d = 3$, Eq. (13) gives $J(\omega) \propto \omega^{-0.53}$. A result which is characteristic of a diffusion in a quasimonodimensional system [$J(\omega) \propto \omega^{-0.5}$] instead of the form $J(\omega) \propto (1 - \frac{3}{8}\sqrt{\omega})$ usually encountered for a homogeneous tridimensional medium. In consequence, we predict for a tridimensional system, a drastic increase of the

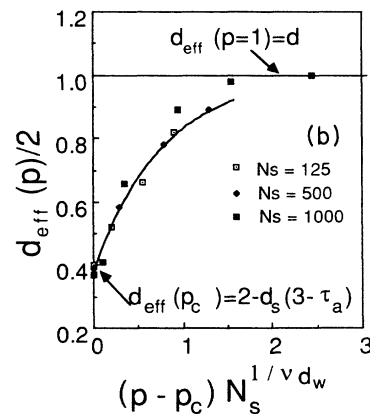
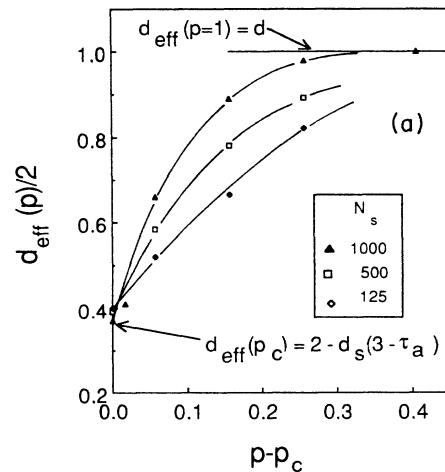


FIG. 6. (a) Concentration dependences of the effective dimensionality $d_{\text{eff}}(p)/2$ for $p > p_c$ when varying the maximum number of unit steps N_s [(125, 500, 1000) here $d = 2$]. (b) Concentration dependences of the effective dimensionality $d_{\text{eff}}(p)/2$ for $p > p_c$ scaled in a single law in term of the dimensionless variable $(p - p_c) N_s^{1/\nu d_w}$. A simple approximate fit $d_{\text{eff}}(p)/2 \sim 1 - 0.62 \exp[-1.3(p - p_c) N_s^{1/\nu d_w}]$ is represented as a solid line. The fit is less correct for $N_s = 1000$ because of the increase of the noise level.

homogeneous NMR linewidth [proportional to $J(0)$] when changing the concentration from $p=1$ to $p=p_c$. Recent NMR experiments in randomly diluted systems agree with this statement.^{1,2}

C. Spin correlation above the percolation threshold

For $p > p_c$, one observes in Fig. 5 that the dipolar correlations after $N_s = 10^3$ unit steps tend to zero according to the following power law:

$$G_N(\tau) \propto \tau^{-d_{\text{eff}}(p)/2}, \quad (14)$$

where the variation of the effective dimensionality d_{eff} with the concentration $p - p_c$ is displayed in Fig. 6(a) for different values of N_s . Actually, it is well known that above p_c , for a sufficiently long time, $\tau \sim N_s$, the square root of the accessible quadratic distance $\langle r^2(\tau) \rangle^{1/2} \sim N_s^{1/d_w}$ exceeds the correlation length $\xi \sim |p - p_c|^{-\nu}$, one has a Brownian diffusion in an homogeneous medium.¹⁷ This means that the effective dimensionality in Eq. (14) is replaced by the Euclidean dimensionality d . Thus, for any values of N_s and p (above p_c), there exists a crossover for $d_{\text{eff}}(p)$ between the reduced dimensionality $d_{\text{eff}}(p_c)$ [Eq. (12b)] and d which is displayed in Fig. 6(b) in terms of the dimensionless variable

$$[\langle r^2(\tau) \rangle^{1/2} / \xi]^{1/\nu} = (p - p_c) N_s^{1/\nu d_w}.$$

One sees that for $(p - p_c) N_s^{1/\nu d_w} < 2$, $d_{\text{eff}}(p)$ is lower than d . Interest of this dimensionless variable is to scale on the same curve the variation with the concentration (system dependent) and the length of diffusion (temperature dependent). This solves the seeming contradiction appearing in the interpretation of NMR results in mixed paramagnetic compounds^{1,2} when using an effective dimensionality. The crossover shown in Fig. 6(b) is also coherent with the evidence, by proton magnetic resonance and relaxation, of a surprising one-dimensional behavior of the microscopic diffusion of ammonium ions in β alumina (a two-dimensional ionic conductor).¹³ We will see in a planned forthcoming paper that the evidence of a very low effective dimensionality will also induce some drastic effect on the temperature dependence of the spin-lattice relaxation rate which could be useful to interpret the diffusion of proton in metallic oxides.¹⁹

IV. CONCLUSION

We have performed Monte Carlo simulations and theoretical calculations of the time decay behavior of the dipolar and spin-exchange autocorrelation functions

$G_N(\tau)$ over a range of concentrations p ($0 < p < 1$) of randomly diluted magnetic species diffusing in a lattice. Interest of these simulations and calculations is to make some reasonable previsions on the behavior of the relaxation quantities in disordered systems which have the fractal geometry of percolating clusters. We have considered successively, squared lattices on both sides of the percolation threshold and at this percolation threshold p_c . For instance, for p below p_c , $G_N(\tau)$ decays exponentially, at long time, with an effective time constant $\tau(p)$ increasing with the concentration. We show that this result is characteristic of a bounded diffusion in a single average cluster explored by the diffusion in the average time $\langle \tau(p) \rangle$. At the percolation threshold $p = p_c$, either for a dipolar or a spin-exchange interaction, $G_N(\tau)$ tends asymptotically towards the same power law $\tau^{-d_{\text{eff}}(p_c)/2}$, where $d_{\text{eff}}(p_c)$ is an effective dimensionality. This proves that the time decay of the spin correlation is mainly controlled by the probability of reencounters rather than by the static interaction. A theoretical calculation of the kinetics of reencounters of two spins diffusing in a distribution of clusters has led to the relation $d_{\text{eff}}(p_c) = 2 - d_s(3 - \tau_a)$, where d_s is the spectral density and τ_a is the critical exponent describing the distribution of clusters. This relation gives $d_{\text{eff}}(p_c) = 0,76$ for $d = 2$, $d_{\text{eff}}(p_c) = 0,95$ for $d = 3$, and $d_{\text{eff}}(p_c) = d_s = \frac{4}{3}$ for $d = 6$. In these cases, the very slow time decay that we observe at p_c is then coherent with a process of anomalous diffusion in a reduced spatial dimensionality. Finally for p above p_c , one finds for each value of p , a power law $G(\tau) \propto \tau^{-d_{\text{eff}}(p)/2}$ with $d_{\text{eff}}(p) < d$. For times sufficiently long that the diffusion length exceeds the correlation length, one shows that there exists a cross over for $d_{\text{eff}}(p)$ between $d_{\text{eff}}(p_c)$ and d . The extension of such crossover depends on the ratio of the length of diffusion $\langle r^2(\tau) \rangle^{1/2}$ (temperature dependent) over the correlation length ξ (concentration dependent). This solves the seeming contradiction appearing in recent interpretation of NMR results in mixed paramagnetic compounds.^{1,2} This is also coherent with the evidence by proton magnetic resonance and relaxation of a surprising one-dimensional behavior of the microscopic diffusion of ammonium ions in β alumina.¹³

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¹G. D'Ariano and F. Borsa, Phys. Rev. B **26**, 6215 (1982).

²M. Engelsberg, J. Albino, O. de Aguiar, Osiel F. de Alcantara Bonfim, and A. Franco, Jr., Phys. Rev. B **32**, 7143 (1985).

³M. A. Vannice, M. Boudart, and J. J. Fripiat, J. Catal. **17**, 359

(1970); P. G. Dickens, D. J. Murphy, and T. K. Halstead, J. Solid State Chem. **6**, 370 (1973).

⁴J.-P. Cohen Addad, J. Chem. Phys. **60**, 2440 (1974); **63**, 4880 (1975).

- ⁵F. Devreux and H. Lecavelier, *Phys. Rev. Lett.* **59**, 2585 (1987).
- ⁶M. H. Cohen and K. S. Mendelson, *J. Appl. Phys.* **53**, 1127 (1982); E. J. Schmidt, K. K. Velasco, and A. M. Nur, *ibid.* **59**, 2788 (1986); K. S. Mendelson, *Phys. Rev. B* **34**, 6503 (1986); M. Lipsicas, J. R. Banavar, and J. Willemsen, *Appl. Phys. Lett.* **48**, 1544 (1986).
- ⁷J. Tabony and J.-P. Korb, *Mol. Phys.* **56**, 1281 (1985); J.-P. Korb, D. C. Torney, and H. M. McConnell, *J. Chem. Phys.* **78**, 5782 (1983).
- ⁸M. A. Klenin and M. Blume, *Phys. Rev. B* **14**, 235 (1976).
- ⁹S. Alexander and R. Orbach, *J. Phys. Lett.* **43**, L625 (1982).
- ¹⁰D. Stauffer, *Introducing to Percolation Theory* (Taylor and Francis, London, 1985).
- ¹¹P. Evesque, *J. Phys.* **44**, 1217 (1983).
- ¹²R. Rammal and G. Toulouse, *J. Phys. Lett.* **44**, L13 (1983).
- ¹³H. Arribart and B. Sapoval, *Solid State Ionics* **9&10**, 323 (1983).
- ¹⁴I. Majid, D. Ben Avraham, S. Havlin, and H. E. Stanley, *Phys. Rev. B* **30**, 1626 (1984).
- ¹⁵D. Petit and J.-P. Korb, *Phys. Rev. B* **37**, 5761 (1988).
- ¹⁶J.-P. Korb, M. Winterhalter, and H. M. McConnell, *J. Chem. Phys.* **80**, 1059 (1984); J.-P. Korb, *ibid.* **82**, 1061 (1985).
- ¹⁷S. Havlin and D. Ben Avraham, *Adv. Phys.* **36**, 695 (1987).
- ¹⁸P. Argyrakis and K. Kopelman, *Phys. Rev. B* **31**, 6008 (1985).
- ¹⁹D. Tinet, P. Levitz, and J.-P. Korb (unpublished).