Diffusion scaling through structural templates given by the 3d dynamic Ising model

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Abstract

We present new results describing diffusion through networks exhibiting dynamic disorder where diffusion 'pathways' are found from dynamic structures obtained from kinetic Monte Carlo (KMC) computer simulations consistent with Kawasaki dynamics in the 3d Ising lattice model. Our simulation results for the diffusion/conductance scaling exponent $s$ are in excellent accord with the most widely quoted theoretical value $s = 2\nu - j$, where $\nu$ and $j$ are 3d static percolation exponents in cubic lattices. This is in contrast to experimentally obtained values for this scaling exponent where there appears to be substantial disparity between many of these prior published results.

1. Introduction

The analysis of diffusion/conductance through disordered media is a problem of continuing interest in many areas of science and engineering [1]. Many of the most successful theories in this area have used percolation concepts to describe the underlying phenomenology and applications have most often been made to problems where the disorder is quenched.

Theory in this area has usually adapted classical static percolation ideas [2] and attempted to derive scaling relationships for transport coefficients in the vicinity of the percolation transition in the network. In the case of classical static percolation theory, however, the diffusion of a random walker throughout the network is restricted to the conducting-site cluster in which the walker initially finds itself. This implies that below the static percolation threshold, the mean square displacement of a walker approaches a finite value after some time, with the concomitant result that the conductivity becomes zero in the long-time limit. This is not the case, however, if the network structure is dynamic [3–6], which is often referred to as the dynamic or stirred percolation problem, the focus of the present work.

In recent work from our group [7,8] we addressed the problem of diffusion through dynamically disordered structures. We described there how kinetic Monte Carlo simulations (KMC) in the dynamic 2d Ising system could be used to generate dynamic network structures throughout which diffusion/conductance occurs. In the present Letter we describe new simulation results for diffusion in dynamic 3d Ising lattice structures. In this case, unlike that of our prior 2d Ising simulations, we were in a position to make direct comparisons between our simulation results and conductivity data taken in microemulsion mixtures.

In the literature there are wide disparities in published experimental values for conductivity scaling exponents in such systems [9–15] (see Table 1), with the range of values provided sometimes approaching a factor of two. This is much greater than the accuracy usually expected when attempting to describe universal scaling behavior in physical systems. This is thus an open issue that partly motivated us to do the current set of simulations.

2. Computational realization of the dynamic network structure

Computer simulations of diffusion usually employ particles called random walkers that diffuse throughout the system by 'hopping' from one conducting-site to another. The rate of diffusion throughout the system depends upon the network structures topological connectivity, as well as kinetic rules governing the RW hopping transition rates.

We modeled dynamic network structures using kinetic Monte Carlo (KMC) simulations, consistent with Kawasaki dynamics (i.e. constant conducting-site density) [16–20], on 3d Ising lattice models [19,21]. At any point during the simulations conducting-site pathways (with density $\phi$) are taken to be given by the network of up spins using the Ising terminology, with the non-conducting-sites represented by the down spins. The thermodynamic properties of this system are well established in terms of the reduced Ising lattice temperature $T'$, where $T$ is the system temperature and in 2d, for example, $T' = T / T_c$ is the critical temperature in which $T_c$ is Boltzmann's constant and $T'$ the spin (site)-spin (site) coupling parameter [22,23].

Given a lattice of size $L \times L$ we pre-equilibrate the system by doing a number of Monte Carlo Steps (MCS), where a MCS consists of a complete sweep of spin exchanges, i.e. $L^2$ updates. After
pre-equilibration we then commence the diffusion simulations. In addition to the ‘usual’ Ising parameters another important feature of our simulation model is the ability to update only a fraction of the conducting sites during any step of the simulation. A (blind) RW is placed on a randomly selected conducting site, and one of its neighboring sites is selected randomly. If this selected site is also a conducting site, the RW moves to it. Otherwise, the RW remains fixed at its current position. We define the number of RW steps taken between consecutive system updates by the symbol \( n_w \) and the fraction of conducting sites updated by \( q \). Thus the number of conducting sites updated each time is \( N_x = qL^d \phi \). Furthermore, we define characteristic time scales for the RW and structure dynamics by the variables \( t_w \) and \( T_q \) (it is easy to show that \( T_q \sim q^{-1} \) and \( t_w \sim n_w^{-1} \)). The ratio of \( t_w \) and \( T_q \) is an essential element in determining the system dynamics. In our simulations \( n_w \) is taken to be one and thus \( T_q(q) \) is the only dynamic variable here. Both RW–site and RW–RW interactions could, in principle, be accommodated with this model, however, in this Letter we do not consider these since they would not be the salient feature in microemulsion mixtures.

### 3. Results

In Fig. 1 we present results obtained from computer simulations of diffusion in dynamic 3d Ising structures at a temperature \( T \rightarrow \infty \), i.e. the random percolation limit. The general pattern of diffusion throughout the network shows three very distinctive modalities: short, intermediate and asymptotically long-time transport regimes. At short times we observe an increase in diffusion that quickly leads to a plateau region, during which the diffusion slow-down occurs since the RW is trapped in its initial cluster. At long-times the system appears to approach a quasi-equilibrium state in which we find regular diffusion behavior over long time scales. We define a cluster escape time \( t_s \) as the time at which the RW escapes the cluster in which it is confined and assume a scaling relationship between \( t_s \) and the distance from the percolation transition as \( t_s \sim (c - \phi)^{\theta_c} \), with \( \theta_c \) a new scaling exponent.

The behavior seen in Fig. 1 is suggestive of systems in which scaling ideas might prove useful for describing the phenomena. Thus we used the general scaling equations derived in detail in our prior publication [24] for fixed \( T, T_q(q) \) with \( \phi < \phi_c \) applied to the most interesting case, involving the slow network re-arrangement regime. We would expect the plateau height \( R \) to exist at short times and to be constant given by [1,25]

\[
R^2 \sim (\phi_c - \phi)^{-2v(z)}.
\]

Above the cluster escape time \( t_s \) and \( \phi < \phi_c \) we expect regular diffusion at long time limit so that

\[
r^2 \sim \phi_c - \phi.
\]

A scaling ansatz [25] that leads to these results is given by

\[
r^2 \sim t(\phi_c - \phi)^{-T(x)/(T_x)},
\]

with the scaling function defined \( T(x) \) such that \( T(x) \sim x^{-1} \) when \( x = 0 \) and \( T(x) \rightarrow \) constant when \( x \rightarrow \infty \), and \( s = 2v - \beta \). This form of the scaling function ensures that the height of the plateau is independent of \( t \) and gives

\[
s = \theta_1 + (2v - \beta).
\]

The scaling equation is thus given by

\[
r^2 \sim \frac{1}{T_q}r(\phi_c - \phi)^{-1}Q\left( \frac{t}{T_q(\phi_c - \phi)^{-\theta_q}} \right),
\]

with \( Q \) an unknown scaling function and \( \theta_q \) an exponent for the diffusion trapping time \( t_s \). We expect this scaling equation to hold where cluster escape dynamics is a central feature of the system behavior.

Using these results we attempted to scale the results shown in Fig. 1. These results are shown in Fig. 2 and illustrate excellent collapse of the data onto a ‘universal’ scaling curve [25]. We repeated these calculations at finite temperatures after first finding the dy-

### Table 1

Conductivity scaling exponents taken from the experimental literature.

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<tr>
<td>( s )</td>
<td>1.21 ± 0.06</td>
<td>1.1–1.6</td>
<td>0.9–1.39</td>
<td>1.20 ± 0.20</td>
<td>1.65</td>
<td>1.17 ± 0.05</td>
</tr>
<tr>
<td>( \mu )</td>
<td>1.63 ± 0.02</td>
<td>1.6–2.2</td>
<td>1.82–2.09</td>
<td>2.00 ± 0.25</td>
<td>–</td>
<td>1.68 ± 0.05</td>
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**Fig. 1.** Simulation results for RW mean square displacement at \( T \rightarrow \infty \) and various values of \( \phi \).

**Fig. 2.** Scaling of mean square displacement data from Fig. 1.
dynamic percolation transition concentration $\phi_t$ employing finite-size scaling methods as we describe as in the next paragraph.

We did this by adopting the method described by Lironis et al. [26] who used the finite-size scaling equation

$$P_c(L, \phi, t) = L^{-\beta} \Phi(\phi - \phi_t)$$

(6)

In this equation $P_c(L, \phi, t)$ is the probability of finding a spanning conducting cluster in a system of size $L$ with the standard static percolation scaling exponents $\beta$, $\nu$ and $\delta \phi \equiv |\phi - \phi_t|$. The various curves cross at the concentration of the dynamic percolation transition.

These finite-size scaling results are shown in Fig. 3. Furthermore, we found the diffusion coefficient $D$ in the system from results like those shown in Fig. 1 at long times and plotted $D$ against the variable $|\phi - \phi_t|$ (see Fig. 4) which represents the ‘distance’ from the dynamic percolation concentration $\phi_t$ which we found for both cases. The values of the diffusion coefficient scaling exponents we found are shown in Table 2 at various temperatures and should be compared with the experimental results given earlier in Table 1.

In appreciating these comparisons we point out that the result for the scaling exponent most frequently cited in prior experimental work appears to have come from the theoretical model of stirred percolation proposed by Laguës [27], who argued that the diffusion/conductivity scaling exponent $s$ should follow the scaling relationship $s = 2\nu - \beta$ where $\nu$ and $\beta$ are the usual static percolation exponents. At the time of that work the best estimates for both $\nu$ and $\beta$ gave rise to a numerical value for $s = 2\nu - \beta \sim 1.2$ but given currently accepted values for $\nu$ and $\beta$, a better value for $s$ would now be considered to be $\sim 1.35$, not an insignificant difference when it comes to validating scaling theories.

We observe that our simulation results for $s$ are in excellent accord with the theoretical result $s = 2\nu - \beta$ that has most often been cited in the prior literature which implies a system where $\nu$ is independent of $\phi - \phi_t$. This, to our best knowledge, is the first time that this has been shown in either a computer simulation study or in experimental data of transport in a dynamic network problem.

### 4. Conclusions

In this Letter we addressed the problem of diffusion through dynamic pathways found by employing the 3d Ising model paradigm to generate network structure dynamics. Our simulation model shows a rich variety of diffusion behavior showing three very distinct diffusion regions: short, intermediate and asymptotically long-time transport regimes.

In a 3d network our simulation results yielded a scaling exponent for the diffusion coefficient that is in good accord with the most widely used theoretical scaling result for this property, which also appears to be at variance with most published estimates of this exponent found from experimental conductivity data in microemulsions. In this regard, there are two points to consider: (1) scaling analysis requires accurate values for the percolation transition point which is difficult to do precisely in experiments and (2) microemulsions can be made from a variety of complex chemical constituents, usually consisting of water, ionic or non-ionic surfactant, and a solvent like oil or a supercritical fluid like carbon dioxide. While ionic effects should be minimal in these mixtures because of screening behavior, we should bear in mind that the Ising system used here represents a class of systems in which short range molecular interactions dominate. Thus, the question of scaling in microemulsions consistent with the $s = 2\nu - \beta$ result that has been used in prior work remains an open issue that would be interesting to see addressed in future experimental work.

### References