Diffusion and Percolation in Systems Exhibiting Dynamic Disorder: Simulation and Scaling Results

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The analysis of diffusion through disordered structures is a problem of widespread interest to many areas of science and engineering, and many of the most successful theories in this area have used percolation concepts. In our presentation we will discuss a novel approach for analyzing the problem of diffusion through heterogeneous network structures exhibiting dynamical disorder. Potential areas of application of this work include a variety of problems including analyzing ionic conduction in polymers, electron-hole recombination in amorphous semiconductors, polymer gelation, turbulent diffusion, the efficacy of corrosion-resistant metal-organic coatings, and ionic conductance through supercritical microemulsion mixtures.

We describe how we use the Ising model paradigm, in conjunction with kinetic Monte Carlo simulations, for generating dynamical network configurations that are consistent with Kawasaki lattice dynamics (i.e. constant conducting-site density). At any point during the simulations conducting-site pathways (with density) are taken to be given by the network of up spins, using the Ising terminology, with the non-conducting-sites represented by the network of down spins.

In addition to the simulation results we provide a theoretical analysis of the problem by firstly providing a rationale as to why we partition the net displacement of the RWs throughout the network into two terms representing: (1) the contribution to transport by ‘hopping' through nearest neighbor conducting sites (the so-called ‘percolation' mechanism) and (2) the self-diffusion of the site itself on which the RW finds itself at any given point in time, respectively. The ‘percolation- diffusion' component exhibits non-trivial scaling behavior, with a new scaling exponent that describes the cage trapping time of the RWs in conducting site clusters. We show how the value of this exponent can be found from computer simulation results and compare our results to conductance measurements in supercritical microemulsions and recently published diffusion data taken in dense colloidal suspensions.

INTRODUCTION

We study the problem of diffusion through network structures exhibiting dynamic disorder, using the Ising model paradigm to generate evolving network configurations. Diffusion is studied using blind random walkers (RW). Furthermore, we partitioned the net displacement of the RWs throughout the network into two terms. These represent the contributions of transport through neighboring conducting sites and the self-diffusion of the site itself on which the RW finds itself at any given point in time.

SIMULATION APPROACH

Dynamic network structures were found with kinetic Monte Carlo (KMC) simulations, consistent with Kawasaki dynamics (i.e. constant conducting-site density) [1,2,3,4], on Ising lattice models [4,5] . At any point during the simulations conducting-site pathways (with density *p*) 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 $\frac{T}{T_c}$, where T is the system temperature and in 2d, for example, $T_c = \frac{\Gamma}{0.44k_B}$ is the critical temperature in which k_B is Boltzmann's constant and Γ the spin (site)-spin (site) coupling parameter [6,7] .

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. In addition to the ''usual'' Ising parameters another feature of our simulation model is the ability to update only a fraction of the conducting sites during any step of the simulation.

After pre-equilibration we perform the diffusion simulations as follows: a RW is placed on a randomly selected conducting site and one of its neighboring sites selected randomly. If the selected site is a conducting site the RW moves to it otherwise the RW remains fixed at its current position. The number of RW steps attempted between consecutive structure updates is defined by the symbol n_w and the fraction of conducting sites updated per lattice sweep by q . Thus, the number of conducting sites updated each lattice sweep is $N_R = qL^2 p$. Furthermore, we define characteristic time constants for the RW and structure evolution dynamics by the variables τ_w and T_R respectively. It follows in straightforward fashion that $T_R \sim q^{-1}$ and $\tau_w \sim n_w^{-1}$ with n_w normalized to the value one. Therefore, $T_R(q)$ represents the relative time scales of structure and RW dynamics.

RESULTS

Given these results we then simulated diffusion in networks at different values of temperature and density *p* starting with a system at the random percolation limit, the results of which are presented in figure 1. In figure 1 (**top**) we show the overall RW mean square displacement with the respective 'component part' transport contributions shown in figure 1 (**middle**) (self –diffusion) and figure 1 (**bottom**) (neighbor hopping). Quite distinctive behavior is observed in these results. The self-diffusion contribution follows regular diffusion behavior, while the neighbor hopping

and overall trajectories show three distinctive modalities: short, intermediate and asymptotically long times. At short times we observe an increase in diffusion that quickly leads to a plateau region, during which time significant diffusion slow-down occurs. Here the RW is trapped within its initial cluster while at long-times the system seems to approach a quasi-equilibrium state in which we find regular diffusion behavior i.e.

$$\left\langle r^2(t) \right\rangle \sim t^{\alpha} \tag{1}$$

with $\alpha = 1$. We observed similar qualitative features in finite temperature simulations. These results were all suggestive of systems in which scaling ideas might play a useful role in collapsing the simulation data into a "universal" curve.

We now discuss this and evaluate a scaling hypothesis with extensive simulation data, in both uncorrelated as well as correlated network structures.

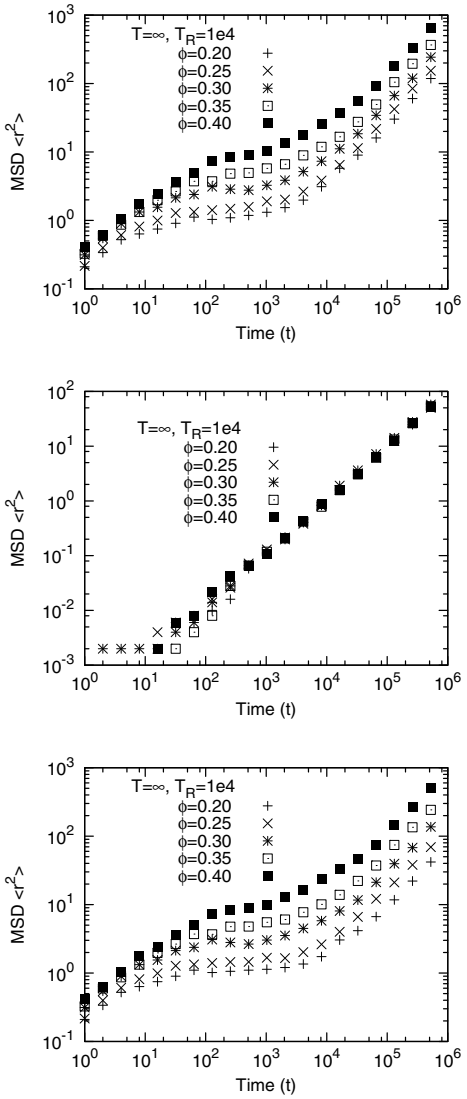

Figure 1: (top) Overall mean square displacement at the limit $T \to \infty$, **(middle)** Self-diffusion contribution to overall mean square displacement at the limit $T \to \infty$, and **(bottom**) Percolation (neighbor hopping) contribution to overall mean square displacement at the limit $T \to \infty$

The overall diffusion behavior seen in these figures is suggestive of a system in which a scaling analysis might play a useful role in collapsing the simulation data into a "universal" curve and in figure 2 we show results using the scaling equations given by Chen et al. [8]. The scaling results seem to capture the physics of diffusion in this system in a satisfactory way.

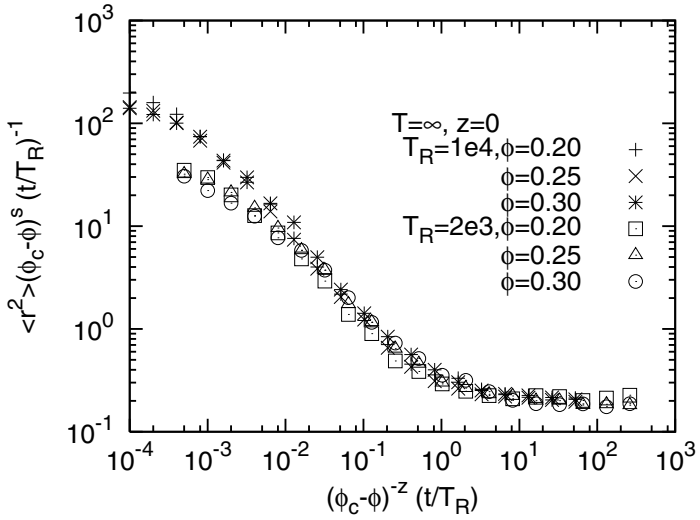

Figure 2: Scaling results for diffusion in the network.

THEORETICAL APPROACH

Fixed $T,\ T_R(q)$

We first analyze system behavior at fixed T and $T_R(q)$ with $p \le p_c$. For the most interesting case involving the slow network re-arrangement regime we expect the plateau height R at short times to be constant and given by

$$R^2 \sim (p_c - p)^{-(2\nu-\beta)}. \tag{2}$$

We define a plateau crossover time t_x in our system to be the time for the trapped random walker to leave the original cluster by either splitting off or the hopping to another new cluster which came in contact. By assuming the scaling relation relations between the crossover time and the distance to the percolation threshold, we have

$$t_x \sim (p_c - p)^z \tag{3}$$

with z a new scaling exponent. Above t_x, $\forall\ p < p_c$ we expect regular diffusion so that

$$r^2 \sim (p_c - p)^{-s} t. \tag{4}$$

A scaling ansatz [9] that incorporates these results is given by

$$r^2 \sim t(p_c - p)^{-s} T\left(\frac{t}{t_x}\right) \tag{5}$$

with the scaling function $T(x)$ defined such that the mean square displacement approaches a plateau at the short time limited $T(x) \sim x^{-1}$ when $x \to 0$ and the mean square displacement approaches the regular diffusion at the long time limit $T(x) \to$ constant, when $x \to \infty$ and $s \equiv 2\nu - \beta$ .Here the scaling relation does not hold for the time $t < (p_c - p)^{\beta - 2\nu - \mu}$, which is the crossover time from subdiffusive to plateau region.

This form of the scaling function ensures that the height of the plateau is independent of *t* and gives

$$s = z + (2\nu - \beta) \tag{6}$$

Note that it has been argued elsewhere that in slow dynamic percolation systems $s = 2\nu - \beta$ [9] so the exponent z defined here represents a deviation from this viewpoint.

Fixed T, varying $T_R(q)$

For the systems vary in different rearrangement time we postulate that the cross over time is proportional to the system rearrangement time to power *x*,

$$t_x \sim T_R^{-x} \tag{7}$$

and at the long time limit, the mean square displacement also scales inverse proportionally to the power *y*, since the slower the rearrangement (longer T_R) the lower the mean square displacement is

$$r^2 \sim \left(\frac{1}{T_R}\right)^y t\,. \tag{8}$$

Following the approach used in the previous section we get that

$$r^2 \sim \left(\frac{1}{T_R}\right)^y tF\left(\frac{1}{T_R}\right) \tag{9}$$

At the plateau, the cluster height is again considered to be independent of both *t* and *q*, which is the case if the scaling function $F(a) \sim a^{-1}$ for $a \sim 1$ and $x = y$. In the slow re-arrangement regime we therefore find that $x = y = 1$. Combing both of these results, for the case when both *p* and $T_R(q)$ can vary, leads to the scaling result

$$r^2 \sim \frac{1}{T_R} t(p_c - p)^{-s} Q\left(\frac{t}{t_x}\right). \tag{10}$$

Since

$$t_x \sim (p_c - p)^z T_R\,, \tag{11}$$

we thus arrive at a complete scaling function explicitly written as follows,

$$r^2 \sim \frac{1}{T_R} t(p_c - p)^{-s} Q\left(\frac{t}{T_R}(p_c - p)^{-z}\right). \qquad (12)$$

The question arises as how to find a value for the exponent z. The simplest way would be to find it from simulation results for RW displacement with time, at various values of $p_c - p$, and fit these results to the scaling function shown in equation (12).

COMPARISON TO EXPERIMENTS

In figure 3 we show these results for scaled diffusion coefficients at various conducting site densities, and temperatures, near the static percolation point in this $2d$ network. The simulation results shown in figure 3 are for a $2d$ system, however, we show that their qualitative agreement with experimental conductivity data taken in a supercritical fluid microemulsion mixture at 35 C is very striking [10,11]. In future work we propose extending this to 3d simulations where experimental data conductivity are available.

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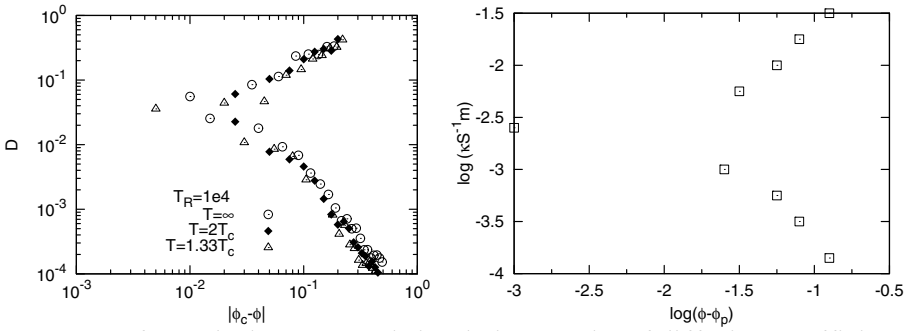

Figure 3: Left graph shows our 2d simulation results of diffusion coefficient scaling at various values of T and ϕ, while the right figure represents data in a supercritical fluid microemulsion [10].

In any computational investigation of the dynamic disorder problem we need to be able to systematically generate structures through which diffusion/conductance occurs. In one set of simulations, in annealing lattice networks, we propose to use kinetic Monte Carlo (KMC) simulations in Ising lattices where temperature will allow us to control the degree of cooperative dynamical correlations between the elements of the conducting network structure itself. For example, we might expect to see transport processes in such systems follow, broadly speaking, a 'trap-and-release' mechanism, a consequence of diffusive particle trapping by surrounding, non-conducting structures, followed by further mobility as the overall conducting network rearranges itself into more favorable configurations for diffusion/conductance to occur. In other related simulations, where self-trapping dynamics are important, we will use KMC simulations with binary (small-large particle) continuum models [13] to emulate structures where a tagged (small) particle's mobility is hindered by surrounding cage-like structures, whose re-arrangements are key to the tagged particles' further mobility (some experimental data, relevant to this project, that displays such features in a self-trapping colloidal suspension are shown in figure 4 [12]).

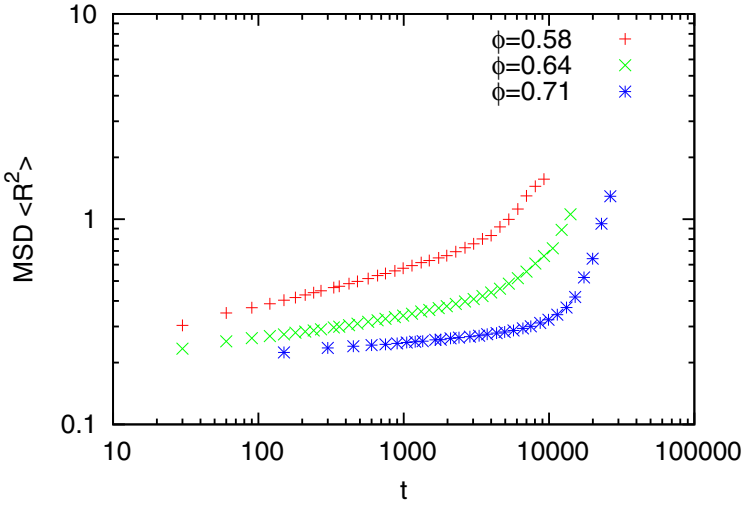

Figure 4: Experimental mean squared displacements of a diffusing particle in a dense colloidal suspension showing plateau (i.e. trap) regions [12].

CONCLUSIONS

Our simulation model shows a rich variety of novel diffusion behavior showing three distinctive diffusion regions: short, intermediate and asymptotically long- time transport regimes. Based upon these observations we used previously postulated scaling functions for diffusion in this system which appeared to universalize the behavior, at both the random percolation limit as well as at finite temperatures (the correlated problem). This first study suggest that the computer model presented here shows potential for being very useful for studying basic phenomena related to diffusion in correlated network structures like ion transport through supercritical microemulsions.

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