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

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Talk Outline

• Motivation and objectives

• Computational approach

• Simulation algorithm

• Scaling analysis

• Results

• Conclusions
Motivation and Objectives

- Transport in dynamic complex network structures is important in many problems, e.g. conduction in microemulsions, proton transport in hydrated membranes and the glass transition, to name just a few areas.

- What characterizes these problems is the appearance of transport plateaus where the diffusion/conducting species ‘waits’ until the network configuration adapts, before further transport occurs.

- There are two relevant time scales: that of the conducting/diffusing species and that of the network rearrangement.
Motivation and Objectives

- How do we ‘realize’ the network templates through which diffusion occurs? We use the dynamic Ising system using kinetic Monte Carlo simulations.

- What is the role of ‘cage-trapping’ by the network and its effects on the plateau region?

- Can scaling theory be used to successfully analyze this problem?

- Do the simulation results hold up vis-à-vis appropriate data and how do we tell this?
Percolation in 2-D Static Lattice

\[ \phi = 0.2 \quad \text{and} \quad \phi \cong \phi_c = 0.6 \]
Structure Generation

- Geometric arrangements
  - Labels: up(+1) down (-1)
- Simulation Update Rules (Kawasaki Dynamics)
  - Spins Conserved
  - Update nearest neighbor pairs
  - Temperature (Metropolis-Boltzmann sampling)
Structural Time Evolution at Finite Temperature $2T_c$

- At finite temperature $T = 2T_c$
- 0 MCS $\rightarrow$ 1 MCS $\rightarrow$ 200 MCS
Random Walker ‘Progress’

• A RW is placed on a Randomly chosen conducting site
• RW moves for a specified number of steps
• Network is updated
• Continue ……
• At long times, we find the slope of the RW Mean Square Displacement v.s. time curve to get diffusion coefficient
Mean Square Displacement

- \( q \): the ratio between the updated sites and the total conducting sites.
- \( T_R \): the System rearrangement time.
- One RW is taken with system updates

\[
q \sim \left( \frac{1}{T_R} \right)
\]

\[
\langle r^2(n) \rangle = \left\langle \left( \sum_{i=1}^{n} e_i \right)^2 \right\rangle
\]
Scaling Analysis: general features

• Diffusion scenario:
  – Short time: diffusion occurs in a fractal structure
  – Medium time: plateau region-’cage trapping’
  – Long time: regular diffusion.

• ‘Scaling’ points of interest:
  – Transition time from plateau region to regular diffusion governed by a ‘crossover’ time
  – Diffusive behavior at long times
Scaling Analysis I

- Transition Crossover Time: $t_x \sim (\phi_c - \phi)^{\theta_z}$
- Plateau height: $R \sim (\phi_c - \phi)^{(2v - \beta)}$
- Regular Diffusion at long times:

$$r^2 \sim (\phi_c - \phi)^{(2v - \beta)}t$$
$$r^2 \sim t(\phi_c - \phi)^{-s}T \left(\frac{t}{t_x}\right)$$

$$T(x) \sim x^{-1} \quad x \to 0$$
$$T(x) \to \text{constant} \quad x \to \infty$$
Scaling Analysis II

- Include influence from: \( T_R(q) \)
- Thus assume: \( t_x \sim (\phi_c - \phi)^{\theta_z} T_R \)
- Final Scaling form:

\[
r^2 \sim \left( \frac{t}{T_R} \right)^{s} Q \left( \frac{t}{T_R} (\phi_c - \phi)^{-\theta_z} \right)
\]

\[
s = \theta_z + (2\nu - \beta)
\]
Simulation Results for Mean Square Displacement, $L=512$

\[ T=\infty, \ T_R=1\times10^4 \]

\[ \phi = 0.20 \]
\[ \phi = 0.25 \]
\[ \phi = 0.30 \]
\[ \phi = 0.35 \]
\[ \phi = 0.40 \]
Finite-Size Scaling Simulation Analysis

- $P_\infty(L, \phi, t) \sim L^{-\beta/\nu} \hat{P}(\delta \phi L^{1/\nu})$
- System Size $L = 64, 128, 256$
Simulation Results for Diffusion Coefficient, L=512
Simulation Results for Scaling Analysis (MSD), L=512

- $\theta_z \sim 0$

- Crossover time does not depend on the density of conducting sites in self-diffusive systems
## Simulation to experiment data comparison

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<thead>
<tr>
<th></th>
<th>theory</th>
<th>simulation</th>
<th>experiment</th>
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<tbody>
<tr>
<td>( s )</td>
<td>1.35</td>
<td>1.3557 ± 0.05168</td>
<td>1.10 – 1.65</td>
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- **Experiment References:**
Confined systems: Self organization in hydrated membranes through ionic groups that facilitate proton transfer.

Perfluorosulfonic acid Polymers

Aromatic, rigid-rod SPI polymers

How does nanostructure influence water uptake and proton transport through percolating water droplet chains?
Conclusions

• Our simulation model captures fundamental features of transport in complex, dynamic network structures

• Scaling theory proposed ‘universalizes’ the diffusion behavior found with KMC simulations-producing diffusion scaling exponents consistent with the theoretical predictions of Lagues’ work – the first time that this has been shown with either simulations and/or experimental data

• Current research is focusing upon the confined network problem - we hope to apply the results to understanding the hydrated membrane problem, e.g. the proton transport problem in hydrated Nafion and similar membrane structures
References


• Finite Size Scaling:
Results for Finite Temperature

• Qualitative behavior (scaling exponents) similar to infinite temperature
• Short Correlation Range
• Infinite Correlation at critical temperature yet to be investigated