Estimating the velocities of interacting random walkers in disordered media

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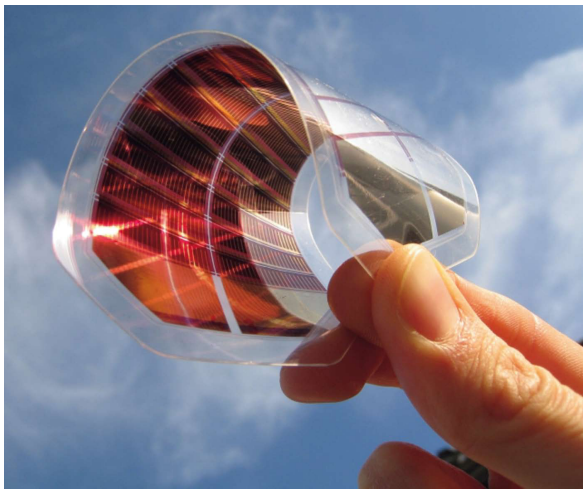
Organic Semiconductors



Organic Solar Cells

OLED Displays

Charge transport in disordered media

- The key quantity of interest when investigating charge transport is charge mobility, μ.

- A electric force, F, is applied to a material in a given direction, $\boldsymbol{e}$. Charge mobility is then defined as

$$\mu = \frac{\nu_{\boldsymbol{e}}}{|F|}$$

Question

How does the microstructure of a disordered material influence charge mobility?

Modeling charge transport

In many disordered media, charge carriers move by 'hopping' between molecules.

Modeling charge transport

- The material is modeled by a geometric graph $G = (V, E)$.
- The vertices, V, represent molecules or segments of polymers.
- The edges, E, represent possible transitions that the charge carriers can make.
- Every vertex has an energy associated with it. We write $\mathcal{E}_i$ for the energy of the ith vertex.

Modeling the material

There are two possible forms of disorder:

- positional
- energetic

Modeling the material

- The classical model of organic semiconductors is the Gaussian disorder model. In this model, the molecules lies on a cubic lattice and their energies are iid normal random variables. This model has energetic disorder but no positional disorder.
- Extensions to this model include correlated energy landscapes and fudges to impose some positional disorder.
- A recent and significant advance has been to model the positional disorder using either molecular dynamics or stochastic geometry (an approach pioneered in Ulm).

Modeling the material

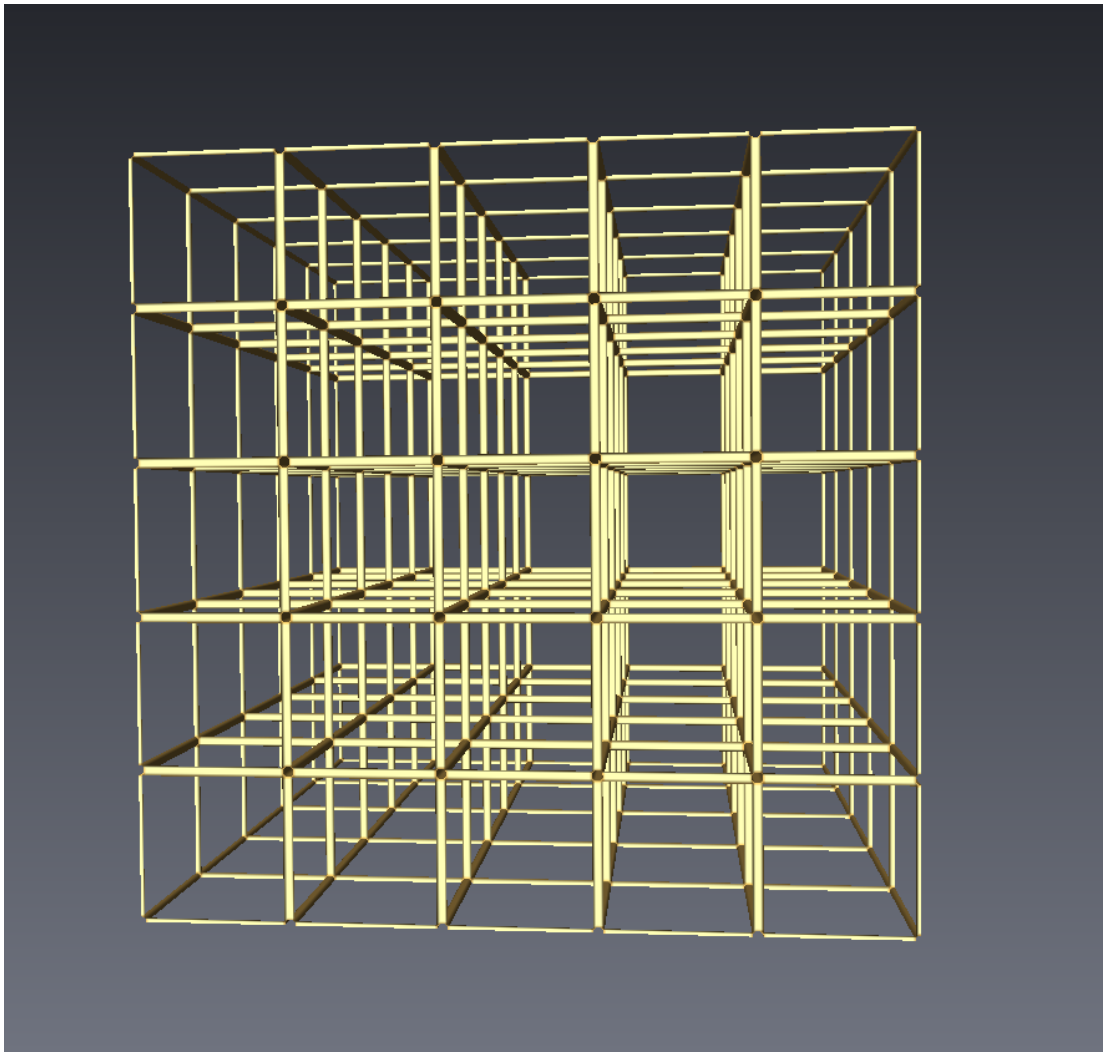


Figure: A 3D lattice for a Gaussian disorder model.

Modeling the material

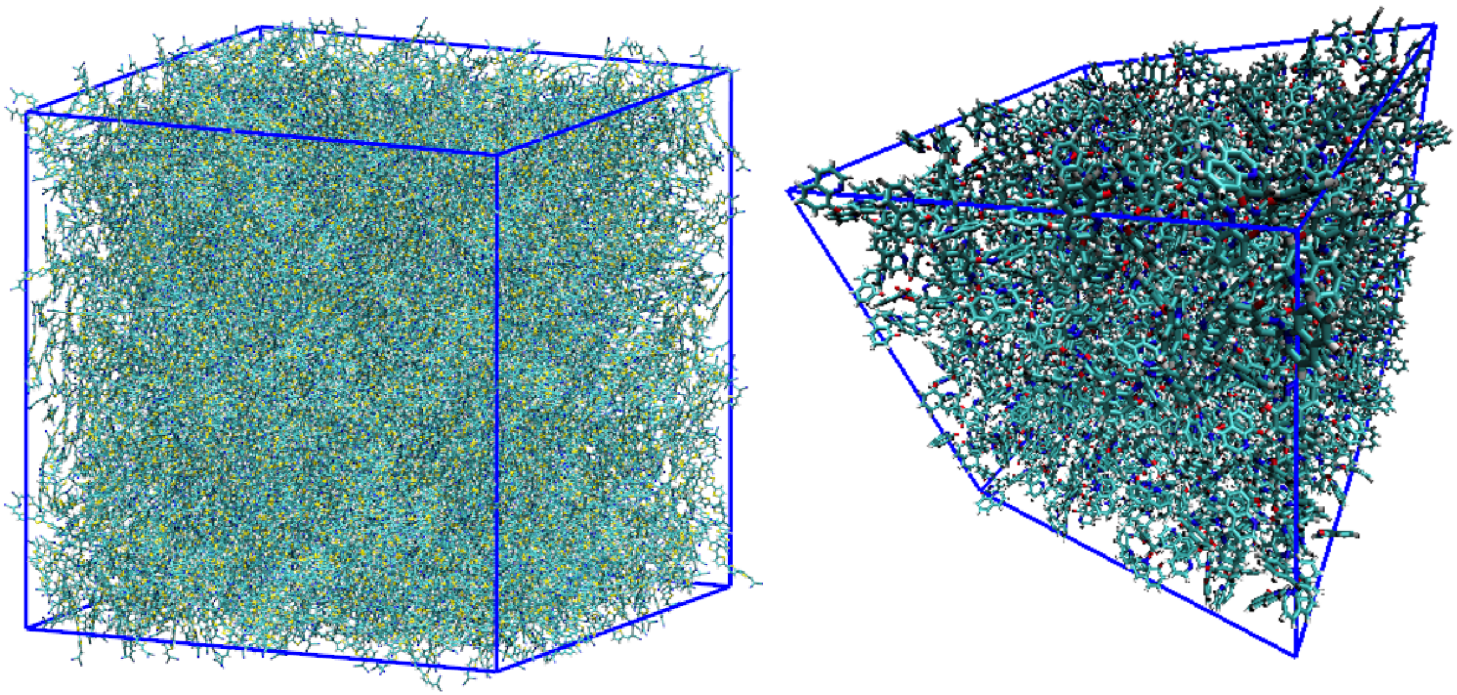


Figure: Left: A molecular network for DCV4T. Right: A molecular network for Alq3.

Modeling the material

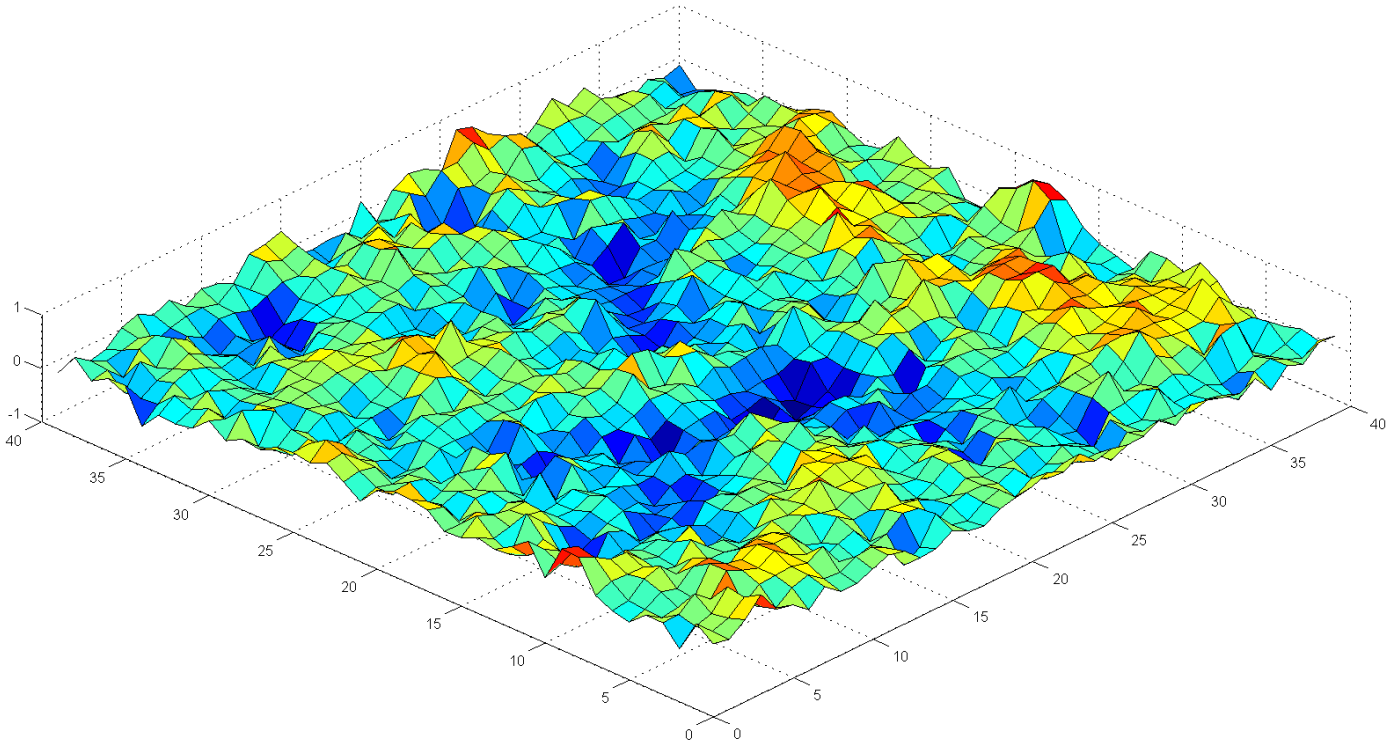


Figure: A correlated energy landscape with trap regions.

Modeling charge transport

In the single carrier case, the motion of a charge carrier is modeled by a continuous time Markov chain (CTMC) taking values in V.

Modeling charge transport

There are two common expressions for the transition rates of the CTMC.

- Miller-Abraham rates

$$q_{ij} = \begin{cases} v_0 \exp\{-2\gamma R_{ij}\} \exp\left\{-\frac{\mathcal{E}_j - \mathcal{E}_i}{k_B T}\right\}, & \mathcal{E}_j > \mathcal{E}_i \\ v_0 \exp\{-2\gamma R_{ij}\} & \mathcal{E}_j \leq \mathcal{E}_i \end{cases}$$

- Marcus rates

$$q_{ij} = \frac{2}{\pi} \frac{J_{ij}^2}{\sqrt{4\pi\lambda k_B T}} \exp\left\{-\frac{(\mathcal{E}_i - \mathcal{E}_j - \lambda)^2}{4\lambda k_B T}\right\}$$

Qualitative features of the rates

The key qualitative feature of the rates are:

1. Charge carriers prefer to hop to molecules with lower energy.
2. The rates with which charge carriers jump from low to high energy states are very small (relative to the other rates).

The effect of disorder

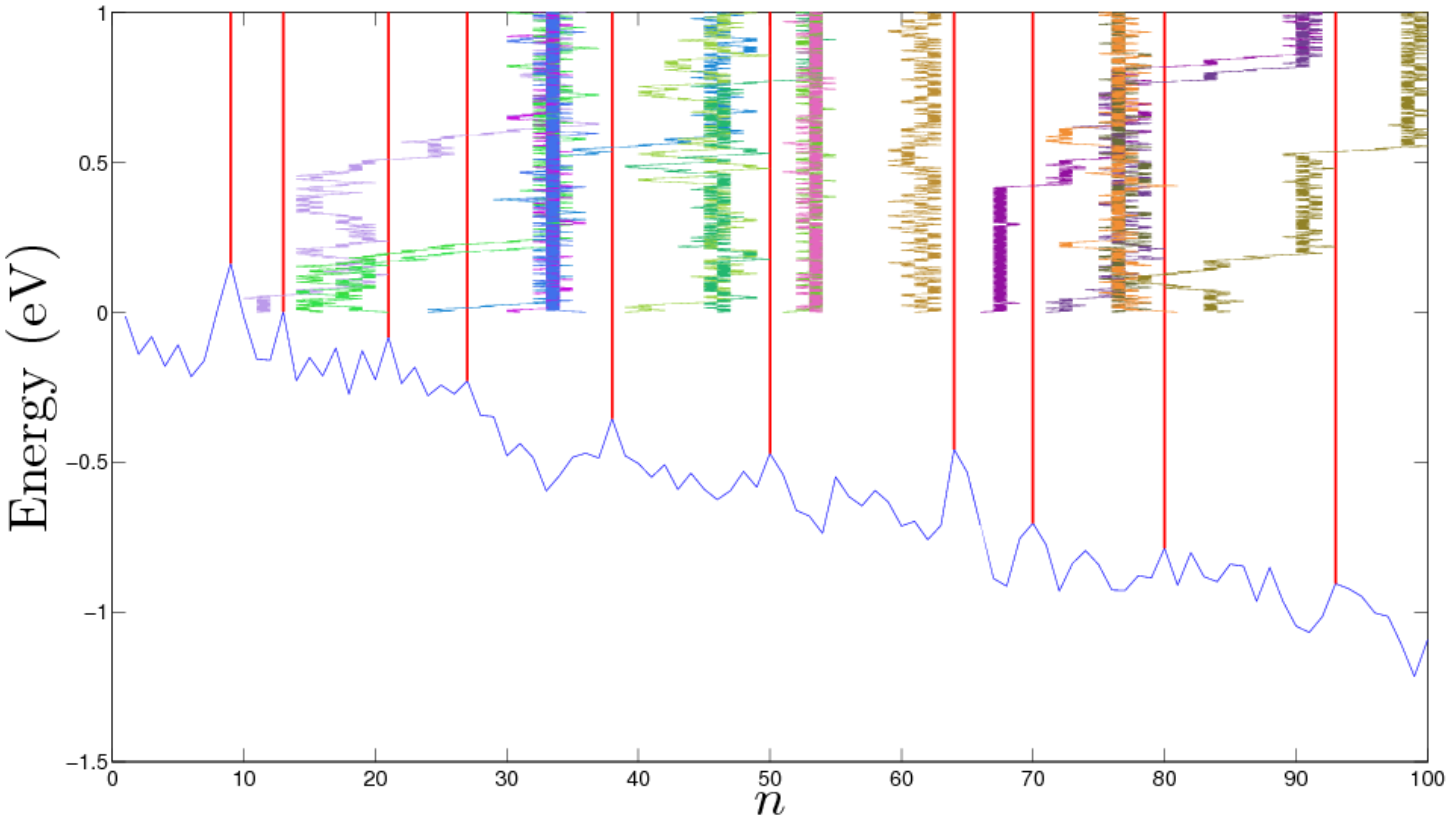
- In organic semiconductors, charge mobility depends heavily on the magnitude of the electric field.
- The main reason for this is the presence of regions of low energy – 'traps' – in which charge carriers become stuck for large amounts of time.

Calculating charge carrier speed

- In order to calculate average speed, we add periodic boundary conditions to the graph.
- We can then calculate speed in terms of the stationary distribution of the CTMC describing the carrier's movement.
- Alternatively, we can use Monte Carlo to estimate speed by

$$\widehat{\nu}_{\boldsymbol{e}} = \frac{d_{\boldsymbol{e},t}}{t}.$$

The limitations of Monte Carlo estimation



The limitations of Monte Carlo estimation

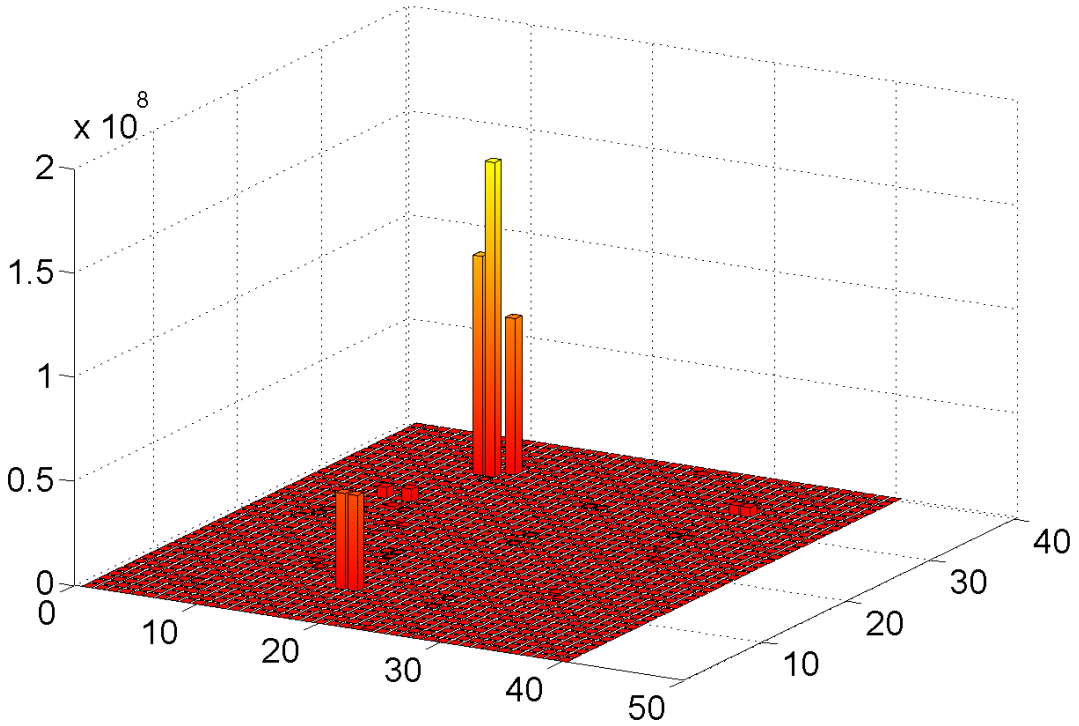


Figure: Number of times each state of a 40×40 lattice is visited in 5×10^8 steps.

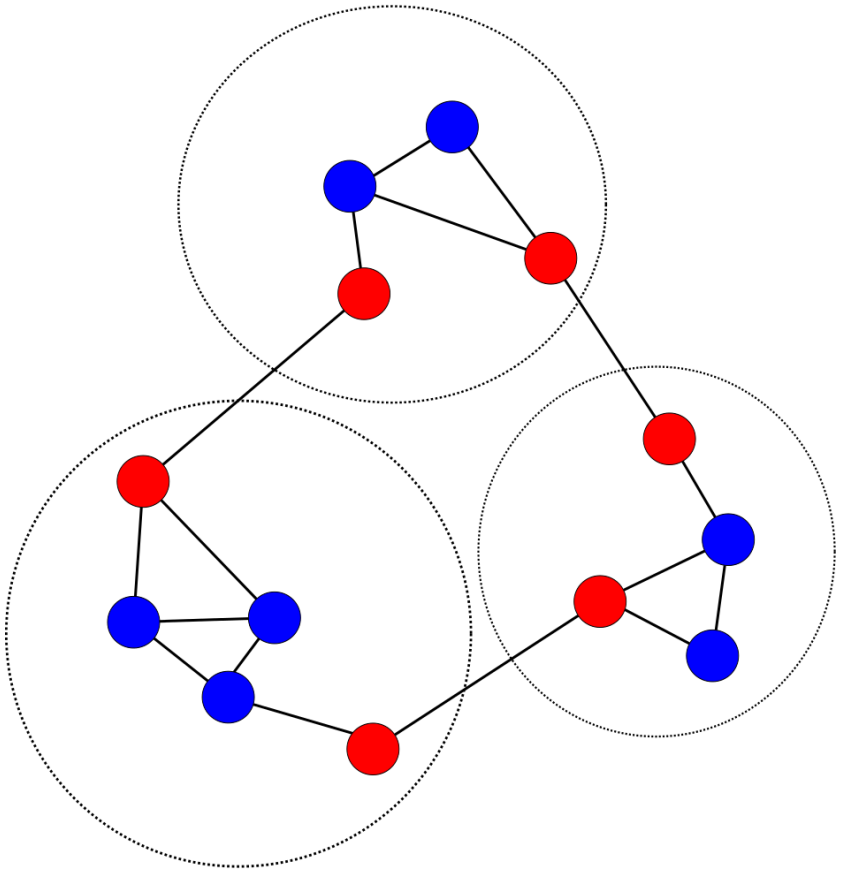
Aggregate Monte Carlo

1. Replace trap regions by single states (called 'super states').
2. Simulate a stochastic process on the coarsened state space.

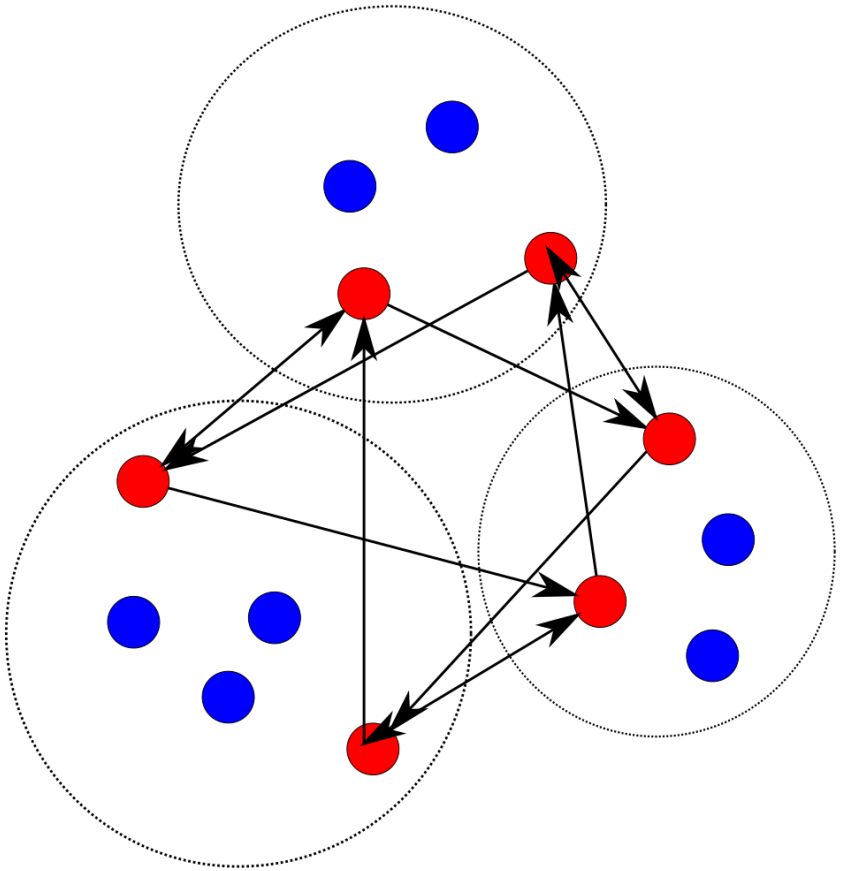
Aggregate Monte Carlo

- We treat each super state as an absorbing CTMC.
- States bordering the super state are treated as absorbing states.
- We then calculate expected times until absorption and the probabilities of exiting the super state into specific bordering states.

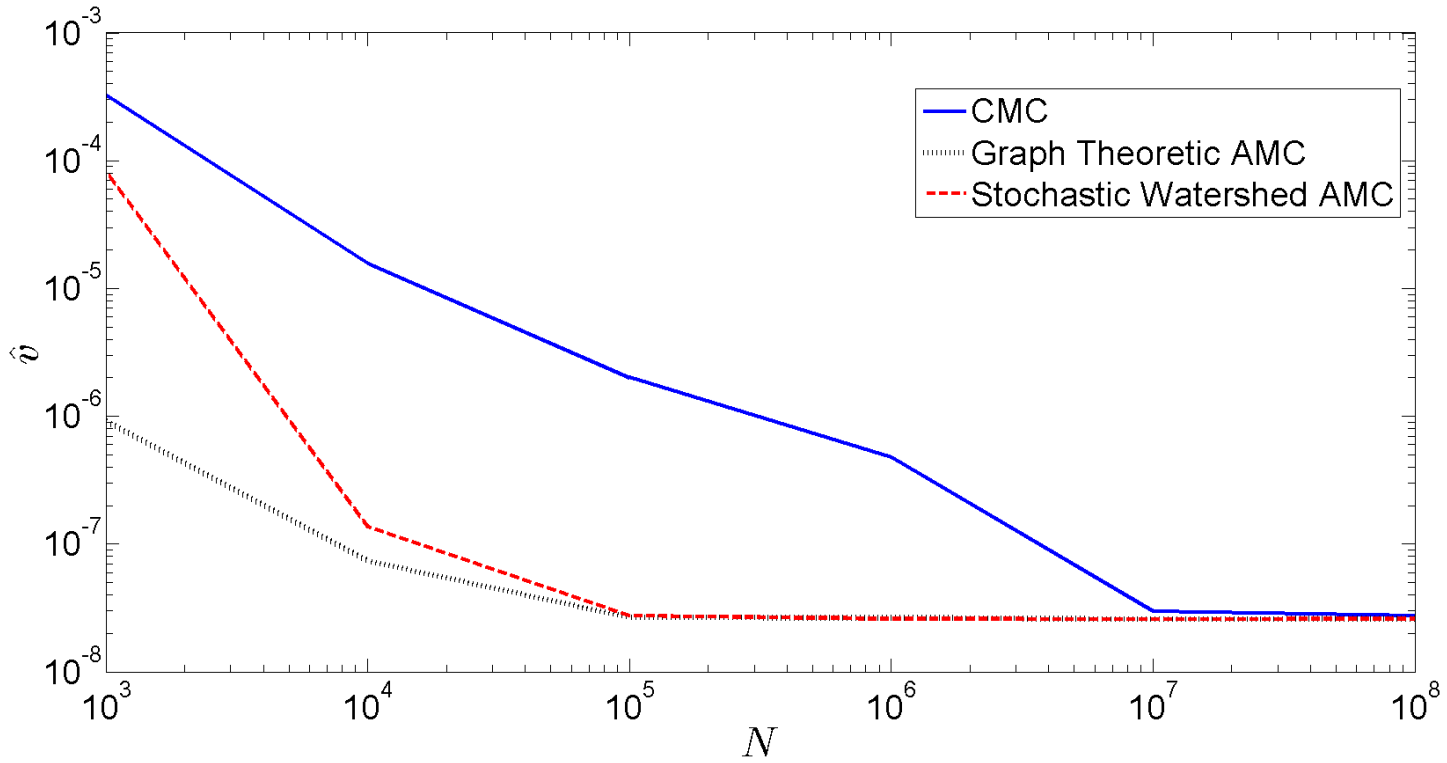
Aggregate Monte Carlo



Aggregate Monte Carlo



Effectiveness



Multiple charge carriers

- In the multiple charge carrier case, we model each charge carrier in the same way as in the single carrier case.
- However, we add the restriction that a charge carrier cannot move to a vertex occupied by another charge carrier.
- Thus we obtain an exclusion process.

Multiple charge carriers

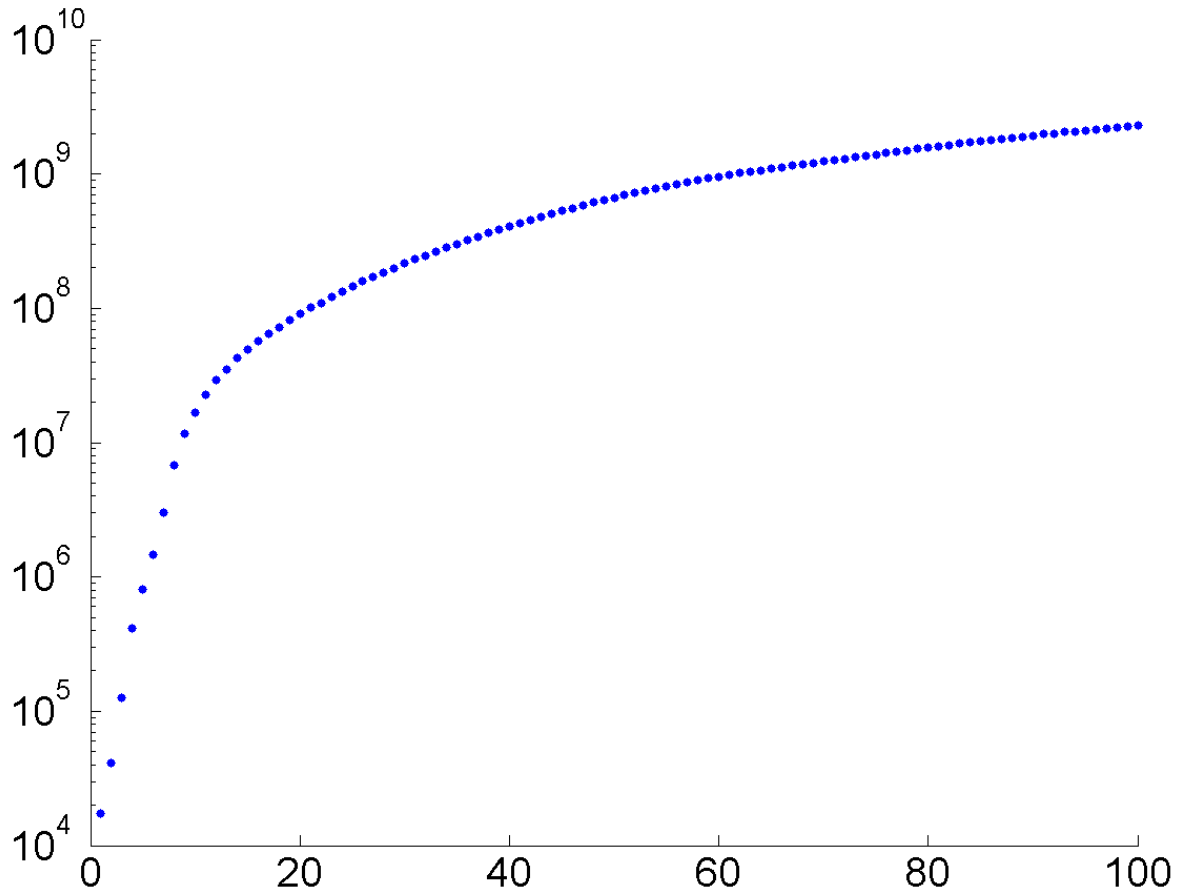


Figure: Charge carrier velocity for 40×40 lattice as a function of number of carriers.

Estimating velocity for multiple charge carriers

- If we have k charge carriers, the size of the state space is

$$\binom{|V|}{k}.$$

- This prohibits us from solving for the stationary distribution or even constructing the rate matrix of the whole process directly.

Aggregate Monte Carlo

- Again, we want to collapse the trap regions into super states.
- Problem: now we need to keep track of what is happening inside super states.

Aggregate Monte Carlo

More precisely, we need to be able to simulate:

- The (random) time until a charge carrier exits a super state.
- The state to which the exiting charge carrier tries to jump.
- (If necessary) the locations of charge carriers within the super state at a given time.

Dual Chain Approach

- We can use a dual chain!
- That is, a process $\{Y_t\}_{t \geq 0}$ that is easy to simulate and allows us to obtain the necessary information

Dual Chain Approach

- We treat the dynamics in each super state as a CTMC, $\{X_t\}_{t\geq 0}$, with a single absorbing state, Δ (representing the surrounding states).
- We consider the full Markov chain on this super state (i.e., we model the exclusion process).
- If we have M sites and k particles, we have

$$N = \binom{M}{k}.$$

  transient sites.
- Thus, the CTMC has an $N+1 \times N+1$ rate matrix $\bar{Q}$.

Dual Chain Approach

- We consider Q, the $N \times N$ submatrix of $\bar{Q}$ obtained by removing the row and column corresponding to Δ.
- We assume Q is irreducible and reversible (in the sense that it is in detailed balance with some probability measure) .
- Then, $-Q$ has N real-valued positive eigenvalues $0 < \lambda_1 \leq \lambda_2 \leq \cdots \leq \lambda_N$.
- We can use these to construct a sequence of 'local equilibria' $\{\boldsymbol{\mu}_i\}_{i=1}^N$ and 'death' probabilities $\{d_i\}_{i=1}^N$ with $d_N = 1$.

Dual Chain Approach

- We define a continuous-time Markov chain, $\{Y_t\}_{t\geq 0}$ on the state space $\{1,\ldots,N\}\cup\Delta$.
- This process starts at 1.
- It evolves according to the rate matrix

$$K(i,j)=\begin{cases}-\lambda_{N+1-i} & i=j\in\{1,\ldots,N\},\\ d_i\lambda_{N+1-i} & i\in\{1,\ldots,N\},j=\Delta,\\ (1-d_i)\lambda_{N+1-i} & i\in\{1,\ldots,N-1\},j=i+1,\\ 1 & i=j=\Delta,\\ 0 & \text{otherwise.}\end{cases}$$

Dual Chain Approach

- We can now simulate the absorption time because

$$T_Y = \inf\{t \geq 0 : Y_t = \Delta\}.$$

has the same distribution as

$$T_X = \inf\{t \geq 0 : X_t = \Delta\}$$

- The local equilibria tell us what is happening inside the super state, as one can construct a coupling of $\{X_t\}_{t\geq 0}$ and $\{Y_t\}_{t\geq 0}$ such that

$$\mathcal{L}(X_t \,|\, \{Y_s\}_{0\leq s\leq t}) = \boldsymbol{\mu}_{Y_t}.$$

- We can use the local equilibria to work out where charge carriers jump when they leave the superstate.

Result

At the cost of calculating eigenvalues, we can simulate absorption times while keeping track of charge carrier locations.

Extension

Extend our method to incorporate Coulomb interactions.

References

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Construction

- Let m_0 be the initial distribution of the exclusion process on S.
- For $\ell \in \{0, \ldots, N\}$, define the measures

$$\widetilde{\mu}_\ell = m_0 \prod_{i=0}^{\ell} \left(I + \frac{1}{\theta_{N-i}} Q \right)$$

- For $i \in \{0, \ldots, N-1\}$, define

$$d_i = 1 - \frac{\widetilde{\mu}_{i+1}(S)}{\widetilde{\mu}_i(S)}.$$

- We have $d_i \in [0, 1]$ for all $i \in \{0, \ldots, N-2\}$ and $d_{N-1} = 1$.

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Construction

- Now, for $i \in \{0, \ldots, N-1\}$, we define the sequence of probability distributions

$$\mu_i = \left(\prod_{j=1}^{N-1} (1 - d_j)^{-1} \right) \widetilde{\mu}_i,$$

called local equilibria.