Mathematical Underpinnings of Diffusive Molecular Dynamics

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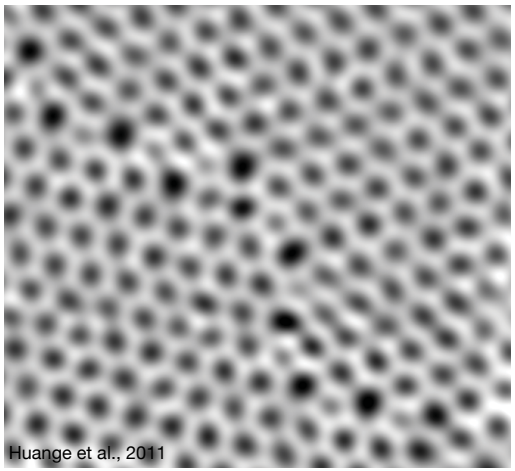
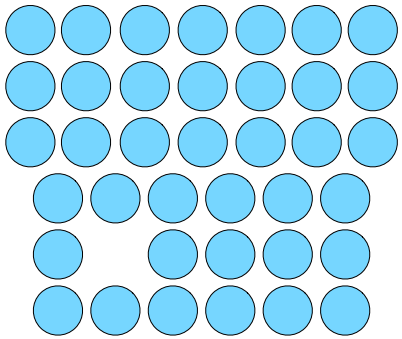
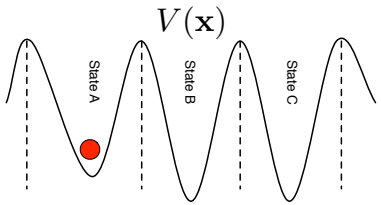
Joint with B. Farmer (U. Minnesota), M. Luskin (U. Minnesota), P. Plechac (U. Delaware)

Metastability







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- Atomic, vibrational, time scale: 10^{-15} s
- Time scale for transitions of defects: $10^{-9} - 10^{-6}$ s

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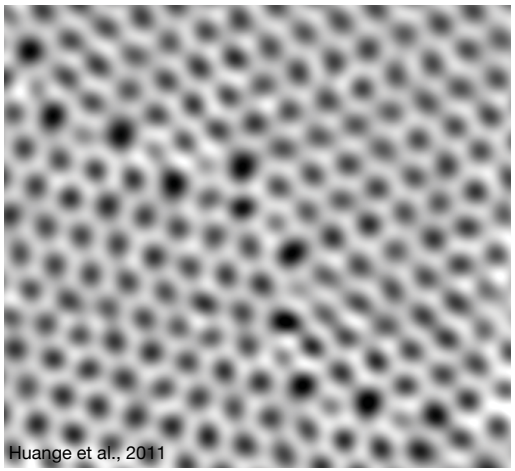

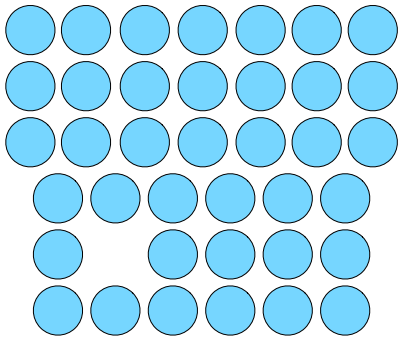

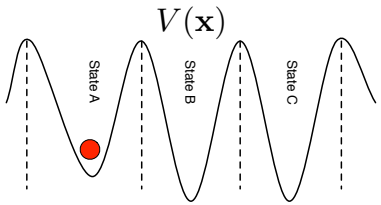

- Real materials (metals, crystals, proteins) contain defects
- Atomic, vibrational, time scale: 10^{-15} s
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- **Metastable States**
- Transitions amongst Metastable States are **Rare Events**
- **Goal – Predictive simulation of metastable systems**

Computational Costs of Classical Molecular Dynamics

- Overdamped Langevin model:

$$dX_t = -\nabla V(X_t)dt + \sqrt{2\beta^{-1}}dW_t, \quad X_t : [0,\infty) \to \mathbb{R}^{3\cdot N} \tag{1}$$

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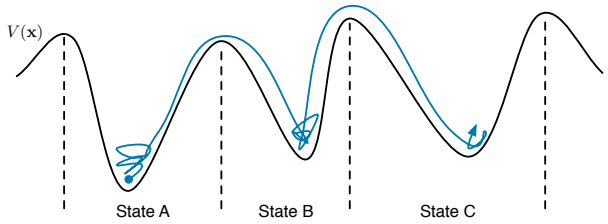
- Each step takes $\approx 10^{-6}$ s of **wall clock time per atom**
- $\approx$ 2.5 hr. per atom
- 10^{-6} s of a 100 atom system $\approx$ 10 days of for direct simulation

Methods for Overcoming the Scale Separation

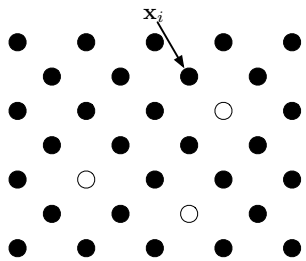
Getting from 10^{-15} s to 10^{-6} s



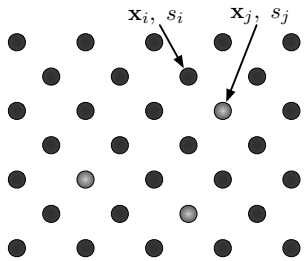
- Accelerated Molecular Dynamics (Voter...)
- (Adaptive) Kinetic Monte Carlo (Henkelman,...)
- ART (Mousseau)
- Markov State Models (Vanden-Eijden, Schütte...)
- Milestoning (Elbert,...)
- Phase Field Crystal (PFC) (Elder, Voorhees,...)
- Others...

Diffusive Molecular Dynamics (DMD)

Sarkar (2011), Phillpot (1994), Perez & Lewis (2006)



Classical MD



DMD

- **Key Idea:** Assign, at each atomic site i, likelihood of occupancy by one of two species, $s_i \in (-1, 1)$

$$\begin{aligned} s_i \sim 1 &\Leftrightarrow \text{High likelihood of species A at site } i \\ s_i \sim -1 &\Leftrightarrow \text{High likelihood of species B at site } i \end{aligned} \tag{2}$$

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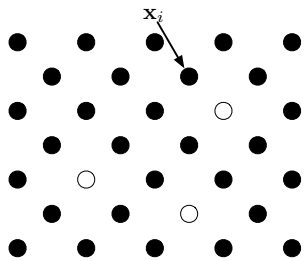

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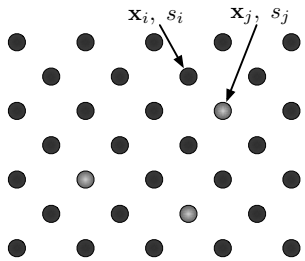

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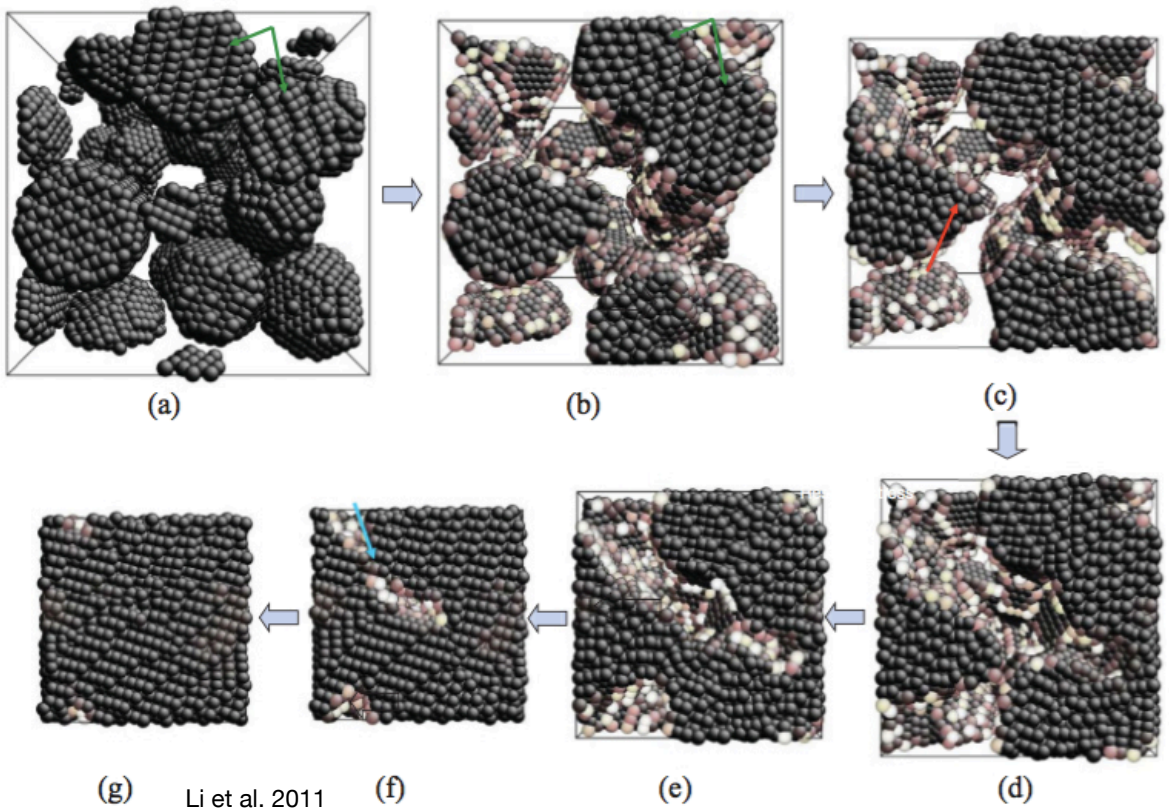
- Evolve s_i under a deterministic flow.
- Allow lattice to quasistatically evolve as composition rearranges

DMD Computations

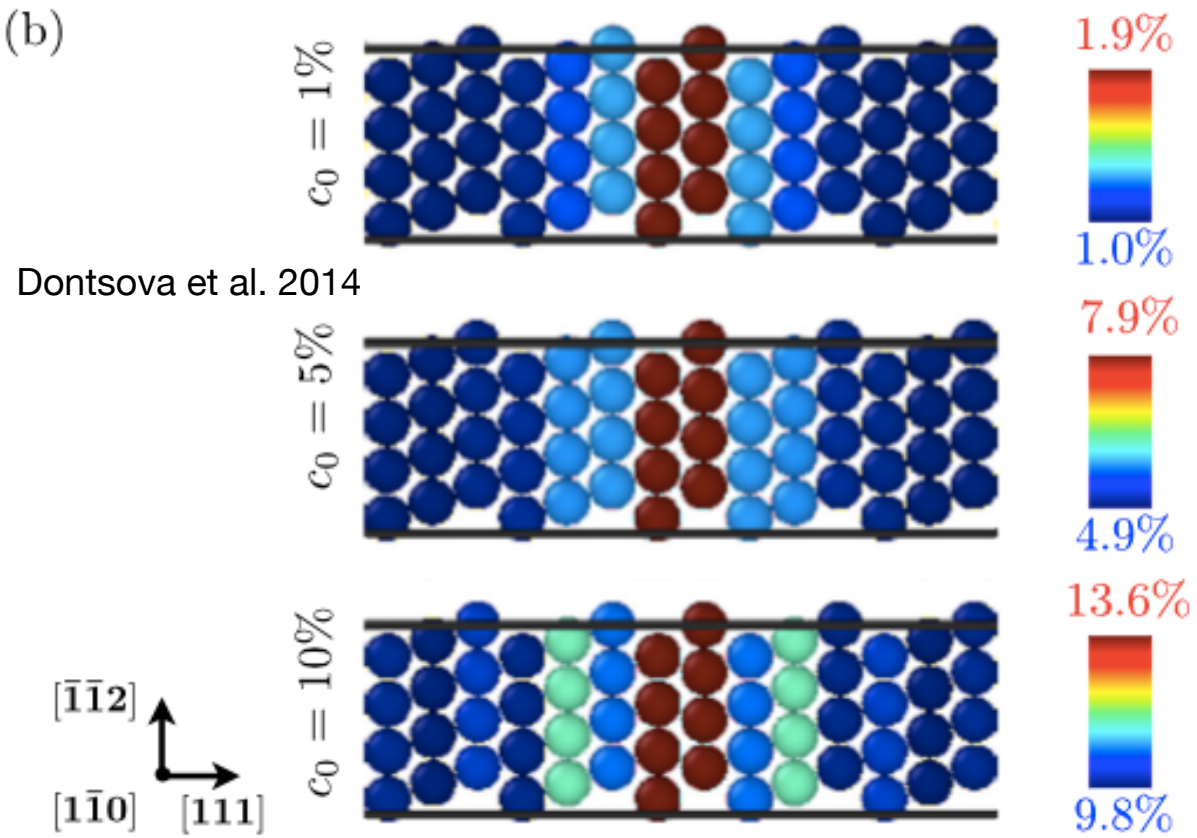
Sintering of Cu – Elemental Material



Li et al. 2011

DMD Computations

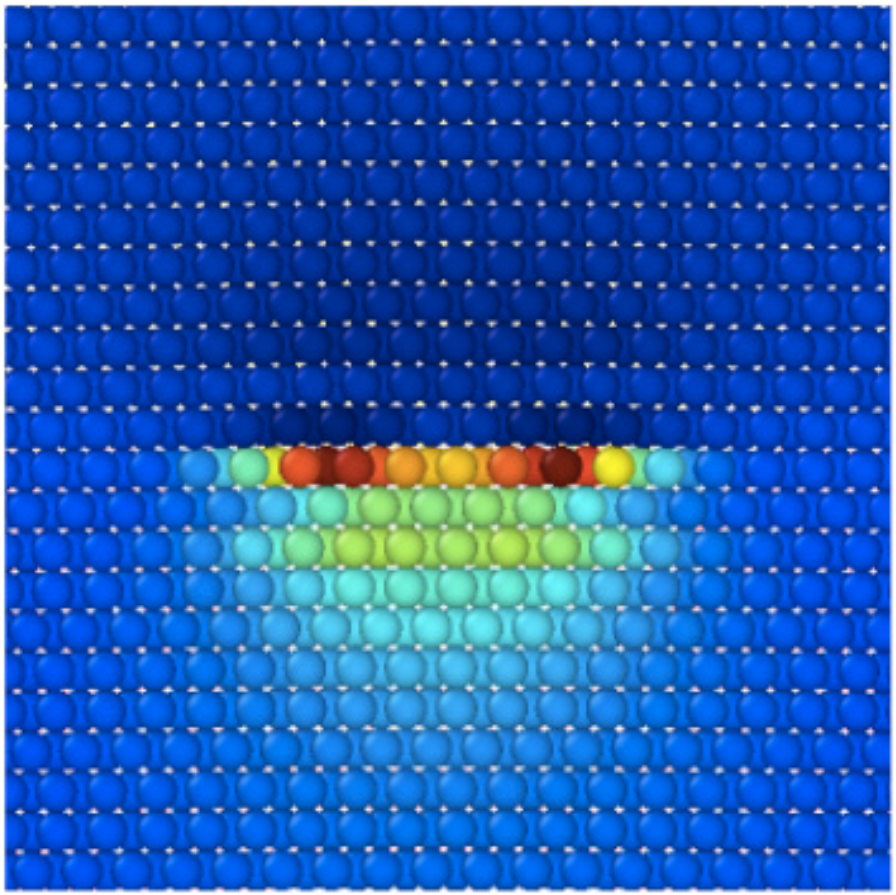
Binary Alloy Segregation in Al-Mg



Dontsova et al. 2014

DMD Computations

Binary Alloy Aggregation near Edge Dislocations in Al-Mg



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DMD Dynamics

Key elements for running DMD

- A "free energy", $\mathcal{F} = \mathcal{F}(\mathbf{X}, \mathbf{k}, \mathbf{s})$, with mean atomic site positions $\mathbf{X}$ and harmonic constants $\mathbf{k}$

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Key elements for running DMD

- A "free energy", $\mathcal{F} = \mathcal{F}(\mathbf{X}, \mathbf{k}, \mathbf{s})$, with mean atomic site positions $\mathbf{X}$ and harmonic constants $\mathbf{k}$
- Given the composition, minimize $\mathcal{F}$ over $(\mathbf{X}, \mathbf{k})$ – quasistatic evolution of the lattice
- With minimizing $(\mathbf{X}, \mathbf{k})$, evolve s_i:

$$\dot{s}_i = \sum_{j \in \mathcal{N}_i} k_{ij} \left(\frac{\partial \mathcal{F}}{\partial s_j} - \frac{\partial \mathcal{F}}{\partial s_i} \right) \tag{3}$$

Mathematical Challenges for DMD

1. Constructing & Evlauating the Free Energy
2. Constructing & Constraining the Evolution Equation – Form of flow and values of coefficients
3. Relating DMD to MD

Main Results

- Spin-Diffusion model – Couple a diffusion (overdamped Langevin) to spin exchange (Ising)
- Using:
  - Time Scale Separation
  - Quasistationary Distributions
  - Low Temperature Approximations
  - Mean field Approximations

  we recover DMD type dynamics

State Spaces and Potentials

Binary Alloy State Space

$$\begin{aligned} \mathbf{x} &= (\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N), \quad \mathbf{x}_i \in D \subset \mathbb{R}^d \\ \boldsymbol{\sigma} &= (\sigma_1, \sigma_2, \ldots, \sigma_N), \quad \sigma_i \in \{\pm 1\} \end{aligned} \tag{4}$$

Pair Potential

$$V(\mathbf{x}, \boldsymbol{\sigma}) = \sum_{i<j} \phi_{\sigma_i, \sigma_j}(|\mathbf{x}_i - \mathbf{x}_j|) \tag{5}$$

Generalizes to more sophisticated potentials (*i.e.*, EAM)

Aside – Elemental Material (Atoms & Vacancies)

- Earliest DMD works were for elemental materials: Single Species & Vacancies:

$$\mathbf{x} = (\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N), \quad \mathbf{x}_i \in D \subset \mathbb{R}^d \tag{6}$$

$$\mathbf{a} = (a_1, a_2, \ldots, a_N), \quad a_i \in \{0, 1\} \tag{7}$$

$$V(\mathbf{x}, \mathbf{a}) = \sum_{i<j} a_i a_j \phi(|\mathbf{x}_i - \mathbf{x}_j|) \tag{8}$$

- Framework could also be extended to multicomponent systems

Ensembles

Generalized Ensemble – Spin-Diffusion

$$\mu(d\mathbf{x}, \boldsymbol{\sigma}) = Z^{-1} e^{-\beta V(\mathbf{x}, \boldsymbol{\sigma})} d\mathbf{x}, \quad Z = \sum{}' \int e^{-\beta V(\mathbf{x}, \boldsymbol{\sigma})} d\mathbf{x} \tag{9}$$

- $\sum \sigma_i = M$ constrains state space

Alternative Ensemble – DMD

$$\nu(d\mathbf{x}, \boldsymbol{\sigma}) = Z_\nu^{-1} e^{-\beta V(\mathbf{x}, \boldsymbol{\sigma}) + \beta \boldsymbol{\lambda} \cdot \boldsymbol{\sigma}} d\mathbf{x}, \quad Z_\nu = \sum \int e^{-\beta V(\mathbf{x}, \boldsymbol{\sigma}) + \beta \boldsymbol{\lambda} \cdot \boldsymbol{\sigma}} d\mathbf{x} \tag{10}$$

- No constraint on state space
- λ_i chosen such that $\mathbb{E}^\nu[\sigma_i] = s_i$, $\sum s_i = M$

True Free Energy

- Working in ν ensemble,

$$F_\nu = -\beta^{-1} \ln Z_\nu + \boldsymbol{\lambda} \cdot \mathbf{s}, \quad Z_\nu = \sum \int e^{-\beta V(\mathbf{x},\boldsymbol{\sigma}) + \beta \boldsymbol{\lambda} \cdot \boldsymbol{\sigma}} d\mathbf{x} \tag{11}$$

- For harmonic potential:

$$\tilde{V}(\mathbf{x}, \boldsymbol{\sigma}; \mathbf{X}, \mathbf{k}) = \sum_i \frac{k_i}{2} |\mathbf{x}_i - \mathbf{X}_i|^2 \tag{12}$$

then

$$F_{\tilde{\nu}} = \beta^{-1} \sum_i \frac{1+s_i}{2} \ln \frac{1+s_i}{2} + \frac{1-s_i}{2} \ln \frac{1-s_i}{2} + \sum_i \frac{d}{2} \ln \frac{\beta k_i}{2\pi} \tag{13}$$

Free Energy Approximation

Variational Gaussian (VG), LeSar *et al.* (1989, 1990)

- **Key Idea:** Approximate the true DMD free energy F by $\mathcal{F}$, a least upper bound, and use $\nabla_{\mathbf{s}}\mathcal{F}$ to drive the dynamics
- Approximate F_ν with $\mathcal{F}$ by finding the best fit "Gaussian" $\tilde{\nu}$ for ν with respect to Relative Entropy:

$$\mathcal{R}(\tilde{\nu}||\nu) = \begin{cases} \mathbb{E}^{\nu}[\log \frac{d\tilde{\nu}}{d\nu}] & \tilde{\nu} \ll \nu, \\ +\infty & \text{otherwise} \end{cases} \tag{14}$$

- Corresponds to minimization over parameters $(\mathbf{X}, \mathbf{k})$

$$\begin{aligned} \mathcal{F} = \mathbb{E}^{\tilde{\nu}}[V] + \beta^{-1} \sum_{i=1}^{N} \frac{1+s_i}{2} \log \frac{1+s_i}{2} + \frac{1-s_i}{2} \log \frac{1-s_i}{2} \\ + \frac{3}{2}\left(\log \frac{\beta k_i}{2\pi} - 1\right) \end{aligned} \tag{15}$$

Aside – Why Relative Entropy?

- For classical problem, let V and $\tilde{V}$ be two different potentials for the same system (*i.e.*, N atoms in a box Ω). Gibbs distributions are:

$$\nu(d\mathbf{x}) = Z^{-1} e^{-\beta V(\mathbf{x})} d\mathbf{x}, \quad \tilde{\nu}(d\mathbf{x}) = \tilde{Z}^{-1} e^{-\beta \tilde{V}(\mathbf{x})} d\mathbf{x}, \tag{16}$$

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- Non-negativity of $\mathcal{R} \Leftrightarrow$ Gibbs-Bogoliubov inequality:

$$\underbrace{-\beta^{-1} \log Z}_{\text{Free Energy for } V} \leq \underbrace{\mathbb{E}^{\tilde{\nu}}[(V - \tilde{V})] - \beta^{-1} \log \tilde{Z}}_{\text{Upper Bound}} \tag{18}$$

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- Generalizes to extended state space
- $\mathcal{R}(\tilde{\nu}||\nu)$ vs. $\mathcal{R}(\nu||\tilde{\nu})$

DMD Dynamics – Fast/Slow Processes

- Minimize $\mathcal{F}$ over harmonic parameters $(\mathbf{X}, \mathbf{k})$

$$\mathcal{F} = \mathbb{E}^{\tilde{\nu}}[V] + \beta^{-1} \sum_{i=1}^{N} \frac{1+s_i}{2} \log \frac{s_i+1}{2} + \frac{1-s_i}{2} \log \frac{1-s_i}{2} + \frac{d}{2}\left(\log \frac{\beta k_i}{2\pi} - 1\right) \tag{19}$$

- Free Energy Gradients – conserves mass, reduces free energy

$$\dot{s}_i = \sum_{j \in \mathcal{N}_i} k_{ij} \left(\frac{\partial \mathcal{F}}{\partial s_j} - \frac{\partial \mathcal{F}}{\partial s_i} \right)$$

- "Master Equation"

$$\dot{s}_i = \sum_{j \in \mathcal{N}_i} (1+s_j)(1-s_i)\Gamma_{j \to i} - (1+s_i)(1-s_j)\Gamma_{i \to j} \tag{20}$$

Outstanding Questions

- What motivates the form of the dynamics?
- What is the relationship between DMD and MD?

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State Space $\boldsymbol{\sigma} \in \{\pm 1\}^N$, $\mathbf{x} \in \mathbb{R}^{d \cdot N}$

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Spin Exchange Process Given $\mathbf{x}$, swap $\boldsymbol{\sigma} \to \boldsymbol{\sigma}'$ with rates satisfying detailed balance:

$$r(\boldsymbol{\sigma} \to \boldsymbol{\sigma}'; \mathbf{x})e^{-\beta V(\mathbf{x}, \boldsymbol{\sigma})} = r(\boldsymbol{\sigma}' \to \boldsymbol{\sigma}; \mathbf{x})e^{-\beta V(\mathbf{x}, \boldsymbol{\sigma}')} \tag{22}$$

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Joint Process $L_\epsilon = \epsilon^{-1}L_x + L_\sigma$; ϵ reflects a scale separation

Equilibrium Since $e^{-\beta V(\mathbf{x}, \boldsymbol{\sigma})}$ is invariant for each process, it is invariant for the joint process and preserves $\sum \sigma_i = M$

Spin-Diffusion and MD

- Assume $V(\mathbf{x}, \boldsymbol{\sigma})$ is invariant to simultaneous change of labels in both arguments: For any admissible $\boldsymbol{\sigma}_\star$

$$Z = \sum_{\boldsymbol{\sigma}}{}' \int \exp(-\beta V(\mathbf{x}, \boldsymbol{\sigma}))d\mathbf{x} = \binom{N}{N_{\mathrm{A}}} \int \exp(-\beta V(\mathbf{x}, \boldsymbol{\sigma}_\star))d\mathbf{x}. \tag{23}$$

  where $N_{\mathrm{A}} + N_{\mathrm{B}} = N$ and $N_{\mathrm{A}} - N_{\mathrm{B}} = M$
- Spin-diffusion can be used to estimate $e^{-\beta V(\mathbf{x}, \boldsymbol{\sigma}_\star)}$ averaged observables also invariant to permutation (*i.e.* internal energy)

Scale Separation & Metastability

- Assume $V(\mathbf{x}, \boldsymbol{\sigma})$ has a finite number of minima and associated basins of attraction. Then:

$$\mathbb{R}^{d \cdot N} = \cup_{\ell=1}^{n} D_\ell(\boldsymbol{\sigma}), \quad D_\ell(\boldsymbol{\sigma}) \cap D_{\ell'}(\boldsymbol{\sigma}) = \emptyset \quad \text{if } \ell \neq \ell' \tag{24}$$

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- Time for diffusion to transit amongst $D_\ell(\boldsymbol{\sigma})$ at fixed $\boldsymbol{\sigma}$ is long relative to time to sample $D_\ell(\boldsymbol{\sigma})$ (**metastable states**) – approximate using Quasistationary distributions (QSDs):

$$Z = \sum_{\boldsymbol{\sigma}}{}' \sum_{\ell=1}^{n} Z_\ell(\boldsymbol{\sigma}) \approx \sum_{\boldsymbol{\sigma}}{}' \sum_{\ell=1}^{n} \check{Z}_\ell(\boldsymbol{\sigma}), \tag{26}$$

QSDs for Diffusions

- For just a diffusion (for now):

$$d\mathbf{x}(t) = -\nabla V(\mathbf{x}(t))dt + \sqrt{2\beta^{-1}}d\mathbf{W}(t)$$

and let D be a subset of the state space (*i.e.*, a basin of attraction) with $\mathbf{x}(0) \in D$:

$$T = \inf\{t \geq 0 \mid \mathbf{x}(t) \notin D\}$$
$$\check{\mu}(d\mathbf{x}) = \lim_{t\to\infty} \mathbb{P}(\mathbf{x}(t) \in d\mathbf{x} \mid T > t)$$

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- QSD $\check{\mu}$ is the distribution of the diffusion, conditioned on never leaving D.
- For spin-diffusion, given a set $D_\ell(\boldsymbol{\sigma})$ at **fixed** $\boldsymbol{\sigma}$, QSD $\check{\mu}_\ell(\bullet \mid \boldsymbol{\sigma})$:

$$\check{\mu}_\ell(\bullet \mid \boldsymbol{\sigma}) = \lim_{t\to\infty} \mathbb{P}(\mathbf{x}(t) \in \bullet \mid T > t) \tag{27}$$

QSDs for Diffusions, Continued

- Generator of the diffusion is

$$L = -\nabla_x V \cdot \nabla_x + \beta^{-1} \Delta_x$$

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- Conditioning on not leaving D corresponds to putting zero Dirichlet boundary conditions on L

QSDs for Diffusions, Continued

- Generator of the diffusion is

$$L = -\nabla_x V \cdot \nabla_x + \beta^{-1}\Delta_x$$

- Conditioning on not leaving D corresponds to putting zero Dirichlet boundary conditions on L
- Let λ_i be the eigenvalues of -L:
  - If $\mathbf{x}(0) \sim \breve{\mu}$, then λ_1^{-1} is mean first exit time
  - Starting from an arbitrary initial condition, time scale to relax to QSD is $(\lambda_2 - \lambda_1)^{-1}$
  - Measure of metastability:

$$\frac{\text{Relaxation Time}}{\text{First Exit Time}} \sim \frac{\lambda_1}{\lambda_2 - \lambda_1} \tag{28}$$

Comparison of Distributions for Diffusions

$$\check{\mu}(d\mathbf{x}) = \lim_{t\to\infty} \mathbb{P}(\mathbf{x}(t) \in d\mathbf{x} \mid T > t)$$

$$Z^{-1} e^{-\beta V(\mathbf{x})} 1_D(\mathbf{x}) d\mathbf{x}$$

$$\tilde{Z}^{-1} e^{-\beta \frac{k}{2} |\mathbf{x}-\mathbf{X}|^2} 1_D(\mathbf{x}) d\mathbf{x}$$

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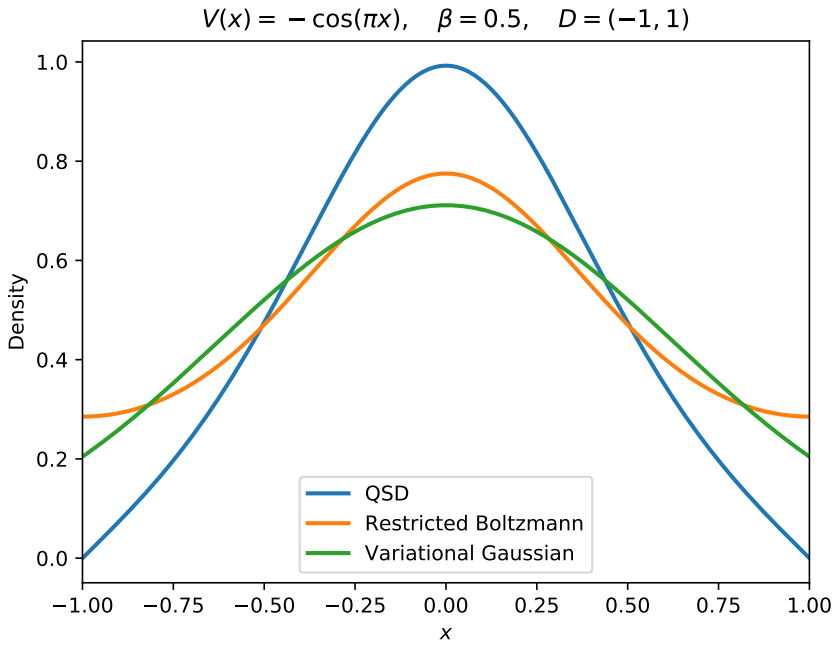

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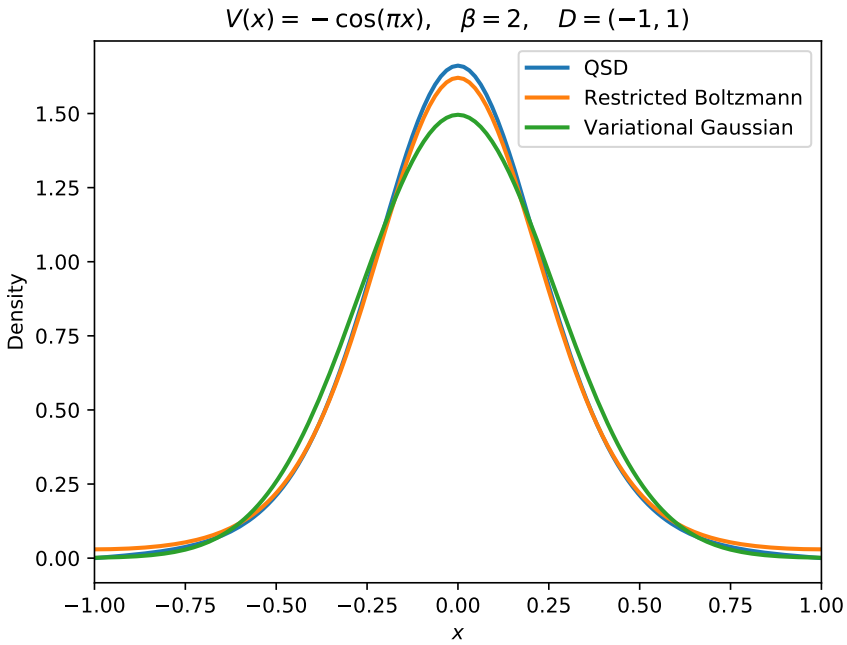

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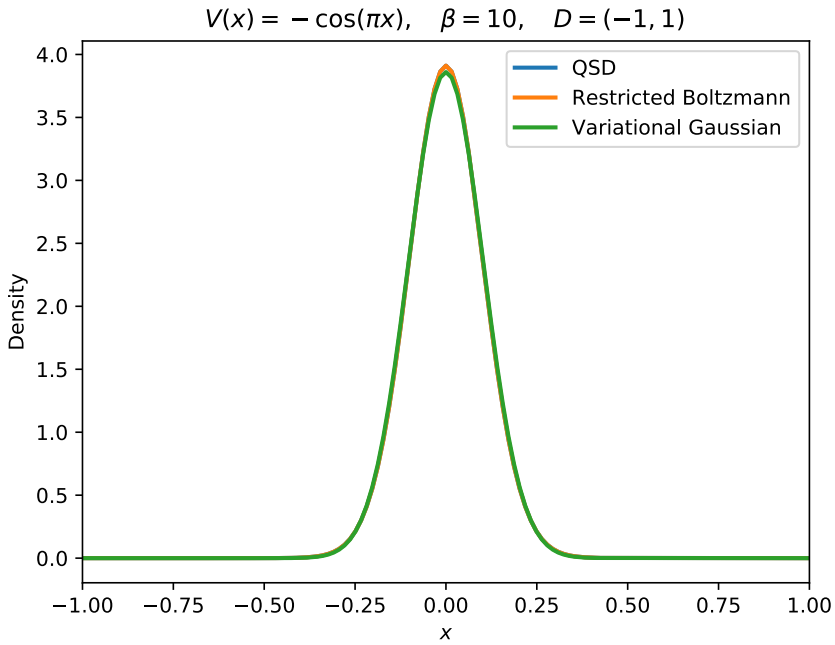


As $\beta \to \infty$, they all agree

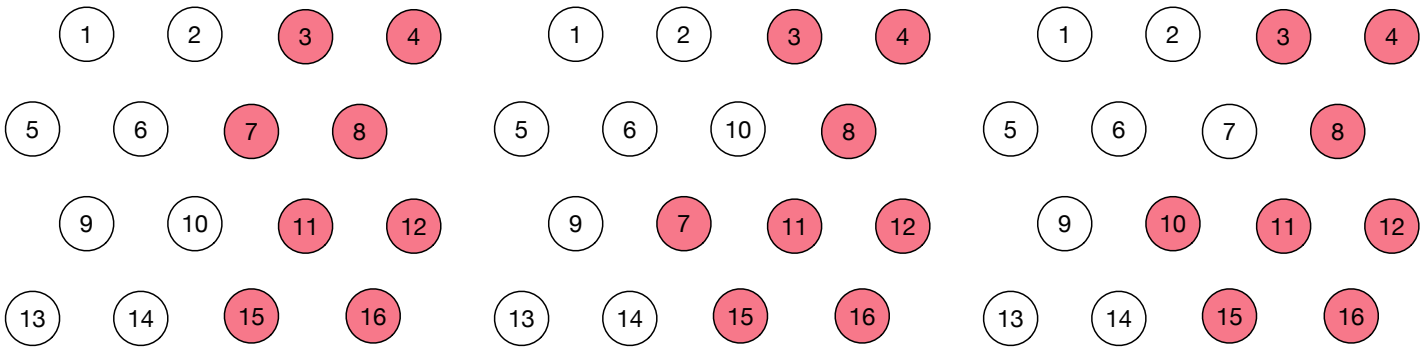
QSD Scale Separation for Spin-Diffusion

- **Assume:** There exists $0 < \epsilon \ll 1$ such that for all $D_\ell(\boldsymbol{\sigma})$

$$\epsilon \sim \frac{\lambda_1(\boldsymbol{\sigma}, \ell)}{\lambda_2(\boldsymbol{\sigma}, \ell) - \lambda_1(\boldsymbol{\sigma}, \ell)} \tag{29}$$

- QSD Idealization of Spin-Diffusion:
  - Diffusions will take so long to exit $D_\ell(\boldsymbol{\sigma})$, approximate this as infinity
  - Conditioned diffusions explores within each basin
  - Spin-Exchange explores across the basins
- Precisely motivates ϵ in $\check{L}_\epsilon = \epsilon^{-1}\check{L}_x + \check{L}_{\sigma,\ell}$ and reaction rates in spin-exchange are O(1) time scale.

QSD Scale Separation for Spin-Diffusion, Continued



- Removes ambiguity of type of transitions – Did this composition arise from a diffusion or a spin-exchange?
- In our model, intrabasin motion is handled by the diffusion, interbasin transits are handled by the spin exchange

Expansion and Averaged Dynamics

- Backwards Kolmogorov: $\partial_t v = \check{L}_\epsilon v$, $v = v_0 + \epsilon v_1 + \ldots$,

$$\text{Leading Order: } \partial_t v_0 = \mathbb{E}^{\check{\mu}_\ell(\bullet|\boldsymbol{\sigma})}[\check{L}_{\sigma,\ell}]v_0, \tag{30}$$

  jump process with **x**-averaged (finite temperature) reaction rates
- By virtue of QSD, jump process is $(\boldsymbol{\sigma}, \ell) \to (\boldsymbol{\sigma}', \ell')$:

$$\dot{v}_0 = \sum_{(\boldsymbol{\sigma}', \ell')} \mathbb{E}^{\check{\mu}_\ell(\bullet|\boldsymbol{\sigma})}[r((\boldsymbol{\sigma}, \ell) \to (\boldsymbol{\sigma}', \ell'); \mathbf{x})](v_0(\boldsymbol{\sigma}', \ell', t) - v_0(\boldsymbol{\sigma}, \ell, t)) \tag{31}$$

Low Temperature Approximation

- For rates to be tractable, approximate QSD as restricted Boltzmann (see Gesú *et al*, 2016)

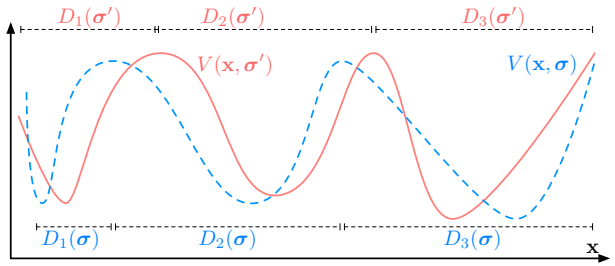
$$\begin{aligned} \check{\mu}_\ell(d\mathbf{x} \mid \boldsymbol{\sigma}) &= \check{Z}_\ell(\boldsymbol{\sigma})^{-1}\varphi_1(\mathbf{x};\boldsymbol{\sigma},\ell)e^{-\beta V(\mathbf{x},\boldsymbol{\sigma})}d\mathbf{x} \\ &\overset{\beta\to\infty}{\approx} \check{Z}_\ell(\boldsymbol{\sigma})^{-1}1_{D_\ell(\boldsymbol{\sigma})}e^{-\beta V(\mathbf{x},\boldsymbol{\sigma})}d\mathbf{x}. \end{aligned} \tag{32}$$

- Then

$$r((\boldsymbol{\sigma},\ell)\to(\boldsymbol{\sigma}',\ell');\mathbf{x})e^{-\beta V(\mathbf{x},\boldsymbol{\sigma})} = r((\boldsymbol{\sigma}',\ell')\to(\boldsymbol{\sigma},\ell);\mathbf{x})e^{-\beta V(\mathbf{x},\boldsymbol{\sigma}')} \tag{33}$$

for $\mathbf{x}\in D_\ell(\boldsymbol{\sigma})\cap D_{\ell'}(\boldsymbol{\sigma}')$

State Space Approximation



- Enumerating all neighboring basins for $(\boldsymbol{\sigma}, \ell) \to (\boldsymbol{\sigma}', \ell')$ is computationally exhausting

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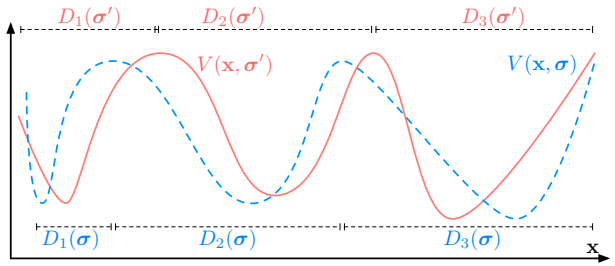

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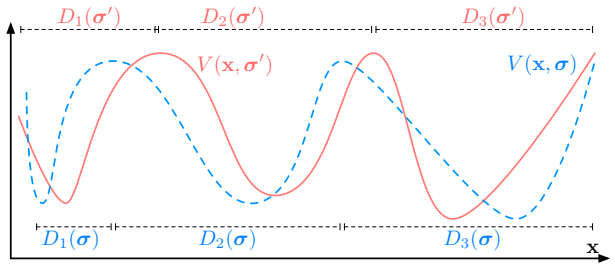

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- $\ell = \ell(\boldsymbol{\sigma})$ and the initial conditions:

$$\dot{v}_0 = \sum_{\boldsymbol{\sigma}'} \mathbb{E}^{\check{\mu}_\ell(\bullet|\boldsymbol{\sigma})}[r((\boldsymbol{\sigma}, \ell) \to (\boldsymbol{\sigma}', \ell'); \mathbf{x})](v_0(\boldsymbol{\sigma}', \ell', t) - v_0(\boldsymbol{\sigma}, \ell, t)) \tag{34}$$

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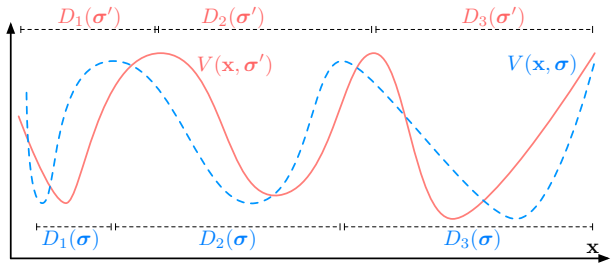

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- Furthermore, $\boldsymbol{\sigma}' = \sigma^{ij}$, a spin exchange between $j \in \mathcal{N}_i$ for each i.

Reaction Rates and Mean Field Approximations

- tanh reaction rates:

$$r(\boldsymbol{\sigma} \to \boldsymbol{\sigma}^{ij}; \mathbf{x}) = \tau^{-1} \left\{ \frac{1}{2} - \frac{1}{2} \tanh \left(\frac{\beta}{2} \Delta_{ij} V(\mathbf{x}, \boldsymbol{\sigma}) \right) \right\}, \qquad (35)$$

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- Assume mean field approximations are valid, the ensemble averaged evolution of $\mathbb{E}[\sigma_i]$ is approximated by

$$\frac{d}{dt} s_i = \frac{1}{2} \tau^{-1} \sum_{j \in \mathcal{N}_i} (s_j - s_i) - (1 - s_i s_j) \tanh \left(\beta \frac{\Delta_{ij} \check{V}^{(\ell(\mathbf{s}))}(\mathbf{s})}{s_j - s_i} \right). \qquad (36)$$

with atomic sites distributed according to $\mathbf{x}(t) \sim \check{\mu}_{\ell(\mathbf{s})}(\bullet \mid \mathbf{s})$

DMD vs. Spin-Diffusion

$$\frac{d}{dt}s_i = \frac{1}{2}\tau^{-1}\sum_{j\in\mathcal{N}_i}(s_j - s_i) - (1 - s_i s_j)\tanh\left(\beta\frac{\Delta_{ij}\check{V}^{(\ell(\mathbf{s}))}(\mathbf{s})}{s_j - s_i}\right) \tag{37}$$

vs.

$$\frac{d}{dt}s_i = \beta^{-1}k_c\sum_{j\in\mathcal{N}_i}\operatorname{arctanh}(s_j) - \operatorname{arctanh}(s_i) - \beta\frac{\Delta_{ij}\tilde{V}(\mathbf{s},\mathbf{X},\mathbf{k})}{s_j - s_i} + \beta\tilde{J}_{ij}(s_j - s_i). \tag{38}$$

In a high temperature, near equilibrium, limit, ($s_i \sim 0$) these agree if

$$\check{V}^{\ell}(\mathbf{s}) \approx \tilde{V}(\mathbf{s},\mathbf{X},\mathbf{k}), \quad \check{V}^{\ell}(\mathbf{s}^{ij}) \approx \tilde{V}(\mathbf{s}^{ij},\mathbf{X},\mathbf{k}) \tag{39}$$

$$k_c \approx \tfrac{1}{2}\beta\tau^{-1} \tag{40}$$

Connecting Spin-Diffusion to DMD

Fast Process – Mechanical Relaxation

$$(\mathbf{X}, \mathbf{k}) \in \operatorname{argmin} \mathcal{R}(\tilde{\nu} || \nu), \quad \mathbf{X} = \mathbb{E}^{\check{\mu}_\ell(\bullet|\boldsymbol{\sigma})}[\mathbf{x}]$$

Both match local basin of V

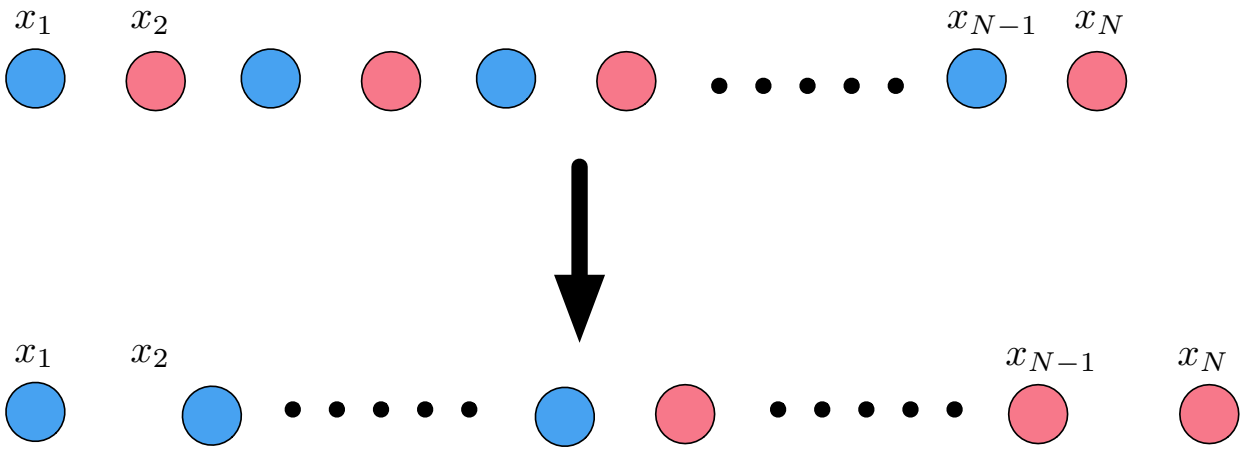
Slow Process – Species Exchange/Migration

$$\dot{s}_i = \sum_j f(s_i, s_j, \partial_{s_i}\mathcal{F}, \partial_{s_j}\mathcal{F})$$

$$\dot{s}_i = \sum_j \mathbb{E}[(\sigma_j - \sigma_i)\check{r}((\boldsymbol{\sigma}, \ell(\boldsymbol{\sigma})) \to (\boldsymbol{\sigma}^{ij}, \ell'(\boldsymbol{\sigma}, \boldsymbol{\sigma}^{ij})))]$$

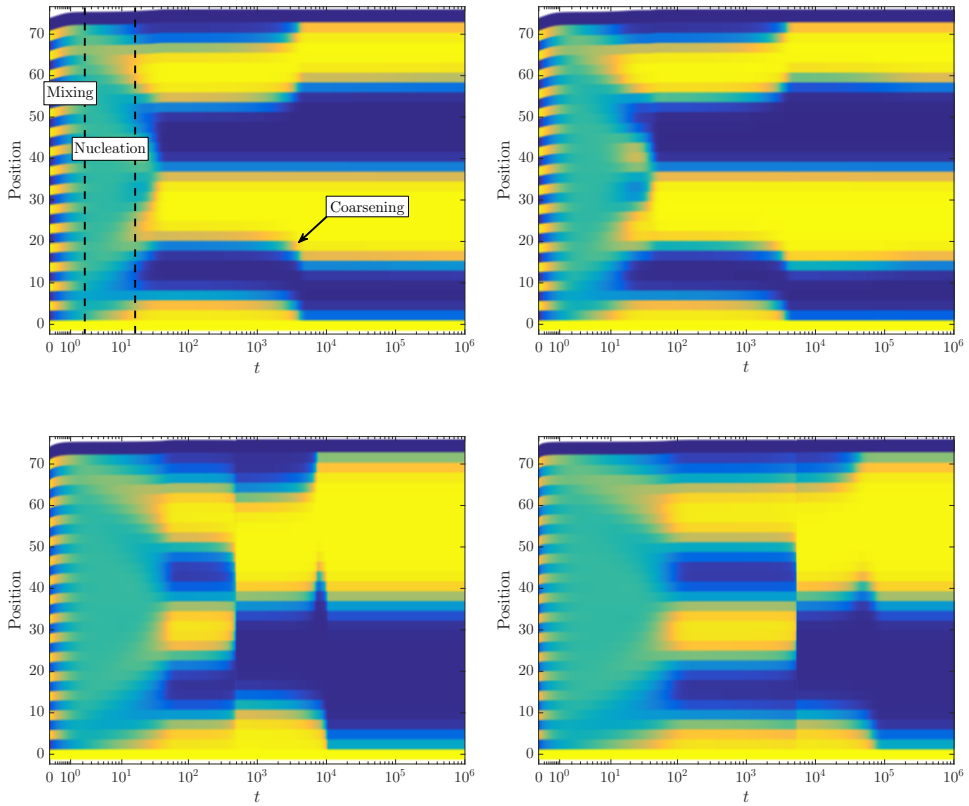
f should approximate the averaged reaction rates

Chain Problem



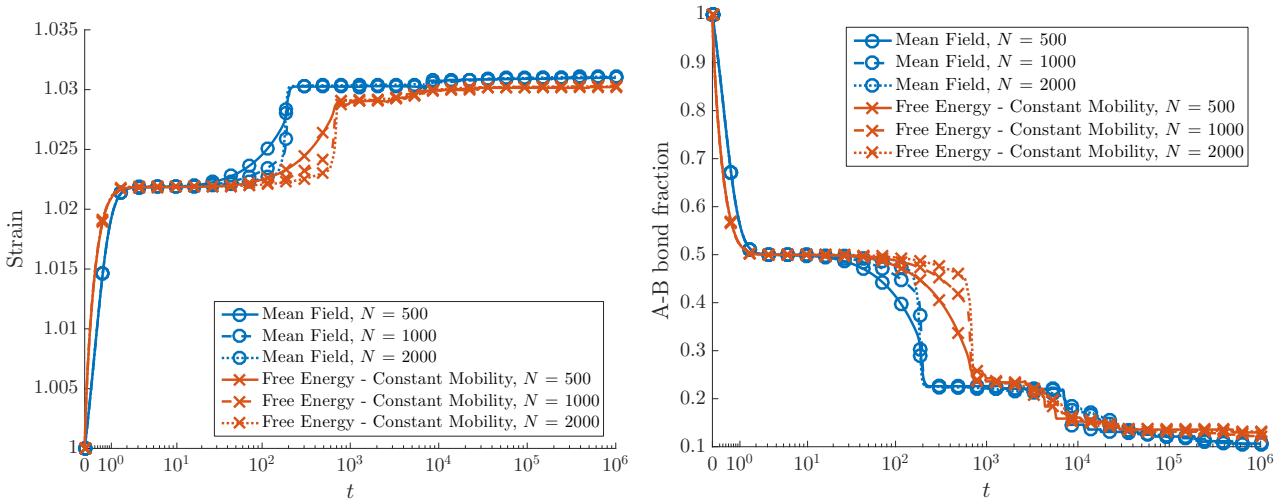
- Pin leftmost atom $x_1 = 0$ with species $\sigma_1 = +1$, and rightmost atom is free to move with species $\sigma_N = -1$
- Energetically favorable for species to segregate
- Interatomic spacing parameters for $A - A$, $A - B$, $B - B$ bonds leads to mechanical deformation

Mean Field Models vs. DMD



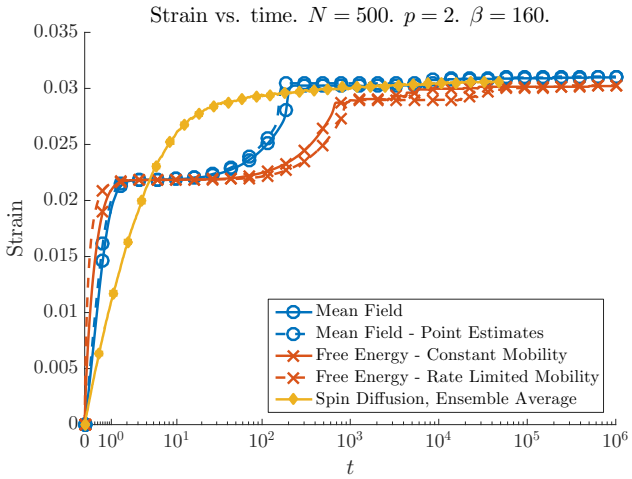
- Top: Approximations of Spin-Diffusion, sharper interfaces, shorter nucleation
- Bottom: DMD, qualitatively similar

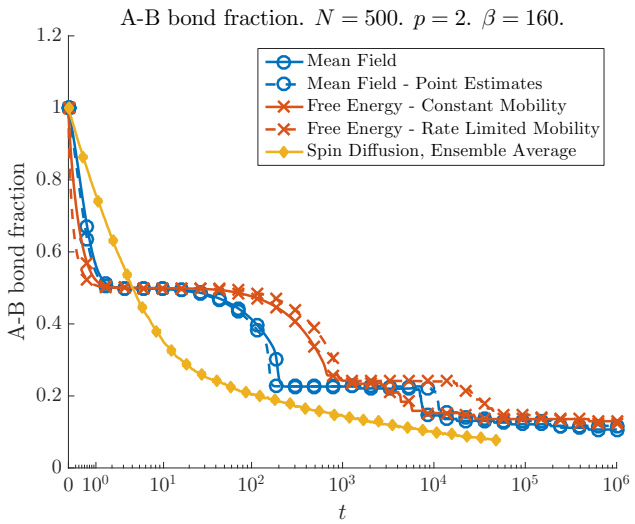
Mean Field Models vs. DMD, Continued



- Behavior is robust to system size
- Qualitatively similar

Mean Field Models vs. Scale Separated Spin Diffusion





- Qualitatively similar – disagreement from short range interactions & mean field approximation
- Equilibrium (large t) behaivor is consistent

Key Assumptions & Approximations for Spin-Diffusion

- Coupled Spin-Diffusion process, $(\mathbf{x}(t), \boldsymbol{\sigma}(t))$
- Assume well defined time scale separation between processes with respect to QSD idealization
- Low temperature approxiatmion to make reaction rates satisfying detailed balance tractable
- State space approximation restricts kMC moves to spin exchanges
- Modelling assumption of reaction rates
- Mean field approximations of true master equation

Interpretation of Spin-Diffusion

Off-Lattice Sites can move, quasistatically

Finite Temperature β present in reaction rates and we are not assumed to be at the quenched configuration

Restricted kMC Only allowed KMC moves are species exchanges

Mean Field An approximate ensemble average to spin-diffusion is made to obtain closed ODEs

Remarks & Open Problems

- Underlying spin-diffusion can be used in place of MD, and this can be approximated with mean field
- Comparison should be in terms of observables

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Remarks & Open Problems

- Underlying spin-diffusion can be used in place of MD, and this can be approximated with mean field
- Comparison should be in terms of observables
- Given physically motivated reaction rates, the approximate spin-diffusion model has closer connections to MD than DMD models
- VG can be used in place of QSD for computational efficiency
- Comparisons of spin-diffusion to its approximate ensemble average remains to be explored
- Substitution of spin-diffusion approximations of the dynamics remains to be implemented in DMD codes.

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Publications Luskin, Simpson, Srolovitz, SIAP (2016)

Preprints `http://arxiv.org/abs/1506.02569`
`http://arxiv.org/abs/1702.01469`

`http://www.math.drexel.edu/~simpson/`