3.320 Lecture 23 (5/3/05)

Faster, faster ,faster …

Bigger, Bigger, Bigger

Accelerated Molecular Dynamics
Kinetic Monte Carlo
Inhomogeneous Spatial Coarse Graining

Problems of Time and Space

Your simulation will always be "too small" and "too short"

Integrated over

Time

Atomistic/Electronic → → Thermodynamics

Continuum matter

Space

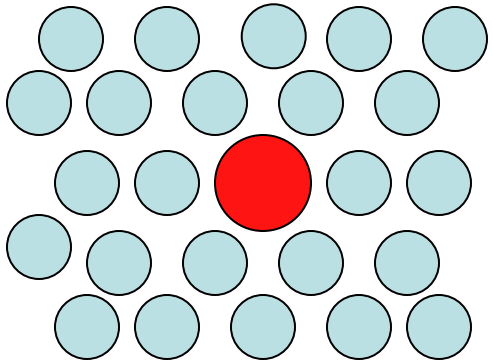
Brute Force Approaches

Conquer more space with more CPU's: *parallelization over space*

How to parallelize *time* ?

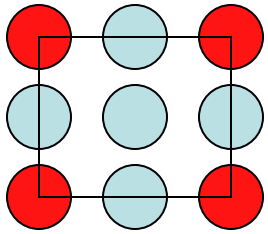
Coarse-graining

Space



e.g. relaxation around a defect
Do you really need all the atoms far away ?

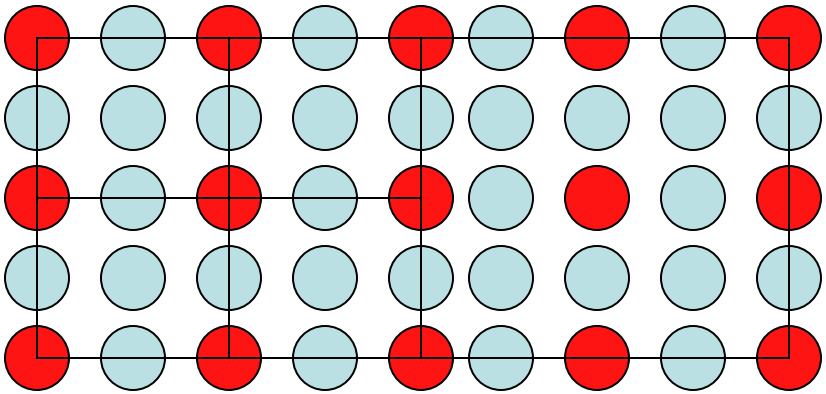
assume homogeneous deformation of groups of atoms



If displacement field for the corner atoms is known, one can interpolate the displacements for the "internal" atoms

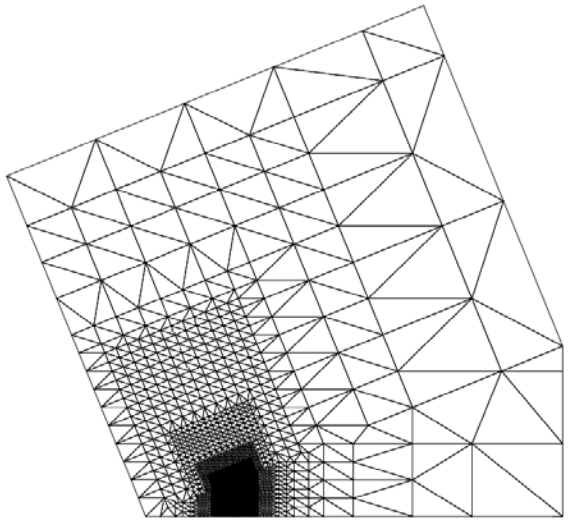
Homogeneous deformation of cell -> can calculate energy without explicitly keeping track of positions of internal atoms

Can Inhomogeneously Coarse-Grain



This is the idea of the quasi-continuum approach (*)

•Atomic extensions of Finite Elements: quasicontinuum



(*) V. B. Shenoy, et al, *Journal of the Mechanics and Physics of Solids* **47**, (1991) 611-42.

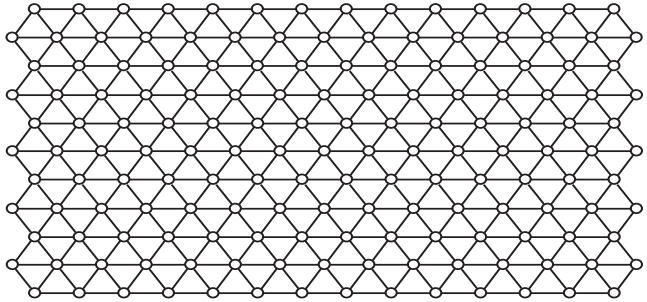
Example: Crack Impinging on Grain Boundary

Photo removed for copyright reasons.

from R. Miller et al. *Modeling and Simulation in Materials Science and Engineering* **6**, (1998) 607.

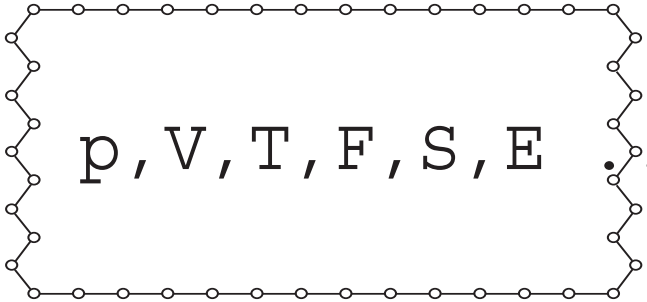
The frontier of coarse-graining: Dynamics

Microscopic dynamics



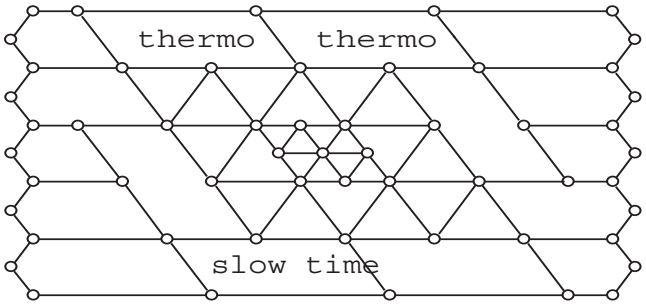
Hamiltonian description
$\{p_i, q_i\}$ of particles, time

Thermodynamics, Elasticity



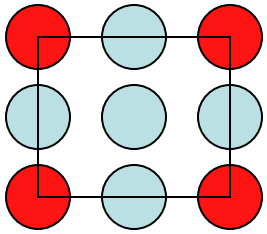
Thermodynamics:
{p,q} of boundaries
T,V,S,E,p ....

Multiscale dynamics: new frontier

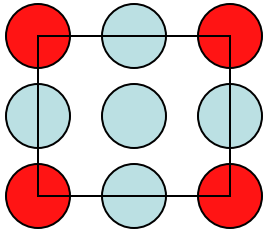


coarse grained models
with thermodynamics
and dynamics

Some suggestions



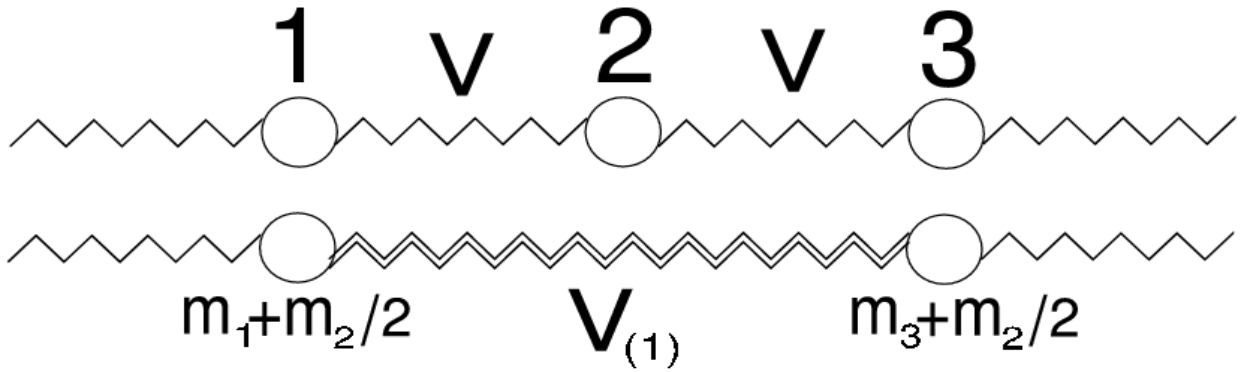
lump mass of removed atoms into node atoms and do MD



Use free energy rather than energy to determine deformation laws inside the elements

Thermodynamic Integration over Degree of Freedom of Removed Atoms

Renormalization of the potential



$$e^{-\beta H_{(1)}(q_1,q_3)} \equiv \frac{1}{h}\int dq_2 dp_2\, e^{-\beta[H(q_1,q_2)+H(q_2,q_3)]}$$

$$\Rightarrow$$

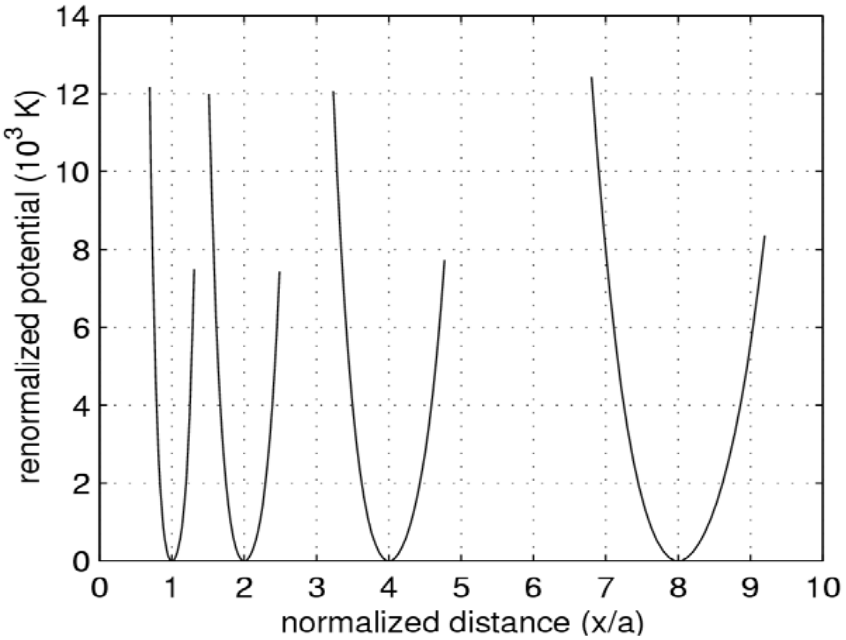
$$e^{-\beta\left[V_{(1)}(q_1,q_3,T)+\tilde{F}_{(1)}(T,q_2)\right]} \equiv \int dq_2 e^{-\beta[V(q_1,q_2)+V(q_2,q_3)]},$$

$$\Rightarrow$$

Renormalization group defines a "potential" tracing out degrees of freedom

S. Curtarolo, G. Ceder. *Dynamics of an Inhomogeneously Coarse Grained Multiscale System*. Physical Review Letters **88**(25). pp. 255504 - (2002).

Renormalized Potentials

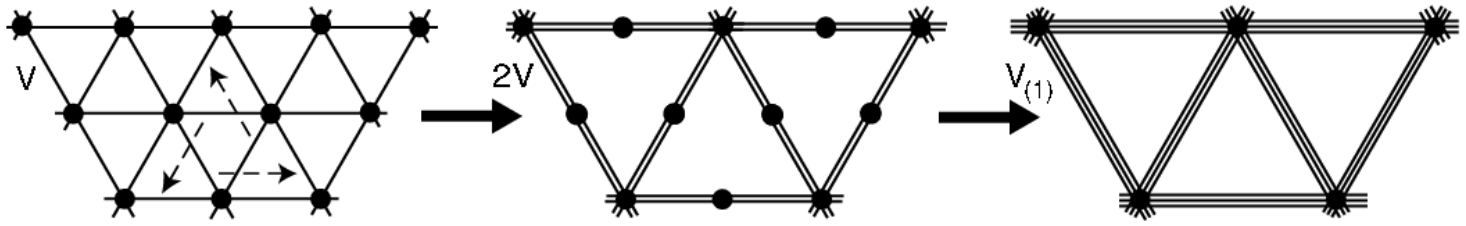


II. lattice spacing is doubled $a_{(1)} = 2a$, time interaction $(1 \leftrightarrow 3)$ is slower than before $(1 \leftrightarrow 2, 2 \leftrightarrow 3)$: $dt_{(1)} = 2^z dt$, z = dynamic exponent, *unknown a priori* ($z \approx 1.45$).

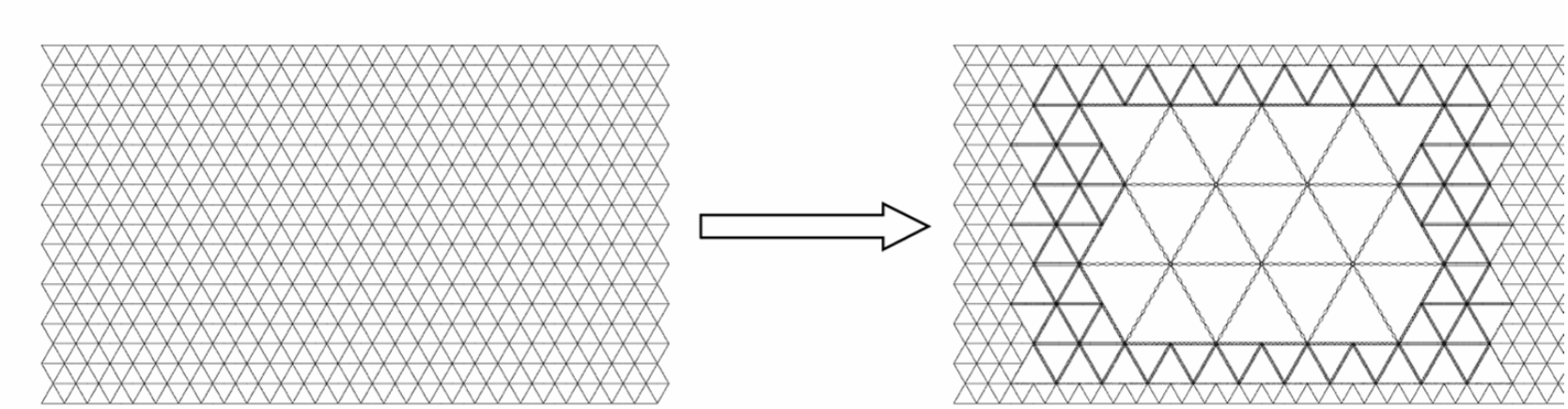
III. Assumption *the renormalized potential* $V_{(1)}$ *describes average dynamic of particles* $(1 \leftrightarrow 3)$ *by averaged interaction of particle 2 during a rescaled time.*

2D-3D Migdal-Kadanoff

bond moving approximation (Migdal-Kadanoff)

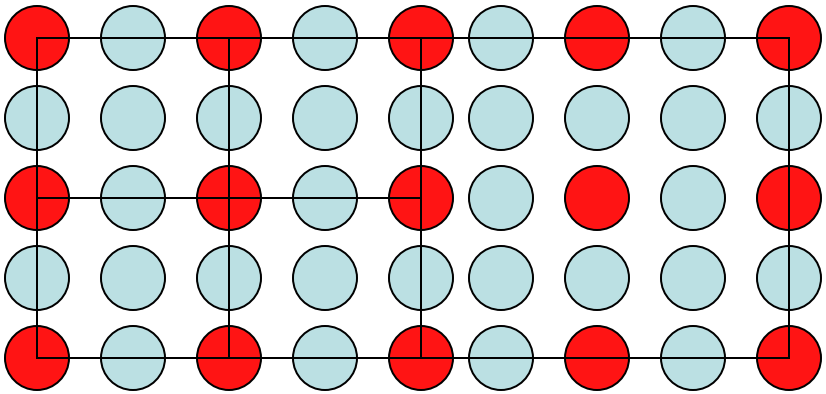


RG: $(V, m) \Rightarrow \left(V_{(1)}, m_{(1)}\right) \Rightarrow \left(V_{(2)}, m_{(2)}\right) \ldots$



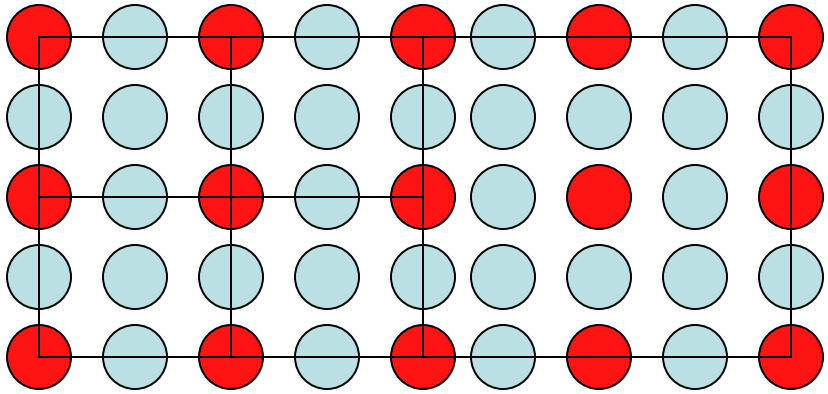
Evaluation Criteria and Problems with Dynamics in Coarse-Grained Models

Phonon reflection into fine regions
Coarse-grained regions can not sustain phonons with short wavelength



Evaluation Criteria and Problems with Dynamics in Coarse-Grained Models

Removing degrees of freedom = removing entropy



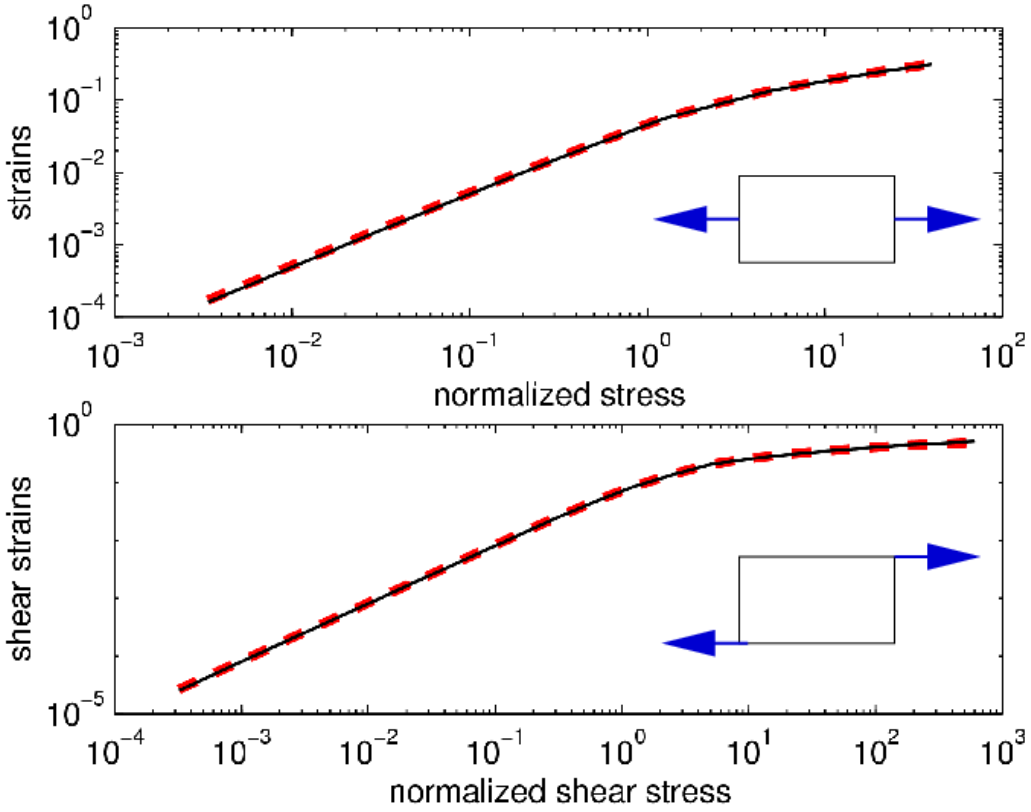
Derivatives of entropy may be wrong

e.g. heat capacity, thermal expansion

How the model works: static properties

2D system

original lattice with 6975 atoms & renormalized lattice with 1510 nodes



tensile strain/stress
------- original
- - - renormalized
4% accuracy

shear strain/stress
------- original
- - - renormalized
5% accuracy

How the model works: *thermal properties*

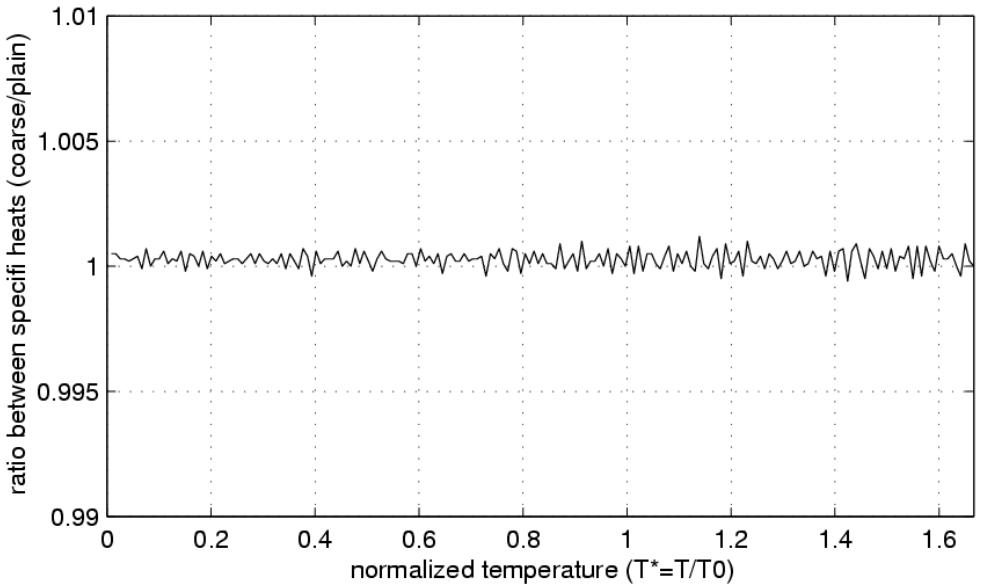
Homogeneous system (h):

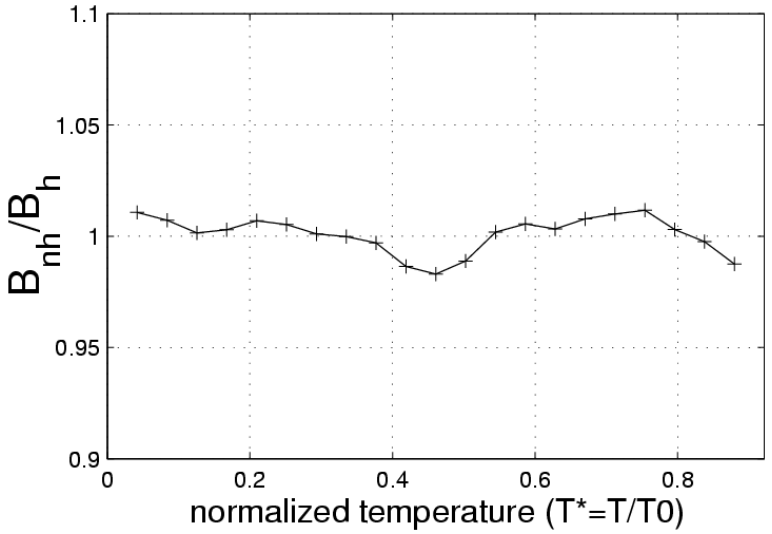
Specific heat C_V due by lattice $C_{Vh} = \partial_T E_h(T)|_{V,N}$.

Non-homogeneous system (nh):

specific heat C_V due by lattice: $C'_{Vnh} = \partial_T E_{nh}(T)|_{V,N}$,

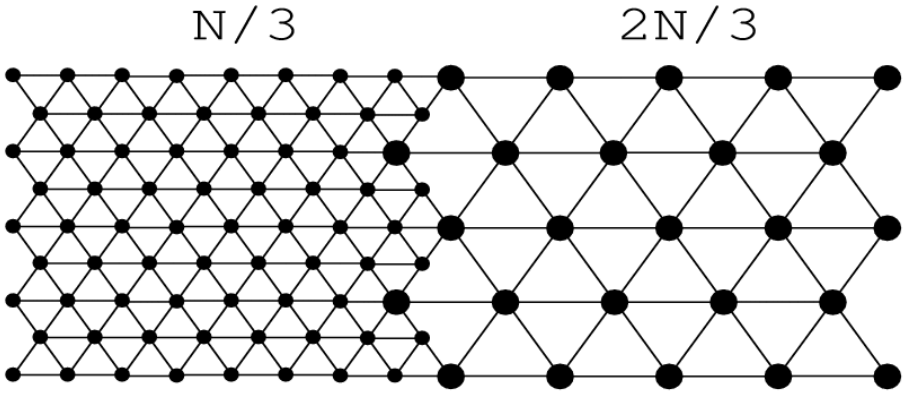
excess free energy contribution $C''_{Vnh} = T\,\partial_T S(T)|_{V,N}$,



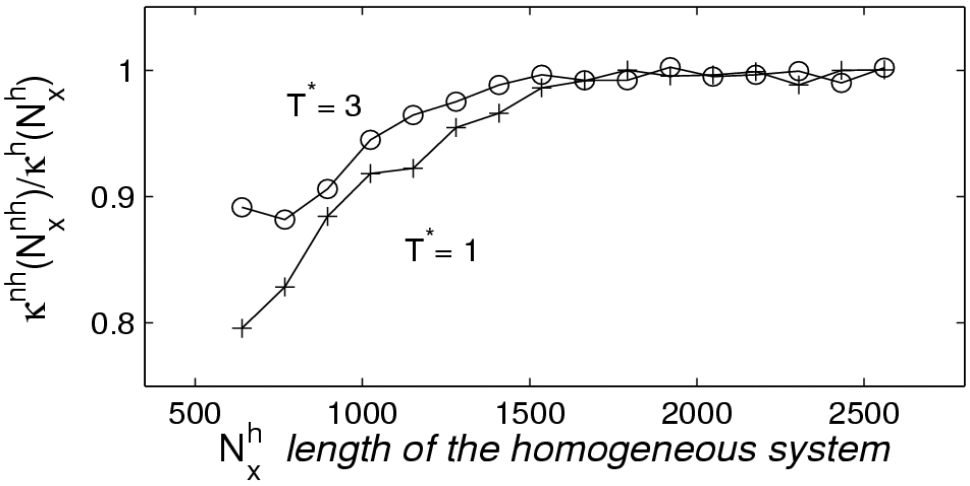


Heat conduction: finite size effect

Run 2D systems with two regions and one interface

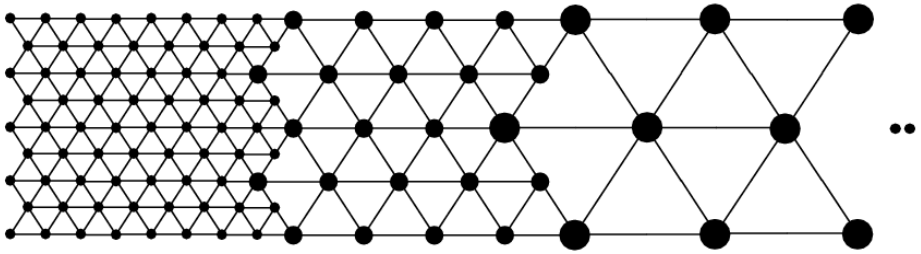


Ratio $\kappa_{nh}(N_{nh})/\kappa_h(N_h)$ vs length.
Regions with nodes>500 give *"accurate"* results.



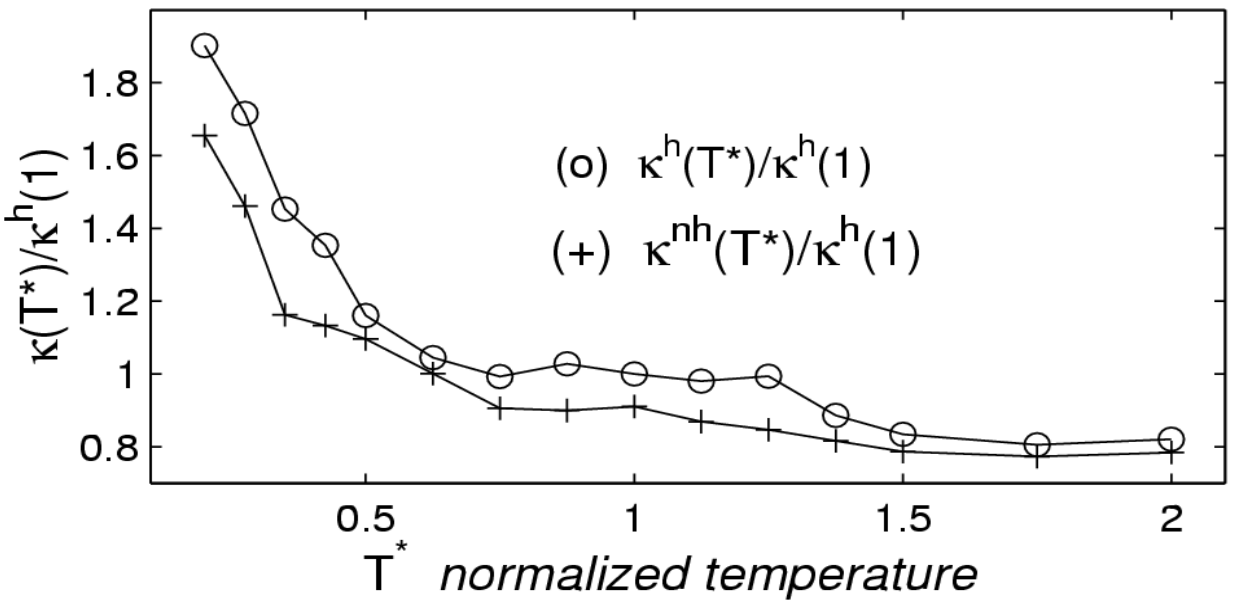
Heat conduction: large system

Compare 2D systems
- homogeneous with $3.5 \cdot 10^5$ atoms
- coarse grained with $6.3 \cdot 10^4$ nodes



- Works better at ***high temperature***
- **15%** underestimation
- interface scattering

homogeneous (o), coarse grained (+)



"constant pressure" properties

- Thermal expansion α_p and specific heat C_p depend on the free energy.

- Models with *"approximated"* free energy have *"approximated"* thermal expansion $\Rightarrow$ build up large internal strains upon changing temperature !

Accelerating time (without Einstein's help)

Do I need to explain why you want faster MD ?

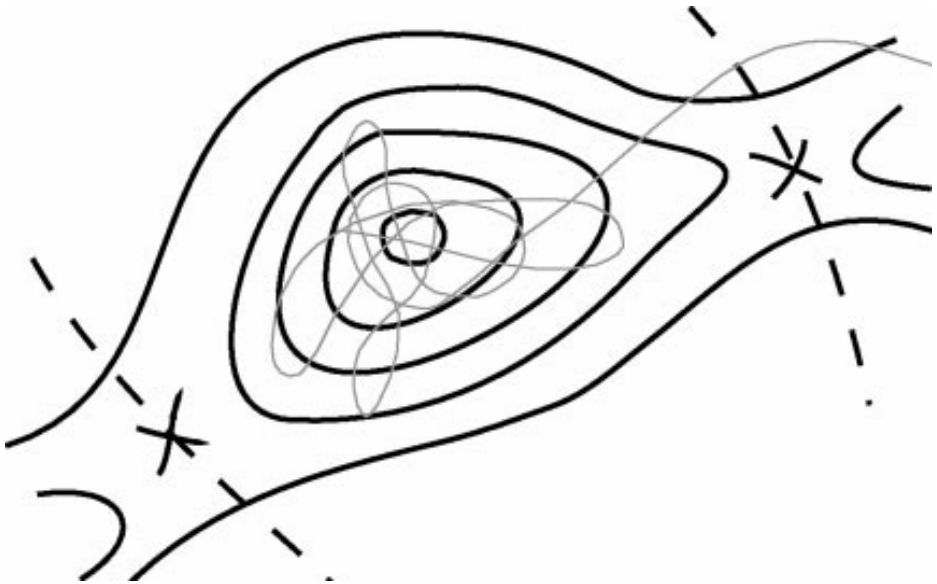
Photo of Star Trek character "Scotty" removed for copyright reasons.

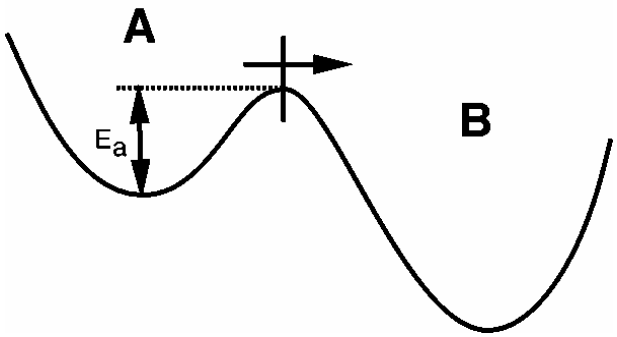
- MD is nano seconds
- For systems where only the equilibrium behavior is of interest, use coarse methods or sampling methods (lattice models, Monte Carlo etc.)
- But no methods available for dynamics in the time regime of μs and greater.

We need more power, Scotty

A.F. Voter, F. Montalenti and T.C. Germann, Extending the Time Scale in Atomistic Simulations of Materials, *Ann. Rev. Mater. Res.,* **32**:321-46 (2002)

The Problem





Well defined minima in phase space with infrequent changes between minima define “infrequent event systems”

$\tau_{rxn} >> \tau_{corr}$

Source: A. F. Voter, F. Montalenti and T. C. Germann. "Extending the Time Scale in Atomistic Simulations of Materials." *Ann. Rev. Mater. Res.,* **32**:321-46 (2002).

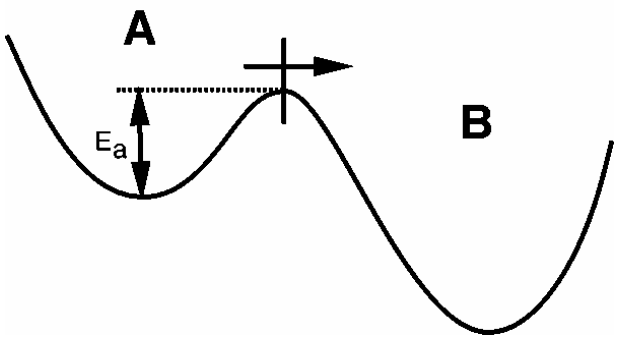
Different Approaches within Molecular Dynamics to Study Infrequent Event Systems

Parallel Replica Dynamics

Hyperdynamics

Temperature Accelerated Dynamics (TAD)

A quick review of Transition State Theory (simplified)



Crossing rate

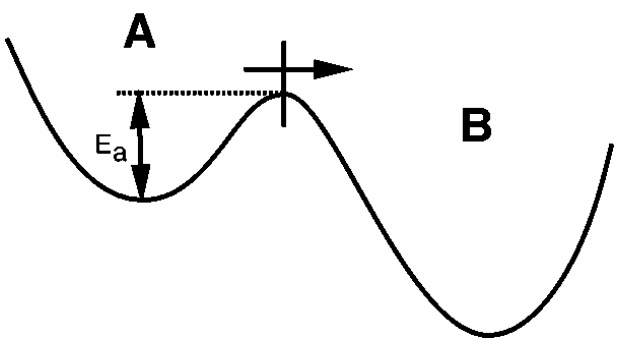
$$k = \nu \exp\left(\frac{-E_a}{k_B T}\right)$$

Source: A. F. Voter, F. Montalenti and T. C. Germann. "Extending the Time Scale in Atomistic Simulations of Materials." *Ann. Rev. Mater. Res.* 32:321-46 (2002).

If one knew all the basins (local minima), and all the transition rates between them, one can do Kinetic Monte Carlo simulation (see later)

Accelerated MD schemes are more appropriate when one can not predefine the transition mechanisms

A quick review of Transition State Theory (simplified)



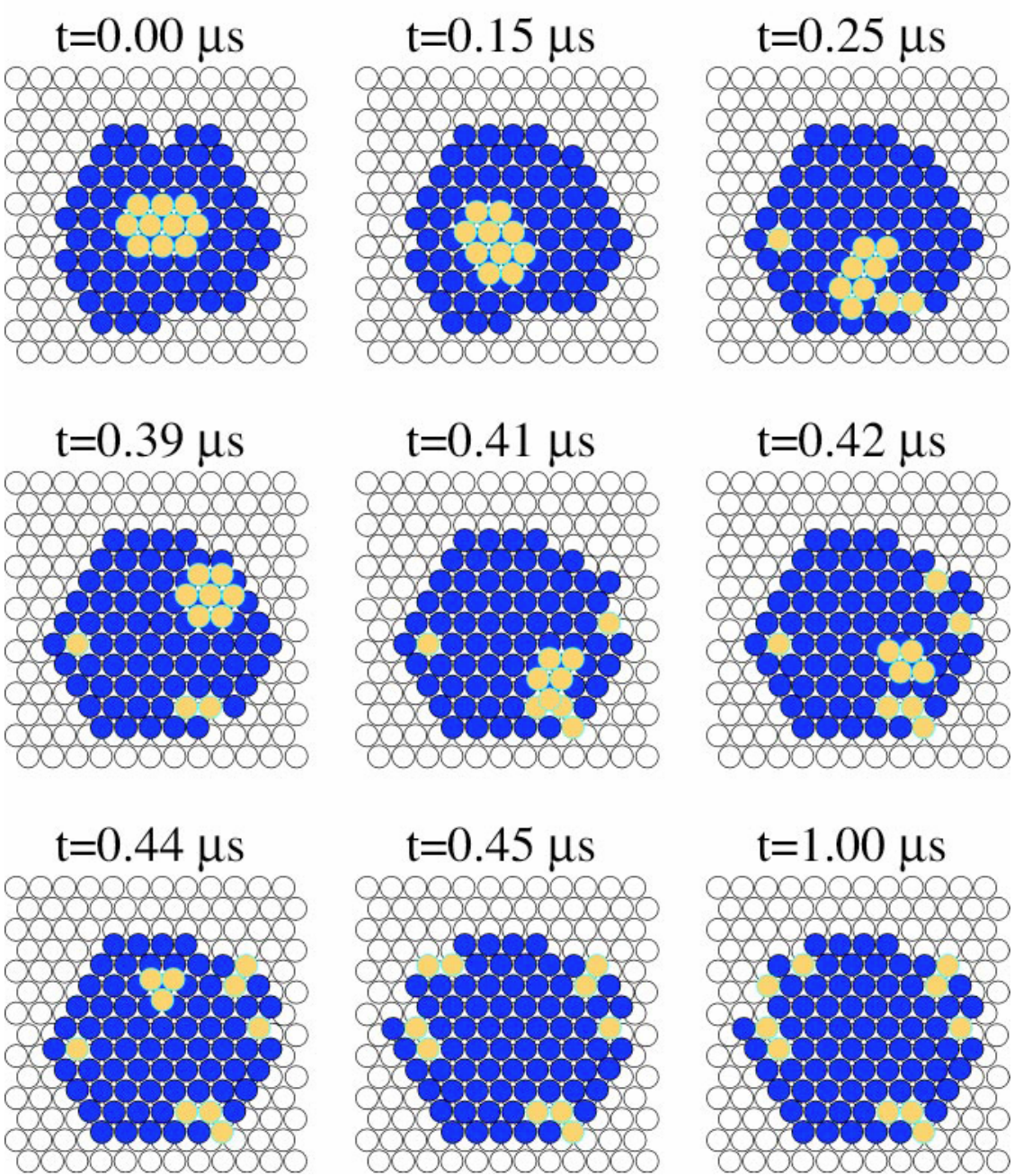
Crossing rate

$$k = \nu \exp\left(\frac{-E_a}{k_B T}\right)$$

Source: A. F. Voter, F. Montalenti and T. C. Germann. "Extending the Time Scale in Atomistic Simulations of Materials." *Ann. Rev. Mater. Res.* 32:321-46 (2002).

If one knew all the basins (local minima), and all the transition rates between them, one can do Kinetic Monte Carlo simulation (see later)

Accelerated MD schemes are more appropriate when one can not predefine the transition mechanisms



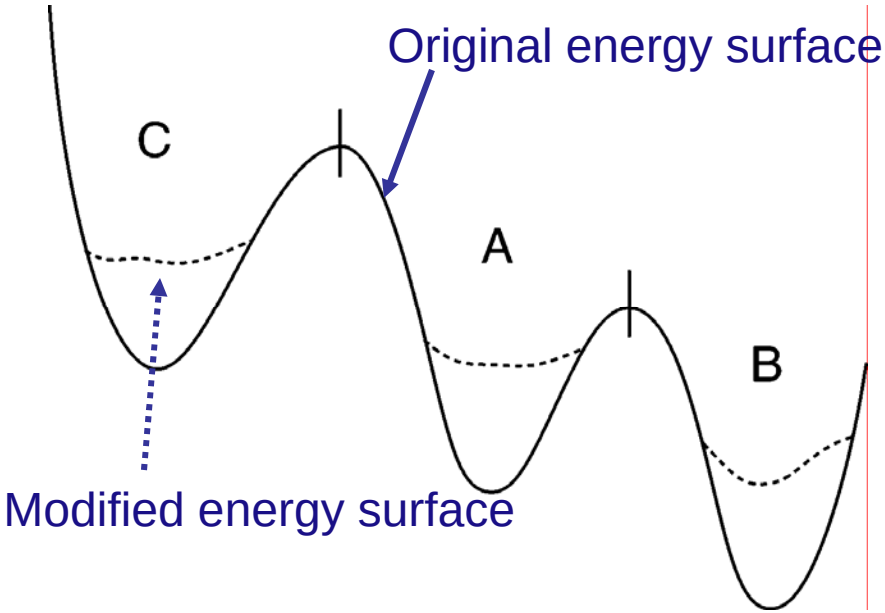
Example of Parallel Replica Simulation: Island on Island on Ag(111) at T=400K

5 days on 32 1GhZ Pentium III (empirical potentials)

Source: A. F. Voter, F. Montalenti and T. C. Germann. "Extending the Time Scale in Atomistic Simulations of Materials." *Ann. Rev. Mater. Res.* 32:321-46 (2002).

Hyperdynamics (briefly):

Elevate the potential wells to make system transition out faster



"Boost" Potential

$$t_{hyper} = \sum_{j=1}^{n} \Delta t_{MD} \exp\left[\frac{\Delta V(r(t_j))}{kT}\right]$$

MD time step

Source: A. F. Voter, F. Montalenti and T. C. Germann. "Extending the Time Scale in Atomistic Simulations of Materials." *Ann. Rev. Mater. Res.* 32:321-46 (2002).

Method is related to Importance Sampling in Monte Carlo (e.g. sample with a bias potential, but correct probabilities (in this case time to reach a state)

Smart choice of Boost potential is key -> Considerable work in this area

Temperature-Accelerated Dynamics (TAD)

Higher temperature gives faster processes. But, one can not simply do MD at higher temperature, since high T and low T may have different processes and equilibrium states

IDEA of TAD

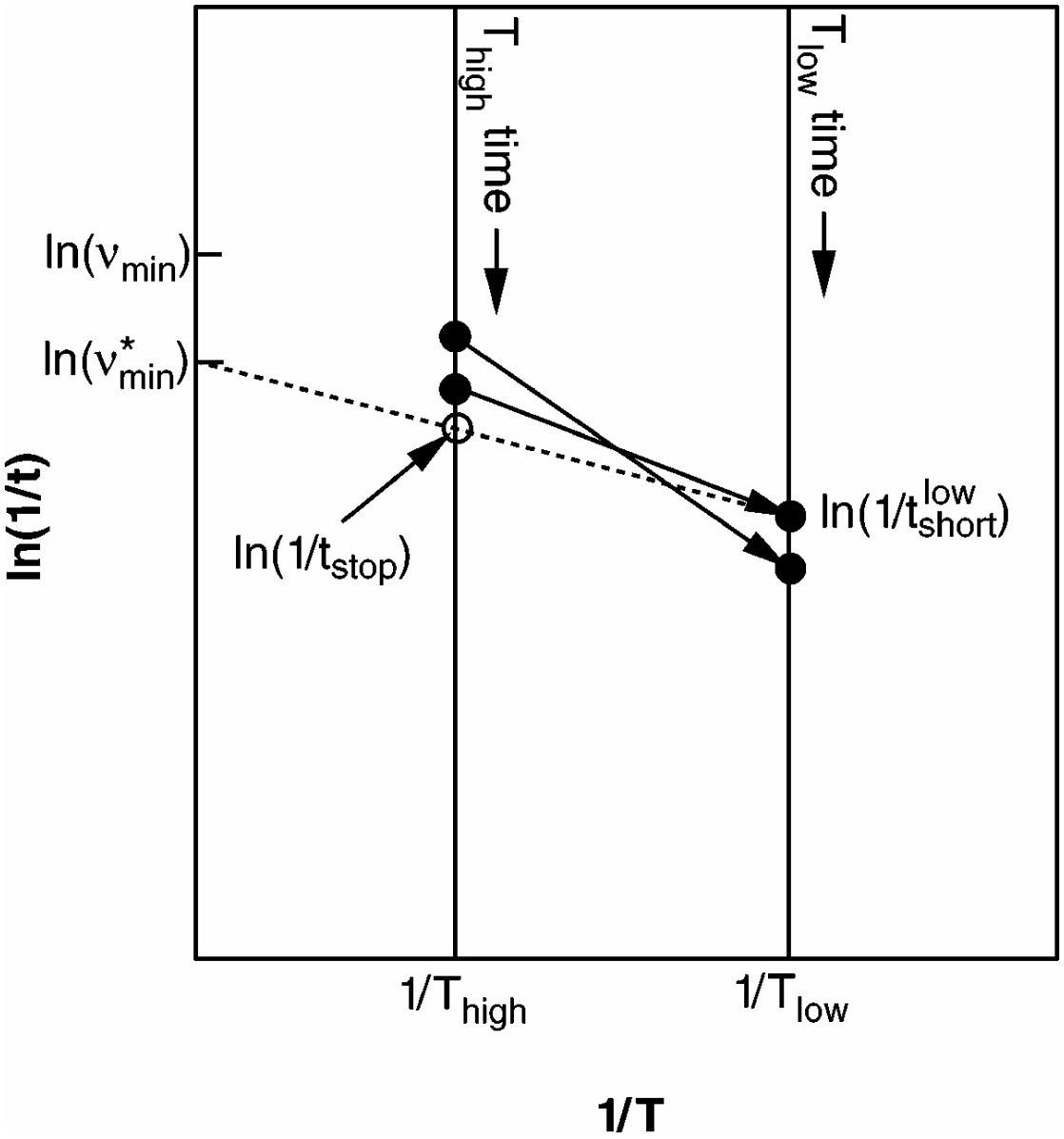
Use Higher temperature to find (sample) possible transitions, but execute them with their correct low-T probability

PROCEDURE

- Run at high-T until transition occurs
- Find E_a for the transition
- Reverse transition and run again at high-T

Leads to a catalogue of transitions and their activation barriers

How to extrapolate to low-T ?



Assume Arrhenius behavior

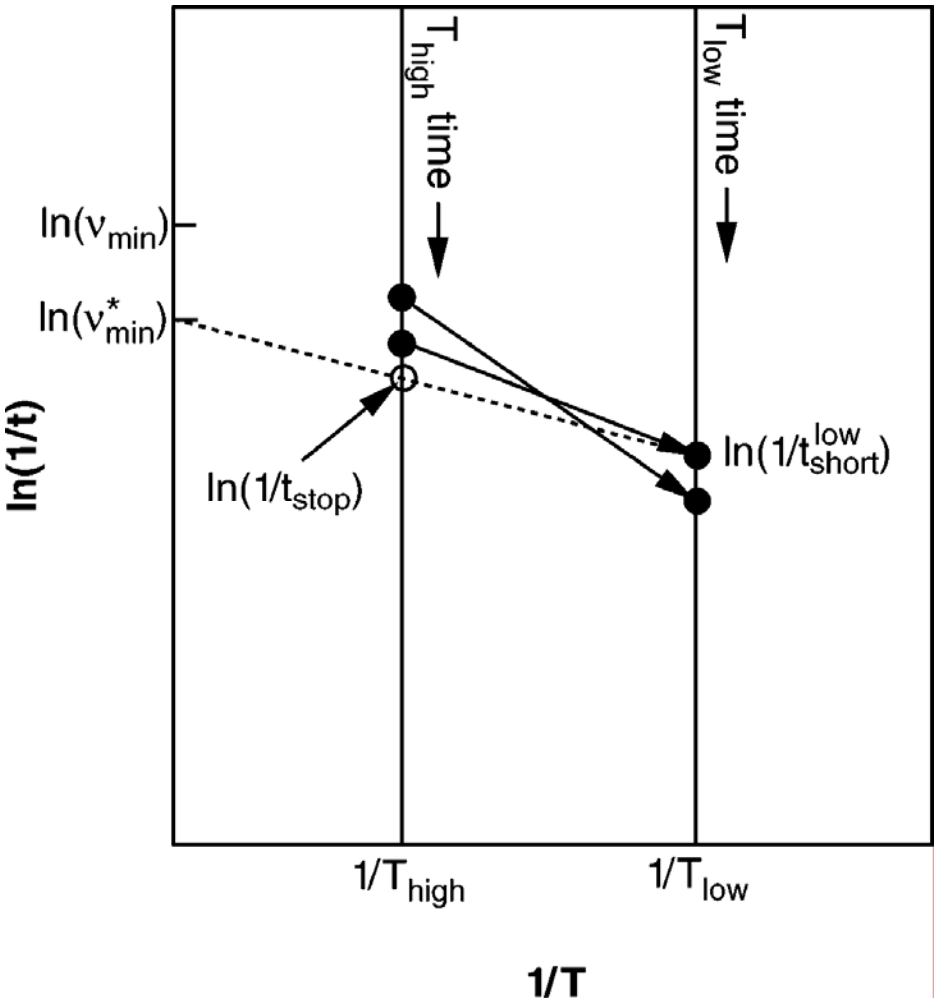
$$k = \nu \exp\left(\frac{-E_a}{k_B T}\right)$$

$$\ln(1/t) = \ln(k) = \ln(\nu) - \frac{E_a}{k_B T}$$

Note: Different processes may occur in different order at high and low T due to the different E_a

Source: A. F. Voter, F. Montalenti and T. C. Germann. "Extending the Time Scale in Atomistic Simulations of Materials." *Ann. Rev. Mater. Res.* 32:321-46 (2002).

Approximations of the method

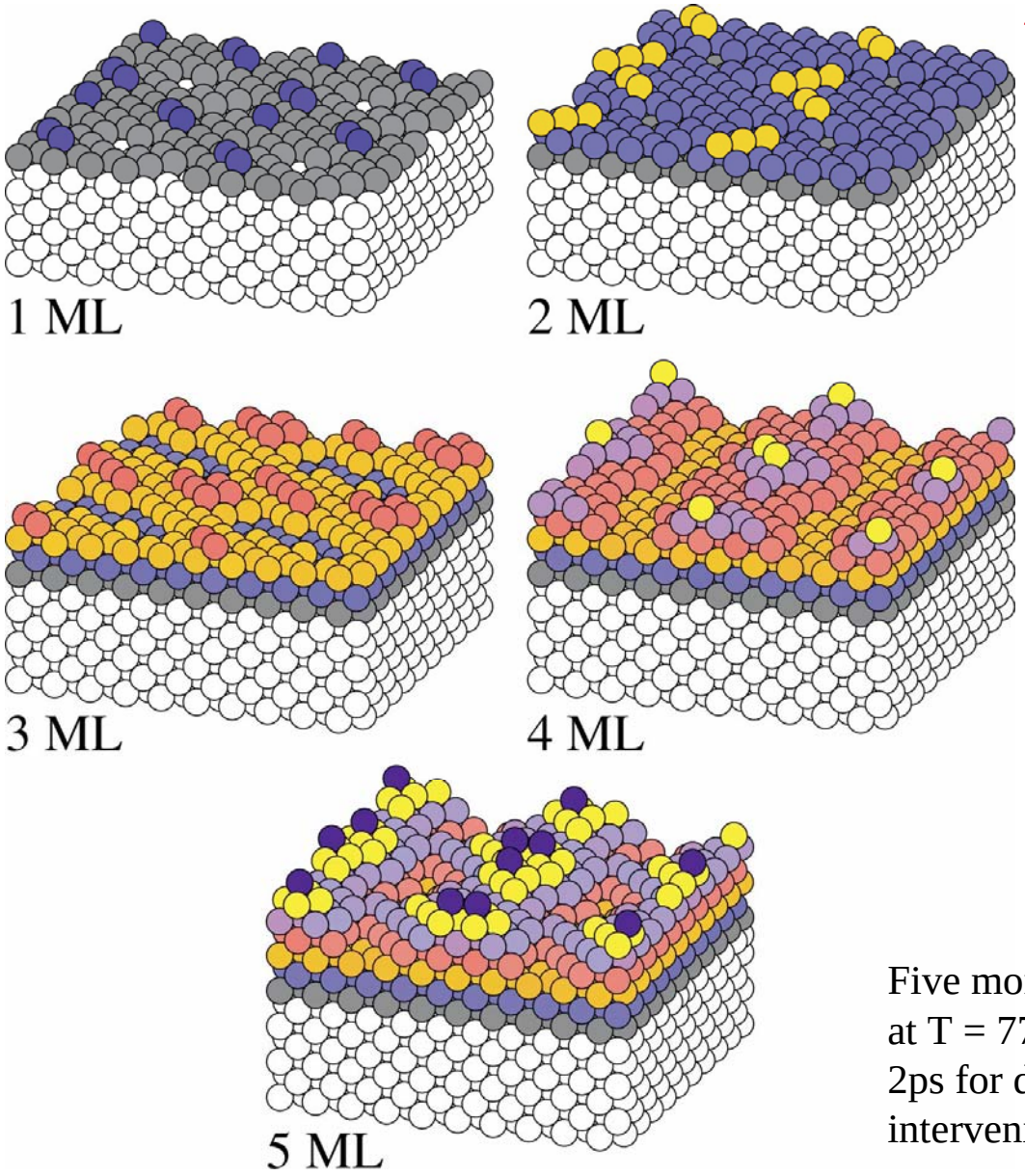


Harmonic TST. Assumes that pre-exponential factor ν is constant.

Need to make sure that have found at high T, mechanism that has highest rate at low T

Source: A. F. Voter, F. Montalenti and T. C. Germann. "Extending the Time Scale in Atomistic Simulations of Materials." *Ann. Rev. Mater. Res.* 32:321-46 (2002).

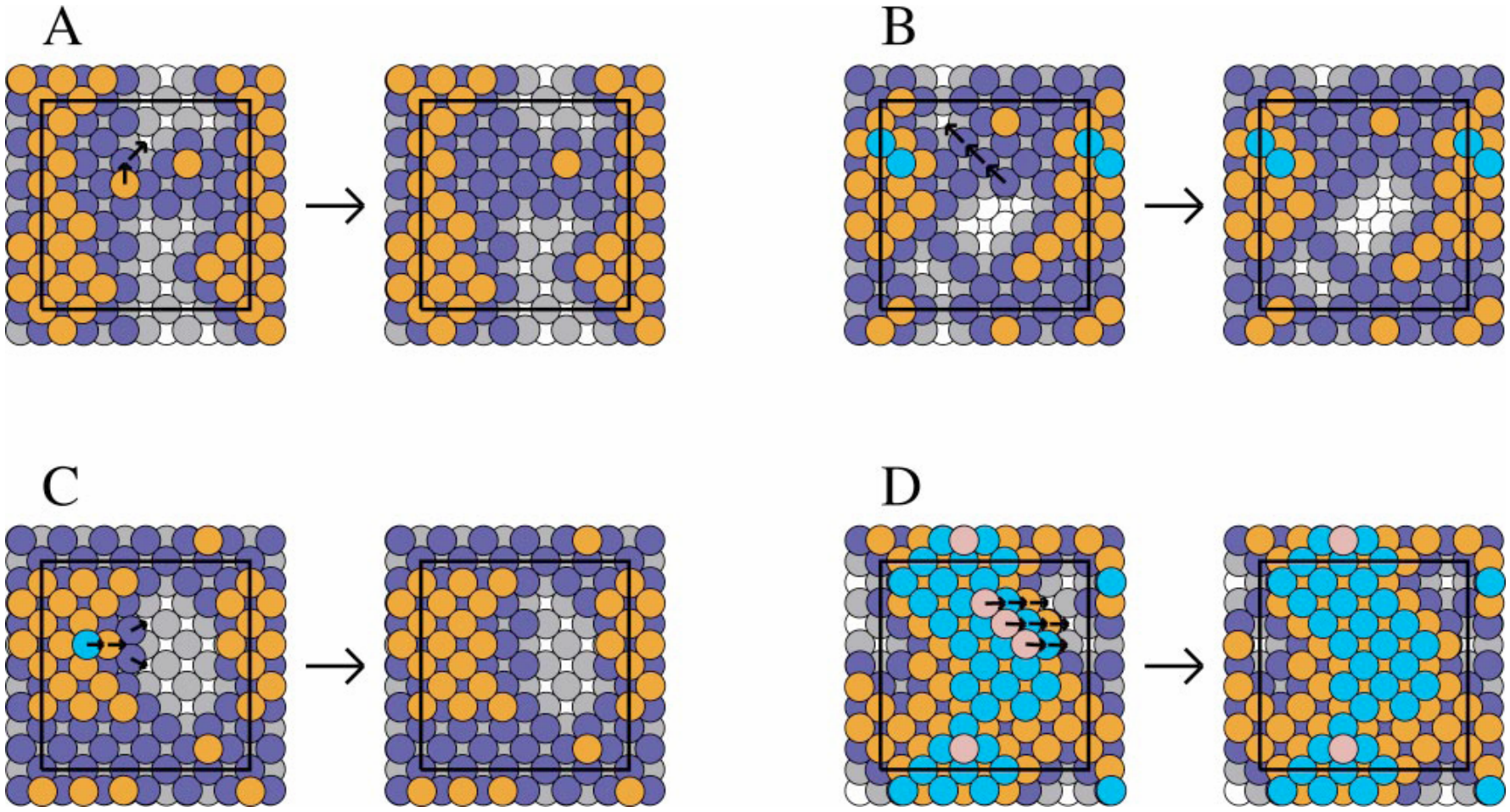
Application of TAD: Cu on Cu deposition



Five monolayer deposition of Cu onto Cu(000) at T = 77K and 0.067 ML/s. Direct MD for 2ps for deposition, with about 0.3s of intervening time with TAD

Source: A. F. Voter, F. Montalenti and T. C. Germann. "Extending the Time Scale in Atomistic Simulations of Materials." *Ann. Rev. Mater. Res.* 32:321-46 (2002).

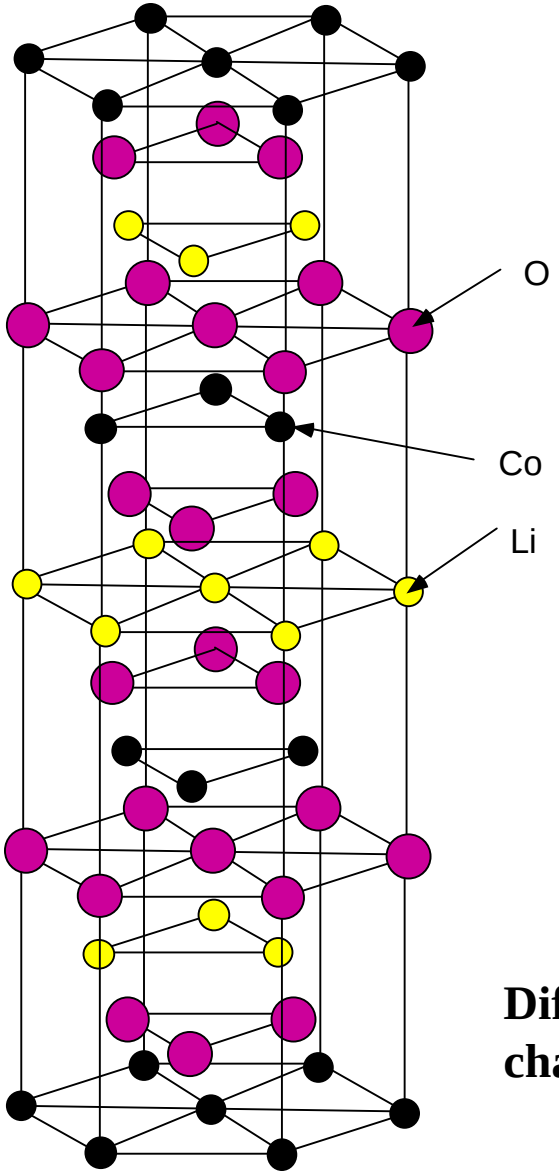
Some “events” during the simulation

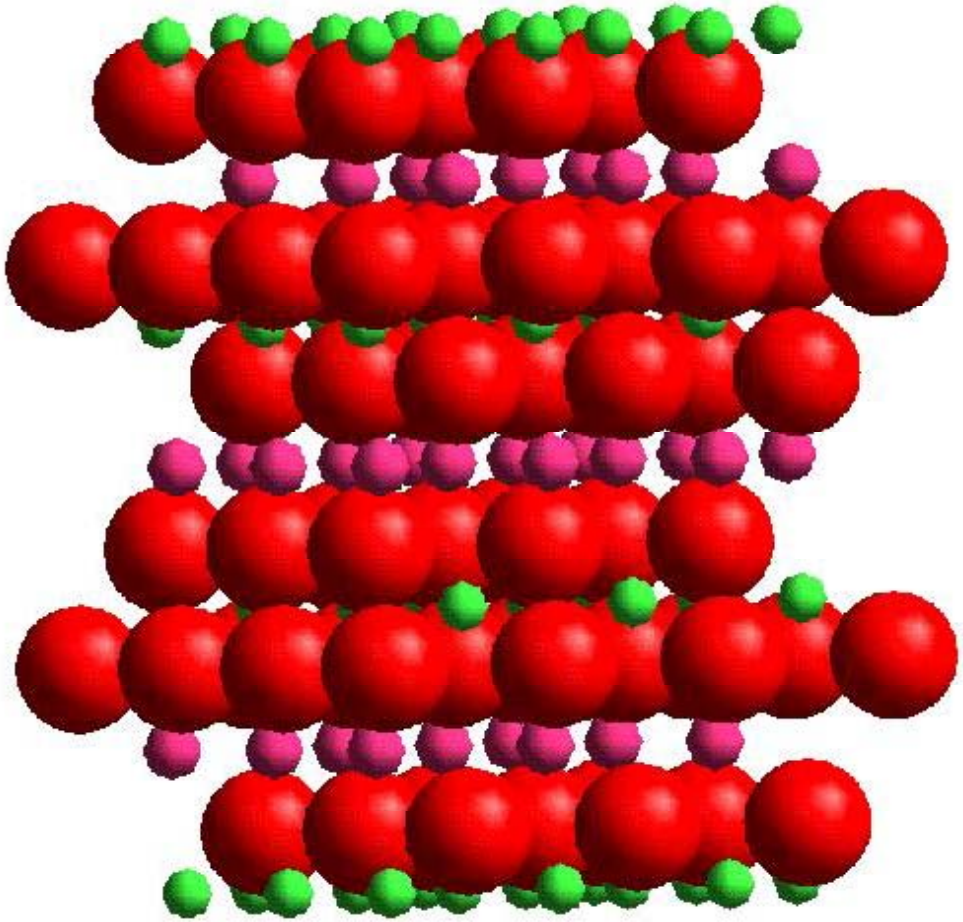


Source: A. F. Voter, F. Montalenti and T. C. Germann. "Extending the Time Scale in Atomistic Simulations of Materials." *Ann. Rev. Mater. Res.* 32:321-46 (2002).

Kinetic Monte Carlo

Example 1: Diffusion in Li_xCoO_2





Diffusivity of Li is key property. Number of vacancies changes as Li is removed.

Dilute Diffusion Theory

From random walk theory

$$D = \nu a^2 f \exp\left(\frac{-\Delta E_a}{kT}\right)$$

When vacancy concentration is high

Activation energy depends on environment

Motion is not random walk (correlated jumping)

f significantly deviates from 1

Need to simulate diffusion

$$D_{self} = \frac{\langle \vec{r}^2 \rangle}{4dt}$$

$$D_{chem} = F\, D_{self}$$

Thermodynamic Factor

Strategy

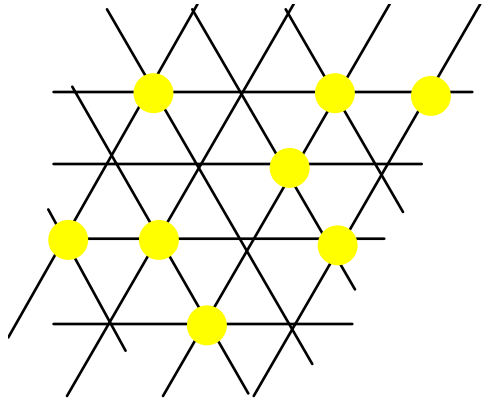
Thermodynamic info

Build lattice model on Li/vacancy sites

Calculate energy of various Li/vacancy arrangements

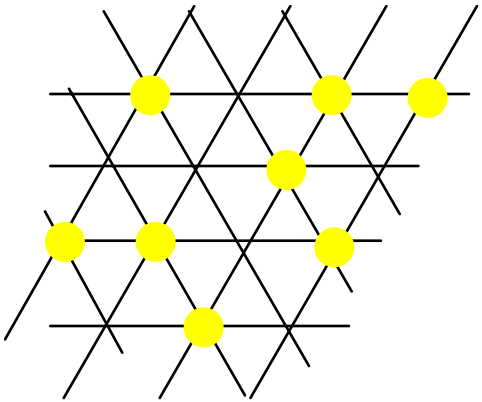
Build Cluster Expansion (Lattice Model Hamiltonian)

Monte Carlo simulation + free energy integration



Graph removed for copyright reasons.

Finite Temperature Configurational Disorder



Parameterize Energy in terms of occupation of lithium sites

Energy(system) = f(lithium site occupation)

$$H(\{\sigma\}) = V_0 + V_1 \sum_i \sigma_i + \frac{1}{2}\sum_{i,j} V_{i,j}\sigma_i\sigma_j + \frac{1}{6}\sum_{i,j,k} V_{i,j,k}\sigma_i\sigma_j\sigma_k + \frac{1}{24}\sum_{i,j,k,l} V_{i,j,k,l}\sigma_i\sigma_j\sigma_k\sigma_l \ \ldots$$

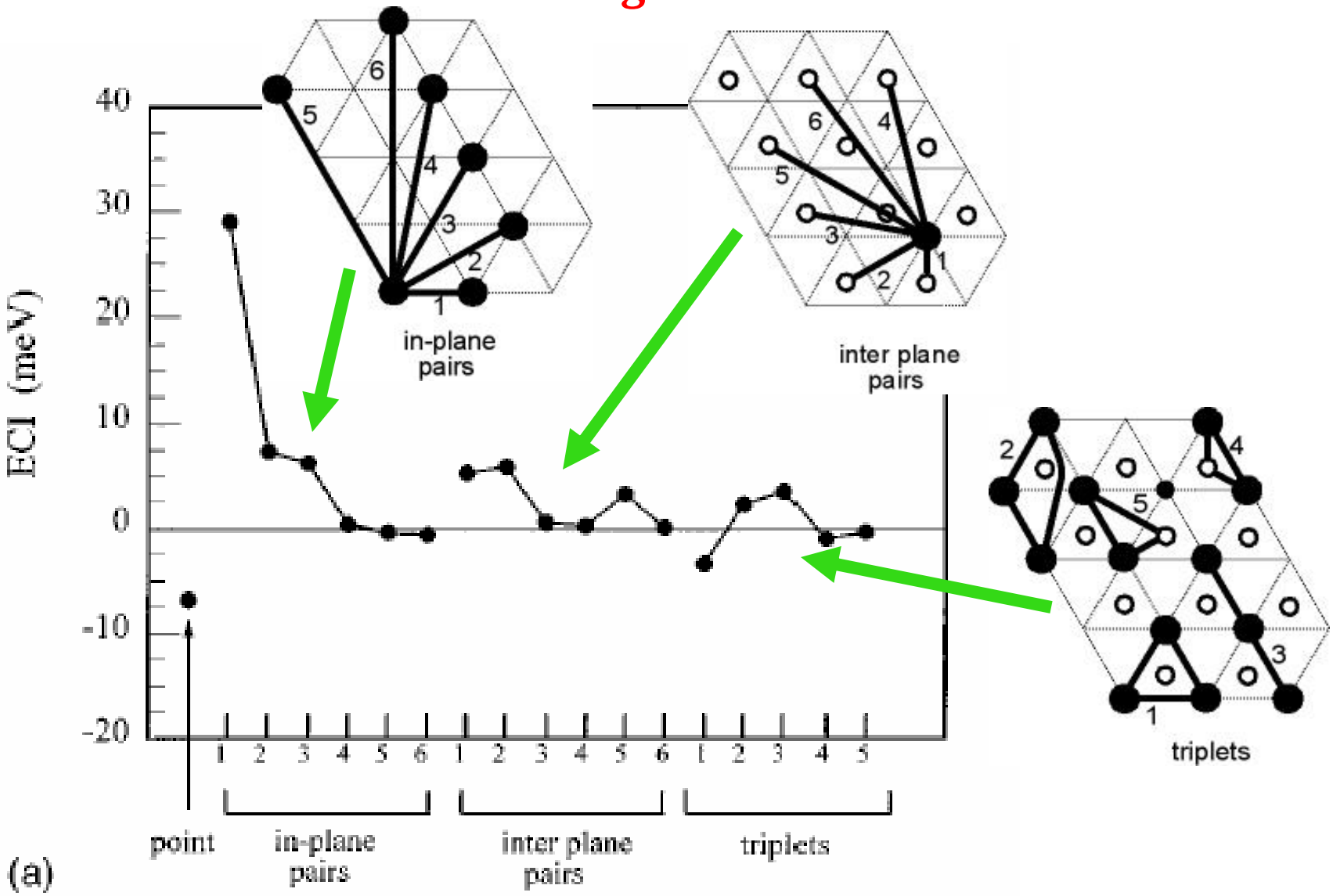
Cluster Expansion

Coefficients **V** -> **Effective Cluster Interactions**

Polynomials in s_i -> **Cluster Functions**

Monte Carlo Simulation → **Free energy and phase diagrams**

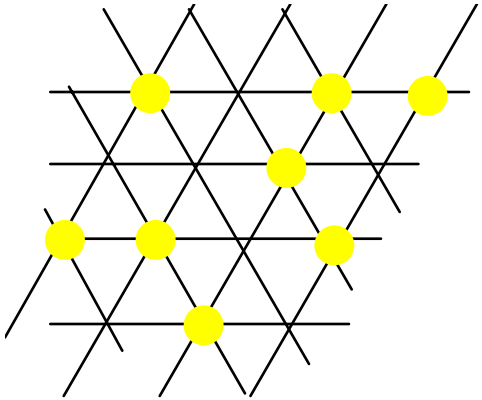
Interactions obtained from Energy Calculations of about 60 configurations



Strategy (continued)

Kinetic Model → **Need model in which $\langle r^2 \rangle$ can be sampled**

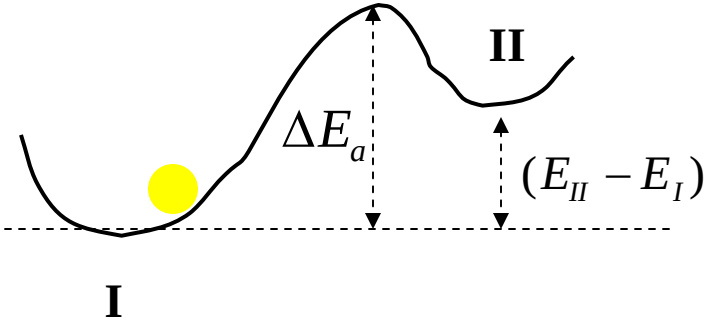
Kinetic Monte Carlo: Monte Carlo perturbations "imitate" real atom hops (diffusive behavior)



$$P_{forward} = \nu \exp\left[\frac{-\Delta E_a}{kT}\right]$$

$$= \nu \exp\left[\frac{-\Delta E_a'}{kT}\right] \exp\left[-\frac{(E_{II} - E_I)}{kT}\right]$$

$$P_{back} = \nu \exp\left[\frac{-\Delta E_a'}{kT}\right]$$



After scaling away the common factor

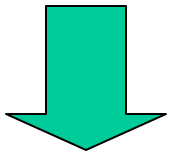
$$P_{forward} = \exp\left[-\frac{(E_{II} - E_I)}{kT}\right]$$ **Metropolis**

$$P_{back} = 1$$

Kinetic Monte Carlo

Know locally stable states of a system

Know kinetic mechanism to move between different states (e.g. hopping of atoms along a particular trajectory)



Perform Monte Carlo simulation over possible states with transition rates similar to the “real” transition rates

Methods to find transition states:

- **Accelerated MD methods**
- **Elastic band**
- **others**

Strategy (continued)

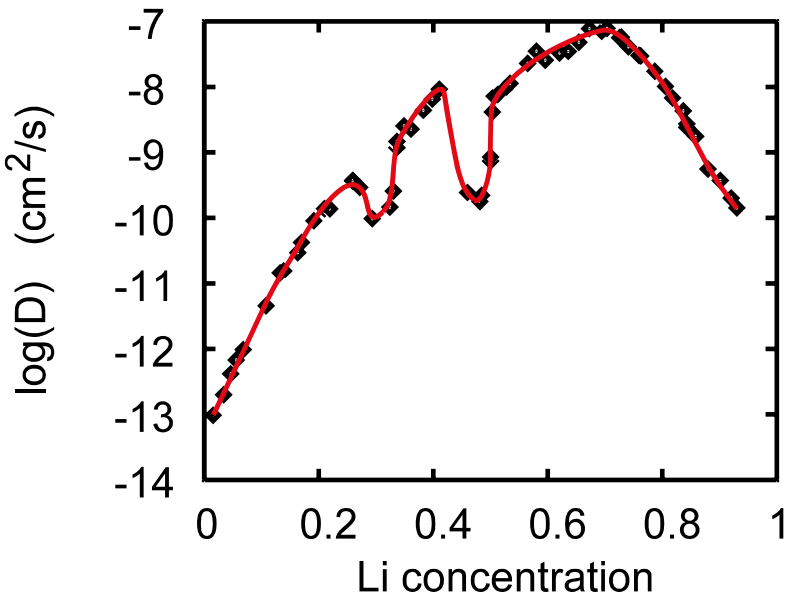
Perform Monte Carlo simulation with nearest neighbor Li-vacancy interchanges

Track RMS displacement of each particle

$$D_{self} = \frac{\langle \vec{r}^{\,2} \rangle}{4dt}$$

Average over all particles

Diffusion Constant



Units of time

1MCS is one hop attempt

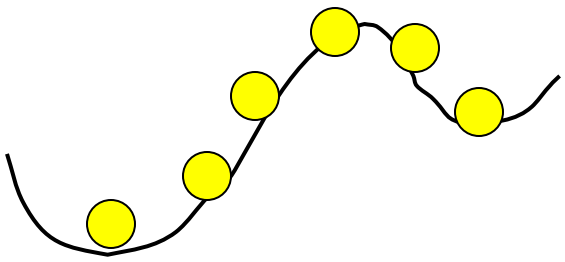
$$1MCS = \left(\nu \exp\left[\frac{-\Delta E_a{}'}{kT} \right] \right)^{-1}$$

Getting activation Barriers: The elastic band method

Sometimes activated state is high symmetry

If not, need to find the activated state

Elastic band method



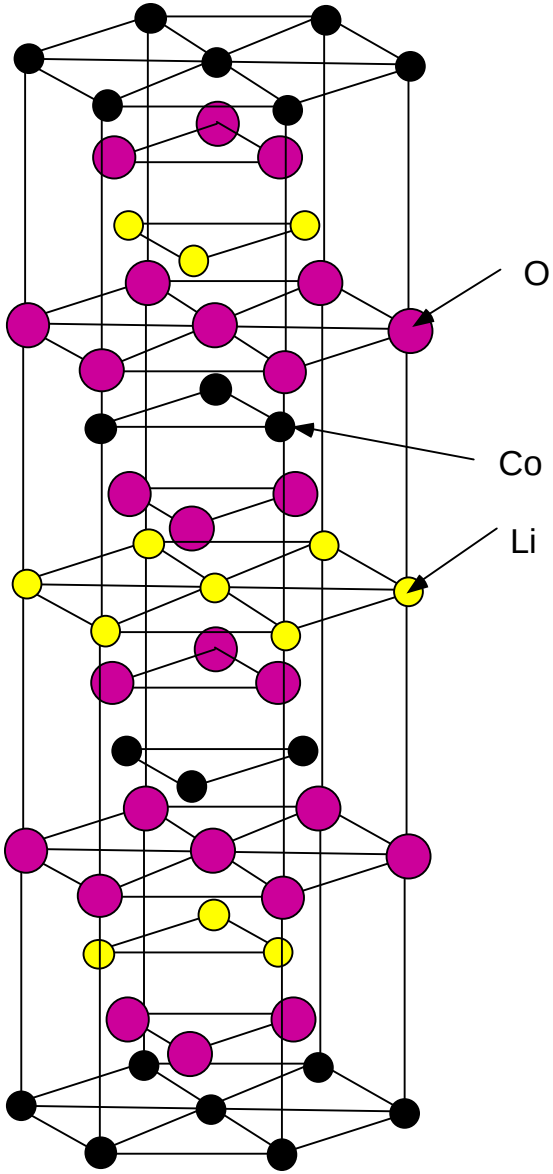
Construct n replica of system

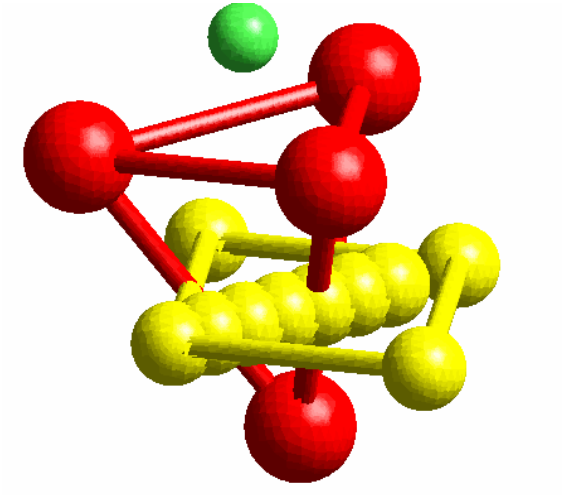
Position of replica is interpolated between initial and final state

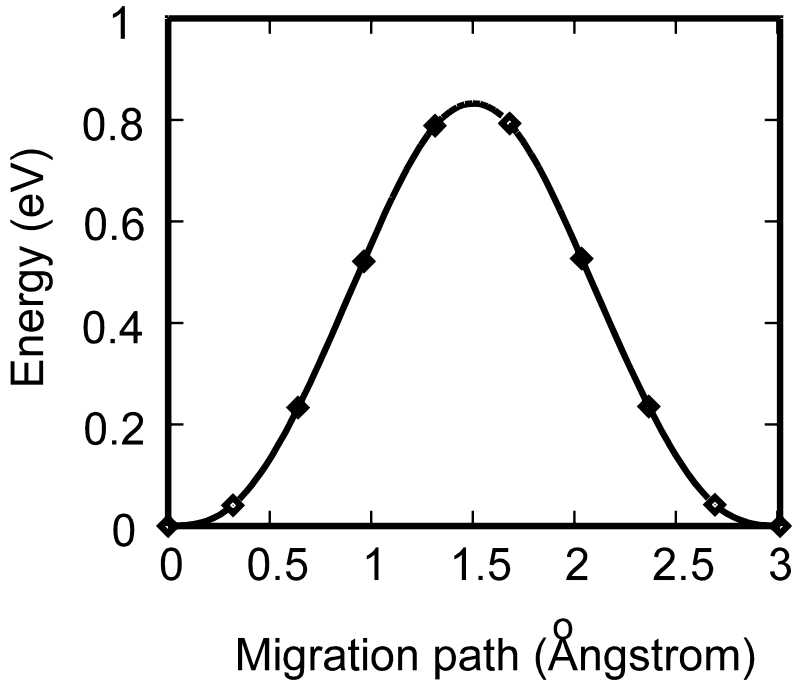
Trajectory is obtained by minimizing

$$\sum_{i=1}^{n} H_i + \sum_{i=2}^{n} k\,(\vec{r}_{i-1} - \vec{r}_i)^2$$

r_i is generalized coordinate vector

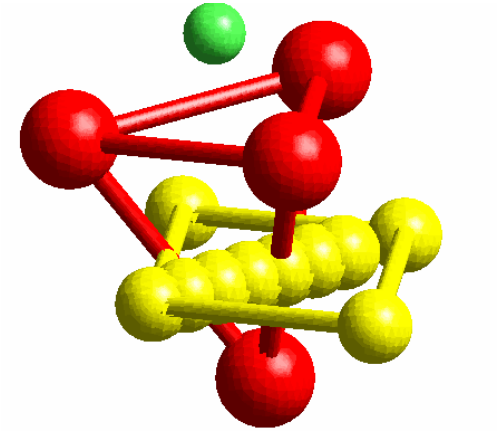

O
Co
Li

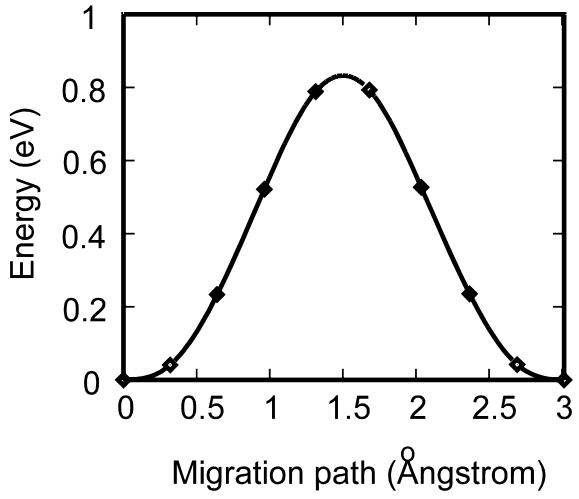


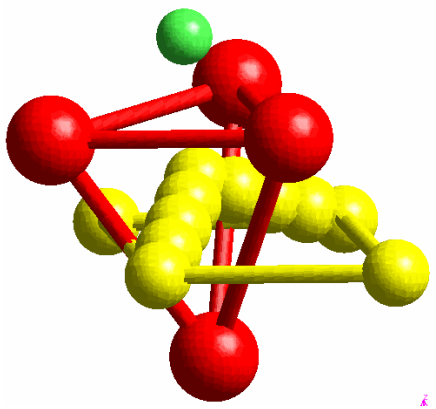

Energy (eV)
0
0.2
0.4
0.6
0.8
1
0
0.5
1
1.5
2
2.5
3
Migration path (Å)

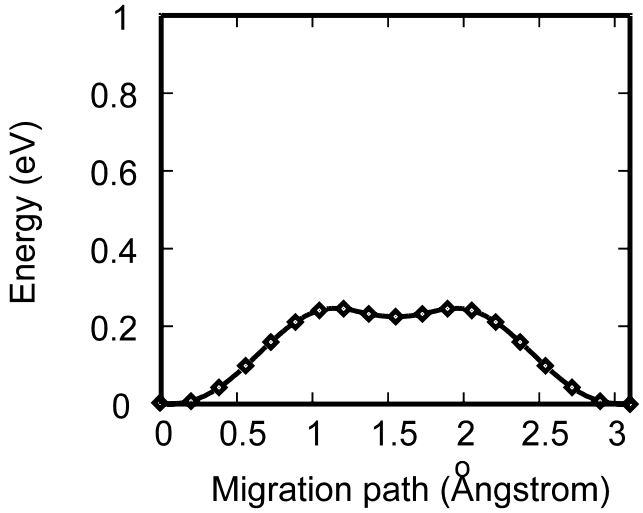
Complications

Multiple mechanisms





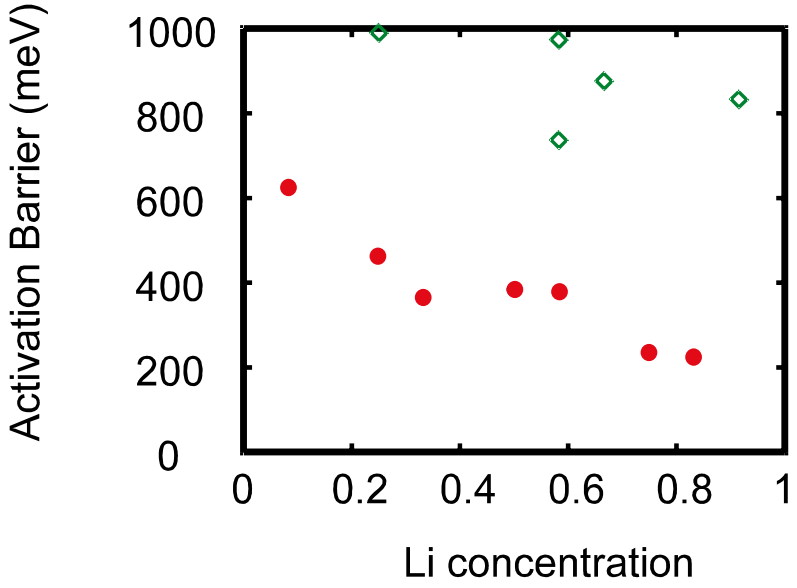




Can only scale the lowest activation barrier away !

Complications

Environment dependent barrier



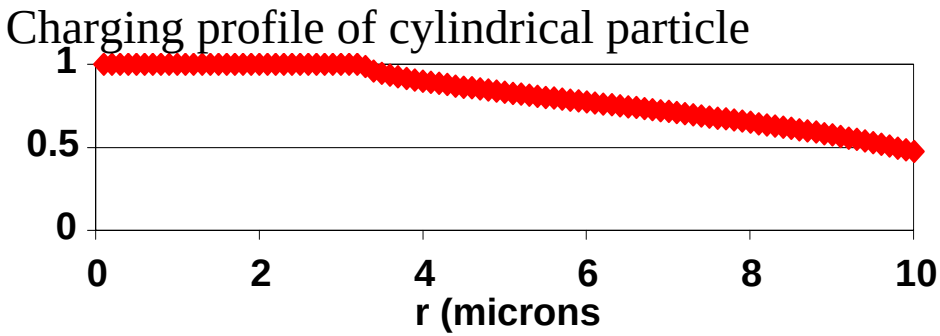
Need to parameterize dependence

e.g. use cluster function formalism

When finding and parameterizing barriers becomes too complicated, MD may be better solution (if timescale can be dealt with).

Use as input in continuum models

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right)$$



References

Quasi continuum method

R. Miller, E. B. Tadmor, R. Phillips, M. Ortiz, *Modeling and Simulation in Materials Science and Engineering* **6**, (1998) 607.

R. E. Miller, E. B. Tadmor, *Journal of Computer-Aided Materials Design* **9**, (2002) 203-239.

Dynamics

S. Curtarolo, G. Ceder, *Physical Review Letters* **8825**, (2002) 255504.

Accelerated MD

A. F. Voter, F. Montalenti, T. C. Germann, *Ann. Rev. Mater. Res.* **32**, (2002) 321-346.

Li_xCoO_2 application of Kinetic MC

A. Van der Ven, G. Ceder, M. Asta, P. D. Tepesch, *Physical Review B* **64**, (2001) 184307.