Solid-liquid interface free energies and structural phase transformations

Atomistic approaches in rare event systems

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Quantum and Atomistic Modeling of Materials Defects

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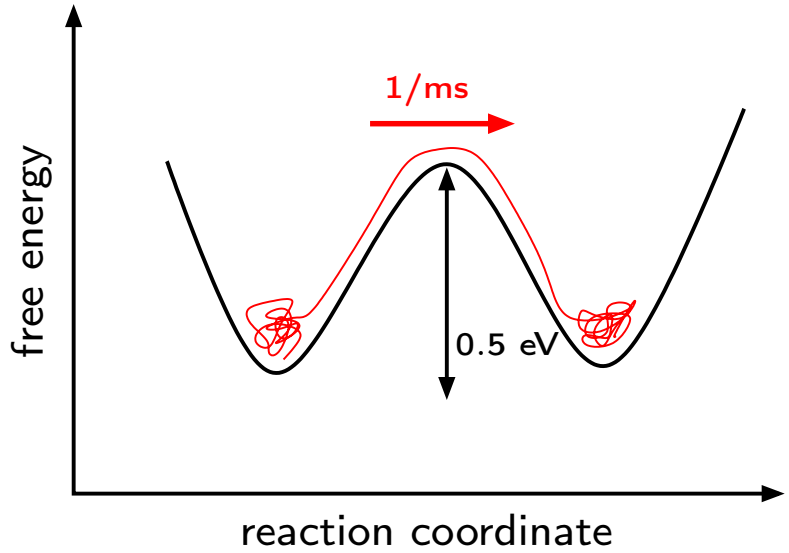
Phase transformations

characteristics

- matter of state: solid, liquid, gas, plasma
- solid-solid: diffusive, displacive
- order/disorder (composition, magnetic)

→ various mechanisms, large range of time scales
→ choose appropriate atomistic simulation techniques

Rare event problem

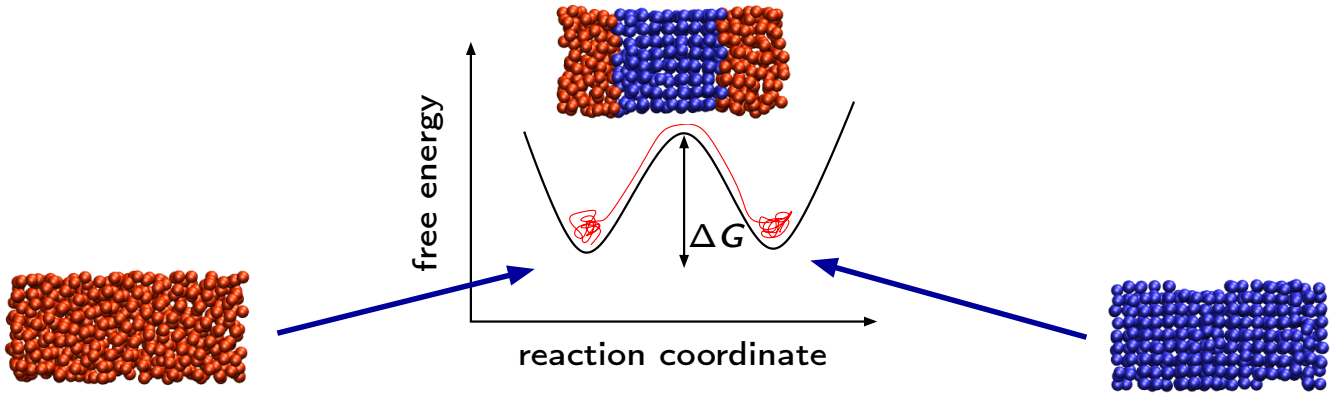


classical molecular dynamics

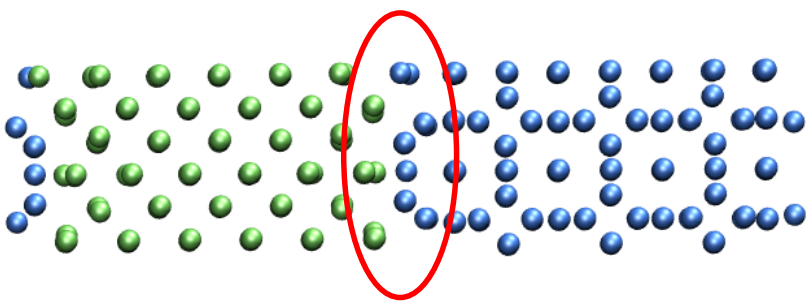
- Newtons equation of motion: $F = ma$
- integration time step Δt determined by fastest motion
- $\Delta t \approx 1$ fs → unfeasible

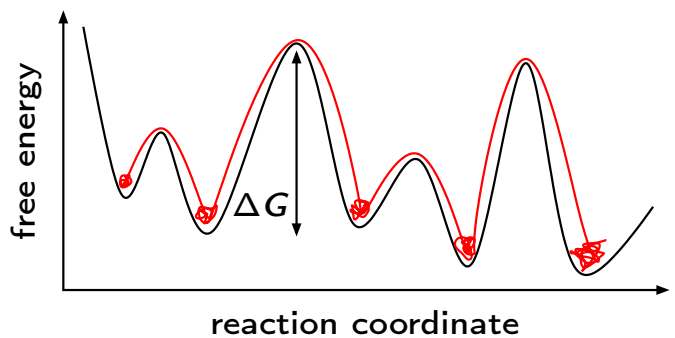
Two examples

solid-liquid interface free energy



structural rearrangement at solid-solid interfaces





Solid-liquid interface free energy

Solid-liquid interface energy

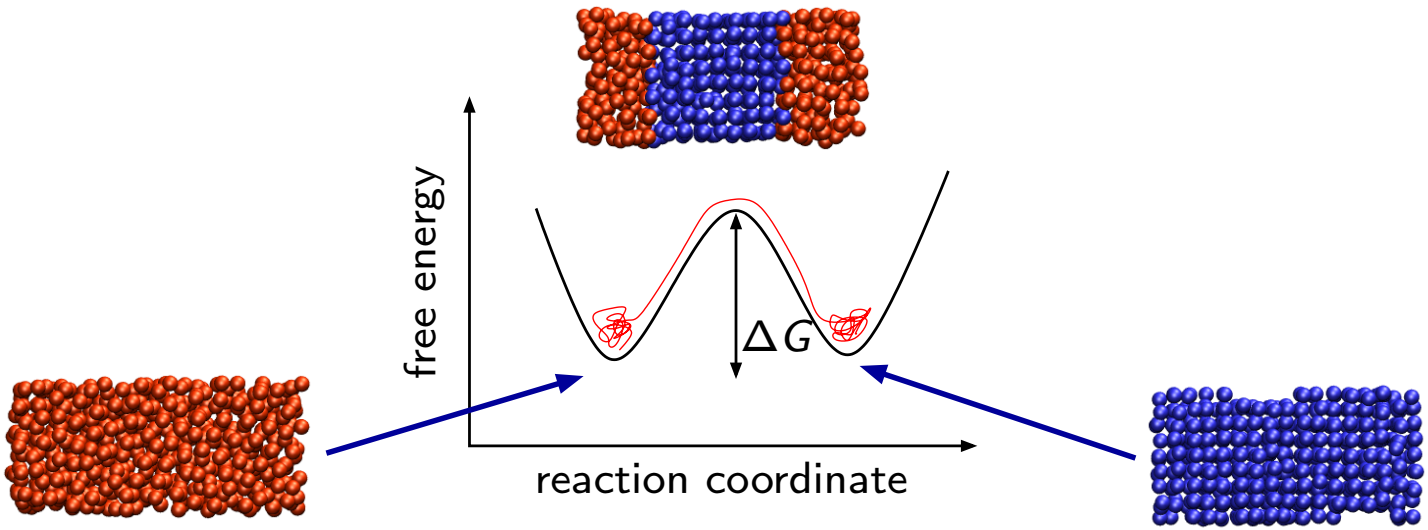
first-order phase transformation

- nucleation and growth
- controlled by interfacial properties → interfacial free energy

solid-liquid interfacial free energy

- capillary fluctuation method
- classical nucleation theory
- various 'cleaving' methods
- here: free energy surface

Solid-liquid interface energy – free energy surface



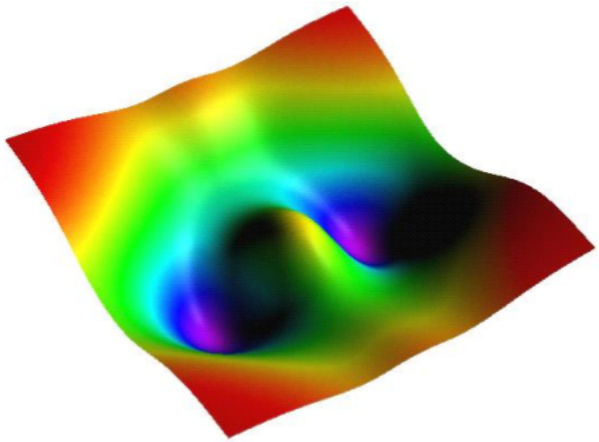
- at the melting T: $\mu_s(P, T_m) = \mu_l(P, T_m)$

$$\begin{aligned} G_{s|l}(P, T_m) &= \mu_{s|l}(P, T_m)N + G_{xs} \\ &= \mu_{s|l}(P, T_m)N + A\gamma_{sl} \end{aligned}$$

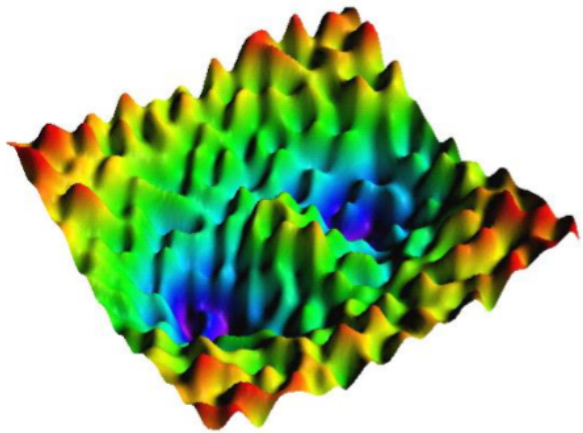
Angioletti-Uberti et al., PRB 81, 125416 (2010)

Sampling rare events

smooth PES



rough PES

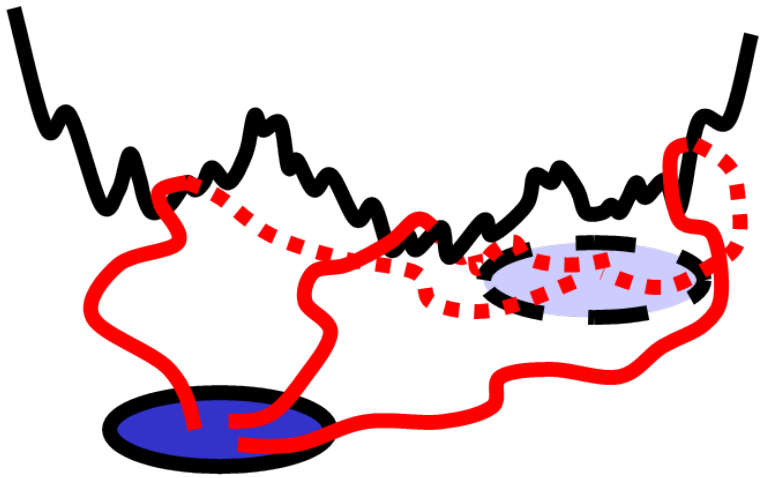


C. Dellago *et al.*, Adv. Chem. Phys. 123, 1 (2002)

rare event techniques

- accelerated molecular dynamics
- stochastic trajectory, kinetic Monte Carlo
- metadynamics, umbrella sampling ($\longrightarrow$ fix collective variable for sampling)
- transition path sampling

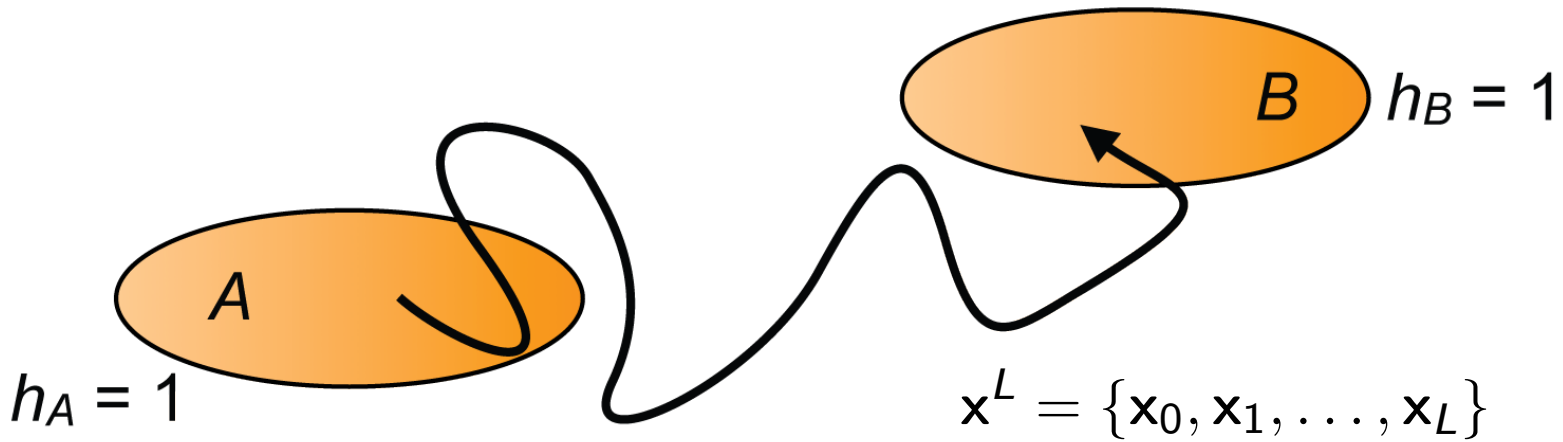
Transition path sampling



C. Dellago, P.G. Bolhuis, P.L. Geissler, Adv. Chem. Phys. **123**, 1 (2002).

- all trajectories that lead over barrier
- Monte Carlo sampling
- calculation of dynamical properties

Transition path ensemble



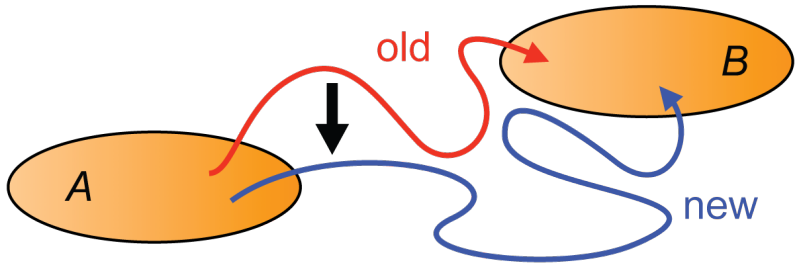
transition path ensemble

$$\mathcal{P}_{AB}[\mathbf{x}^L] = h_A(\mathbf{x}_0)\pi[\mathbf{x}^L]h_B(\mathbf{x}_L)/Z_{AB}$$

$$\pi[\mathbf{x}^L] = \rho(\mathbf{x}_0)\prod_{i=0}^{L-1} p(\mathbf{x}_i \to \mathbf{x}_{i+1}) \qquad Z_{AB} = \int \mathcal{D}\mathbf{x}^L h_A(\mathbf{x}_0)\pi[\mathbf{x}^L]h_B(\mathbf{x}_L)$$

Monte Carlo sampling of pathways

- create a new pathway from the old
  $\mathbf{x}^{L,(\mathrm{o})} \longrightarrow \mathbf{x}^{L,(\mathrm{n})}$



- accept new pathway according to **detailed balance**

$$\mathcal{P}_{AB}[\mathbf{x}^{L,(\mathrm{o})}]\,p[\mathbf{x}^{L,(\mathrm{o})} \longrightarrow \mathbf{x}^{L,(\mathrm{n})}] = \mathcal{P}_{AB}[\mathbf{x}^{L,(\mathrm{n})}]\,p[\mathbf{x}^{L,(\mathrm{n})} \longrightarrow \mathbf{x}^{L,(\mathrm{o})}]$$

$$p[\mathbf{x}^{L,(\mathrm{o})} \longrightarrow \mathbf{x}^{L,(\mathrm{n})}] = P_{\mathrm{gen}}[\mathbf{x}^{L,(\mathrm{o})} \longrightarrow \mathbf{x}^{L,(\mathrm{n})}] \times P_{\mathrm{acc}}[\mathbf{x}^{L,(\mathrm{o})} \longrightarrow \mathbf{x}^{L,(\mathrm{n})}]$$

- satisfy detailed balance with **Metropolis rule**

$$P_{\mathrm{acc}}[\mathbf{x}^{L,(\mathrm{o})} \longrightarrow \mathbf{x}^{L,(\mathrm{n})}] = h_A[\mathbf{x}_0^{(\mathrm{n})}]\,h_B[\mathbf{x}_L^{(\mathrm{n})}]\,\min\left\{1,\ \frac{\mathcal{P}[\mathbf{x}^{L,(\mathrm{n})}]\,P_{\mathrm{gen}}[\mathbf{x}^{L,(\mathrm{n})} \longrightarrow \mathbf{x}^{L,(\mathrm{o})}]}{\mathcal{P}[\mathbf{x}^{L,(\mathrm{o})}]\,P_{\mathrm{gen}}[\mathbf{x}^{L,(\mathrm{o})} \longrightarrow \mathbf{x}^{L,(\mathrm{n})}]}\right\}$$

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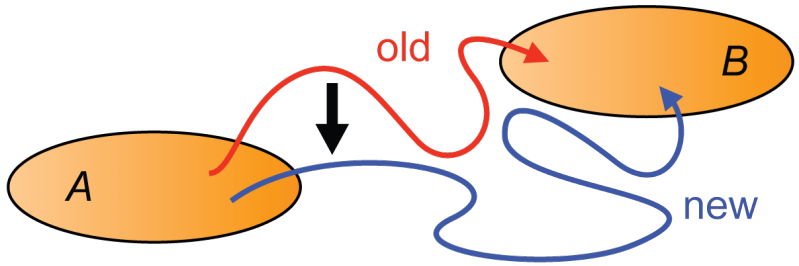

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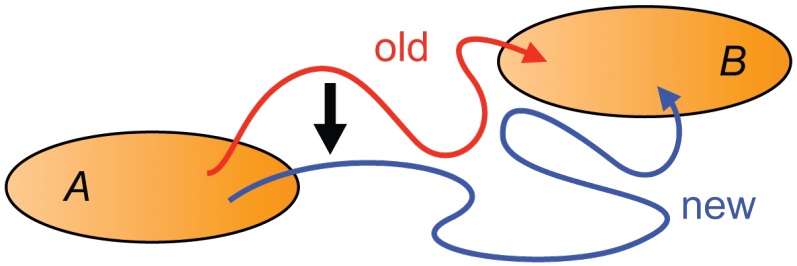

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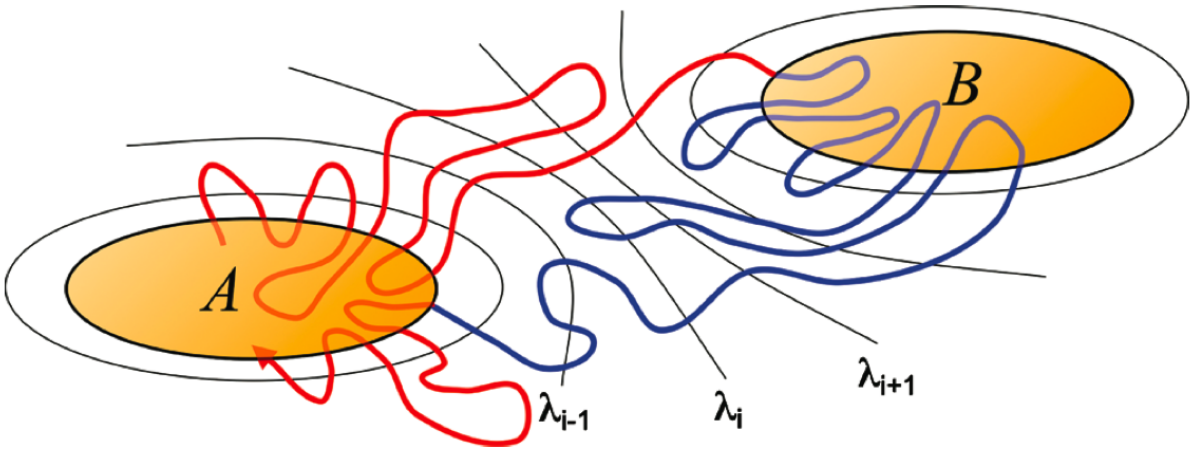
The unbiased path ensemble



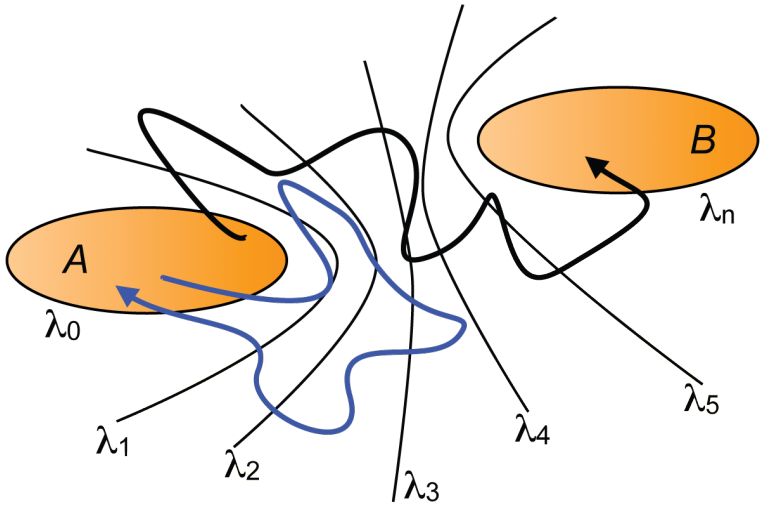
- **unbiased** ensembles for state A and B:

  $\mathcal{P}_A[\mathbf{x}^L] = h_A(\mathbf{x}_0)\pi[\mathbf{x}^L]/Z_A$

  $\mathcal{P}_B[\mathbf{x}^L] = h_B(\mathbf{x}_0)\pi[\mathbf{x}^L]/Z_B$

- allows for direct calculation of all properties: rate constants, free energies, reaction coordinates

Transition interface sampling



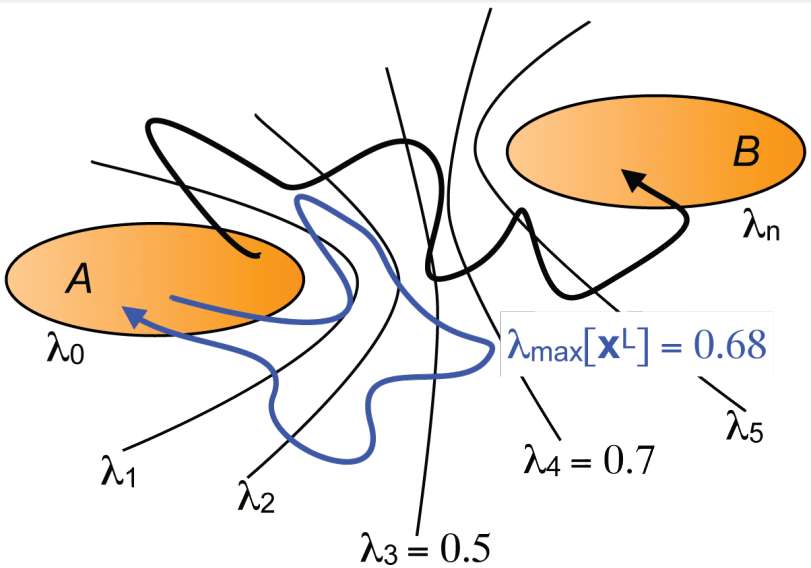
- progress parameter $\lambda(\mathbf{x})$, interfaces as hypersurfaces for $\lambda(\mathbf{x}) = \lambda_i$
- ensemble for **each** interface: $\mathcal{P}_{A\lambda_i}[\mathbf{x}^L] = \tilde{h}_i^A[\mathbf{x}^L]\pi[\mathbf{x}^L]/Z_{A\lambda_i}$
  - start in A
  - cross λ_i
  - end in A or B

T.S. van Erp, P.G. Bolhuis, J. Comp. Phys. **205**, 157 (2005).

TIS crossing probabilities

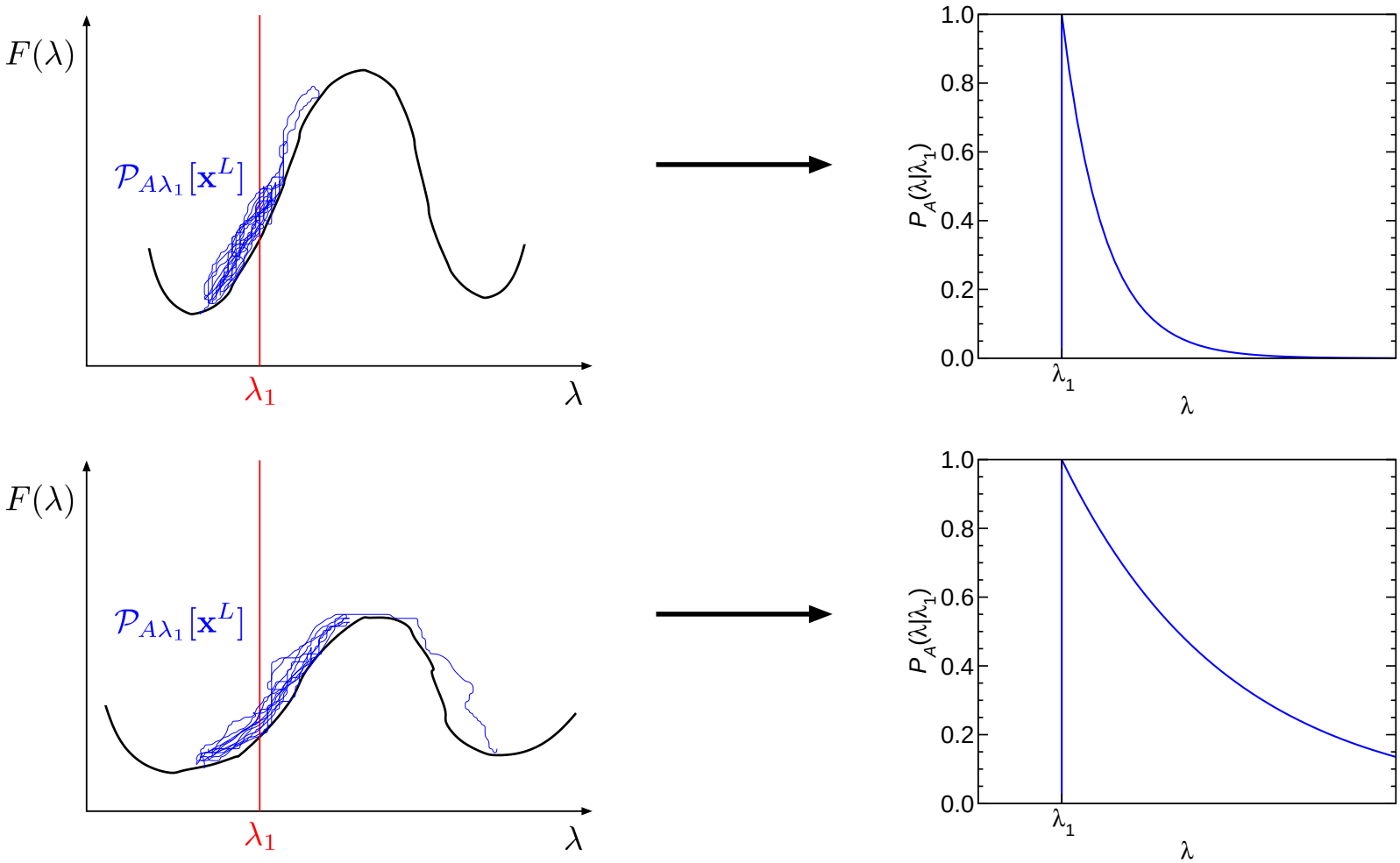
extract crossing probabilities

- path ensemble for λ_i :
  $\mathcal{P}_{A\lambda_i}[\mathbf{x}^L] = \tilde{h}_i^A[\mathbf{x}^L]\pi[\mathbf{x}^L]/Z_{A\lambda_i}$
- crossing probability for $\lambda_i < \lambda < \lambda_n$:
  $P_A(\lambda|\lambda_i) = \int D\mathbf{x}^L \mathcal{P}_{A\lambda_i}[\mathbf{x}^L]\theta(\lambda_{\max}[\mathbf{x}^L] - \lambda)$



$\lambda_{\max}[\mathbf{x}^L] = \max\{\lambda(\mathbf{x_0}), \lambda(\mathbf{x_1}), \ldots, \lambda(\mathbf{x_L})\}$

TIS crossing probabilities



TIS crossing probabilities

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$$P_A(\lambda|\lambda_i) = \int D\mathbf{x}^L \mathcal{P}_{A\lambda_i}[\mathbf{x}^L]\theta(\lambda_{\max}[\mathbf{x}^L] - \lambda)$$

- total crossing probability:

$$P_A(\lambda|\lambda_1) = \sum_{i=1}^{n-1} \bar{w}_i^A \theta(\lambda_{i+1} - \lambda)\theta(\lambda - \lambda_i) \sum_{j=1}^{i} P_A(\lambda|\lambda_j)$$

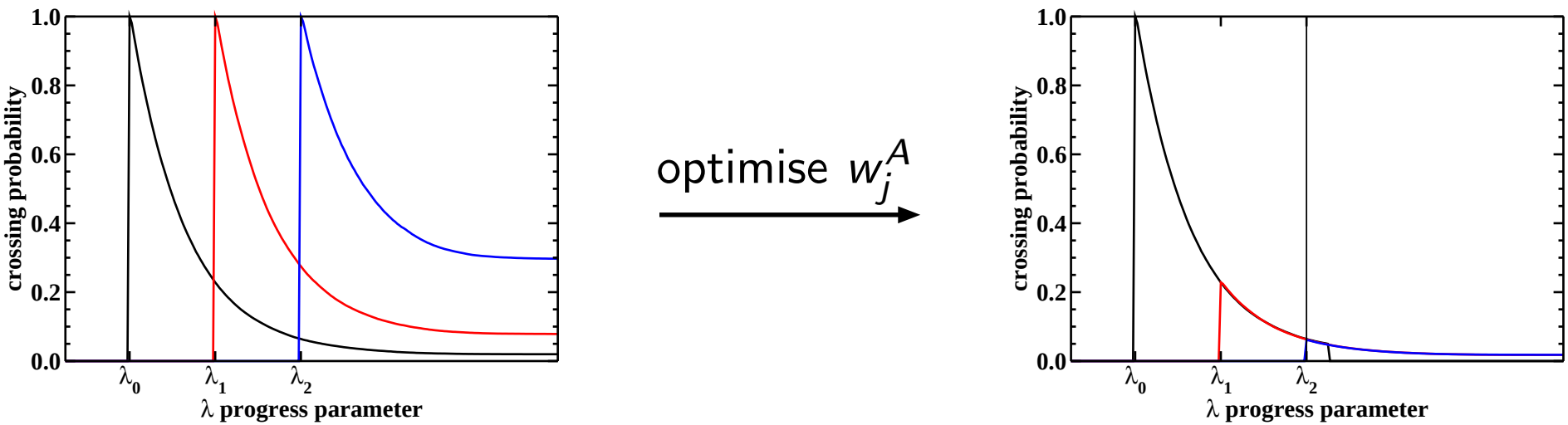
- rate constant: $k_{AB} = \phi_{01} P(\lambda_n|\lambda_1)$

T.S. van Erp, P.G. Bolhuis, J. Comp. Phys. **205**, 157 (2005).

Matching crossing histograms – WHAM

weighted histogram analysis method

- $P_A(\lambda|\lambda_1) = \sum_{i=1}^{n-1} \bar{w}_i^A \theta(\lambda_{i+1} - \lambda)\theta(\lambda - \lambda_i) \sum_{j=1}^{i} P_A(\lambda|\lambda_j)$
- weights : $\bar{w}_i^A = \frac{1}{\sum_{j=1}^{i} 1/w_j^A}$



A.M. Ferrenberg, R.H. Swendsen, Phys. Rev. Lett. **63**, 1195 (1989).

The complete path ensemble from TIS

reweighting the TIS path ensembles

- unbiased path ensemble:

$$\mathcal{P}_A[\mathbf{x}^L] = \sum_{j=1}^{n-1} \mathcal{P}_{A\lambda_j}[\mathbf{x}^L] W^A[\mathbf{x}^L] \quad \text{with} \quad W^A[\mathbf{x}^L] \equiv \sum_{i=1}^{n-1} \bar{w}_i^A g_i^A[\mathbf{x}^L]$$

- complete path ensemble:

$$\begin{aligned} \mathcal{P}_c[\mathbf{x}^L] &= c_A \mathcal{P}_A[\mathbf{x}^L] + c_B \mathcal{P}_B[\mathbf{x}^L] \\ &\quad + c_A w_1^A P_{\lambda_1}^- + c_B w_{n-1}^B P_{\lambda_{n-1}}^+ \end{aligned}$$

J. Rogal, W. Lechner, J. Juraszek, B. Ensing, P.G. Bolhuis, J. Chem. Phys. 133, 174109 (2010)

The complete path ensemble

1. TIS simulation using some λ
2. match crossing histograms using WHAM
3. use WHAM weights to reweight path ensembles $\longrightarrow$ complete path ensemble
4. extract properties like free energy, rate constant, reaction coordinate in any arbitrary collective variable space

free energy

- $F(\mathbf{q}) = -k_\mathrm{B} T \ln p(\mathbf{q}) + \text{const.}$
- probability to find configuration at $\mathbf{q}$:

$$p(\mathbf{q}) = C \int \mathcal{D}\mathbf{x}^L \sum_{k=0}^{L} \prod_{i=1}^{m} \delta(q^{(i)}(\mathbf{x}_k) - q^{(i)}) \mathcal{P}_c[\mathbf{x}^L]$$

The complete path ensemble

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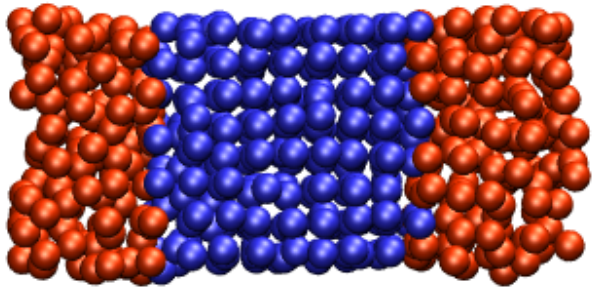
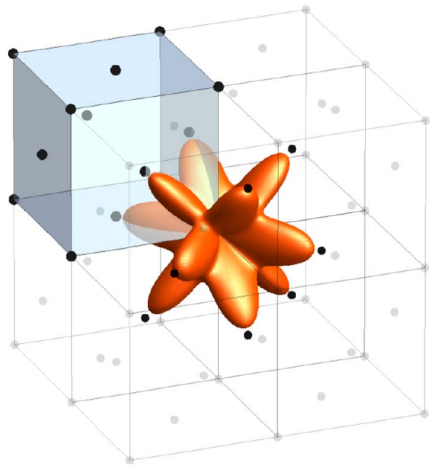
Lennard-Jones: solid-liquid phase transformation

- system:
  - 512 atoms
  - $(4 \times 4 \times 8)$ supercell



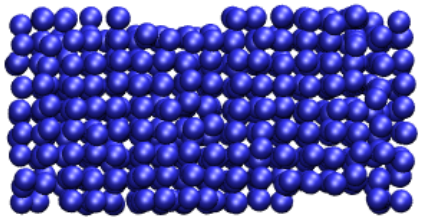
- order parameter Φ:
  - tuned to fcc lattice
  - specific angular function (polynomials, symmetry adapted to cubic point group)

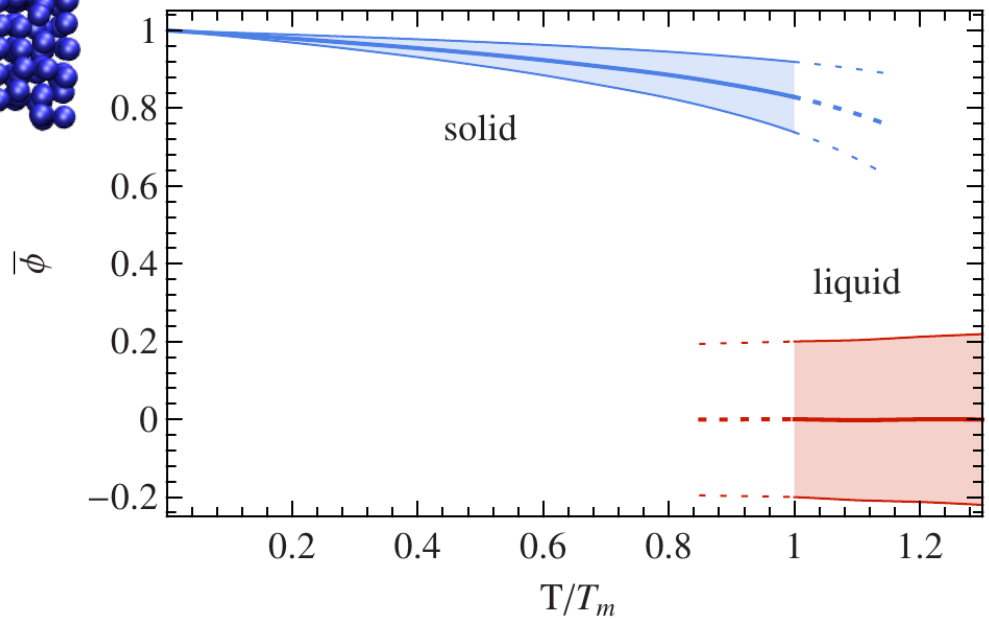


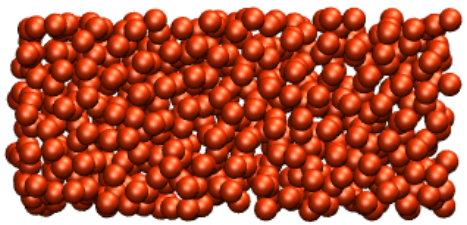
Angioletti-Uberti et al., PRB 81, 125416 (2010)

Order parameter

temperature dependence of Φ







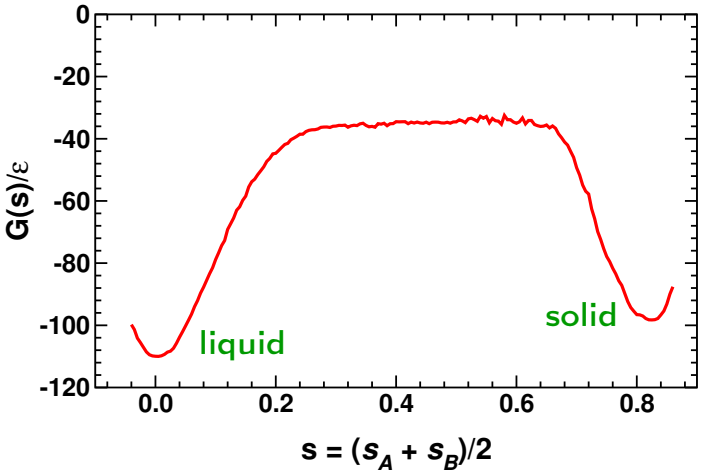
Angioletti-Uberti et al., PRB 81, 125416 (2010)

1D free energy surface

interface energy: $\gamma_{sl} = G_{xs}/A$

reweighted path ensemble

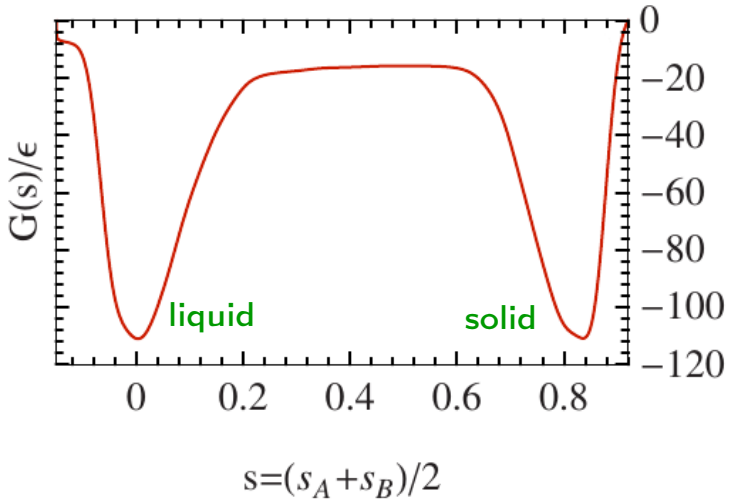
projection



$\gamma_{sl} = 0.30$

metadynamics

sampling



$\gamma_{sl} = 0.37$

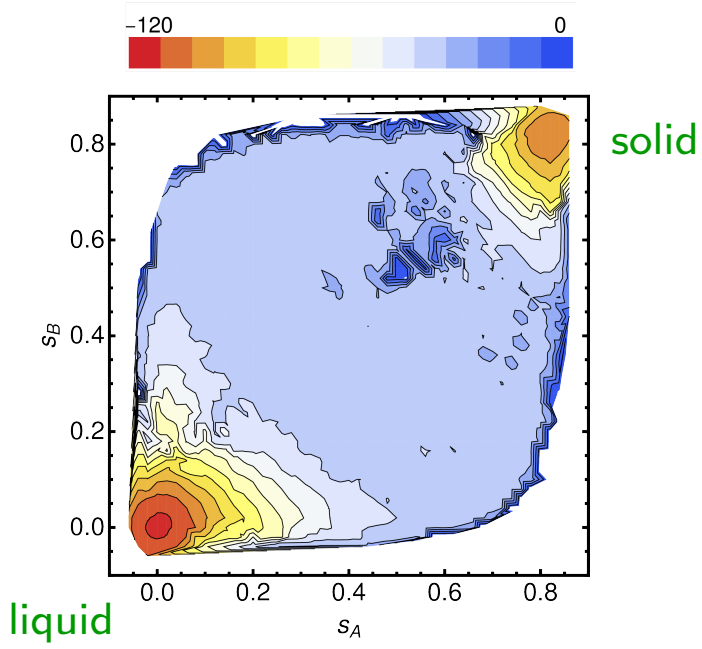
Angioletti-Uberti et al., PRB 81, 125416 (2010)

2D free energy surface

interface energy: $\gamma_{sl} = G_{xs}/A$

reweighted path ensemble

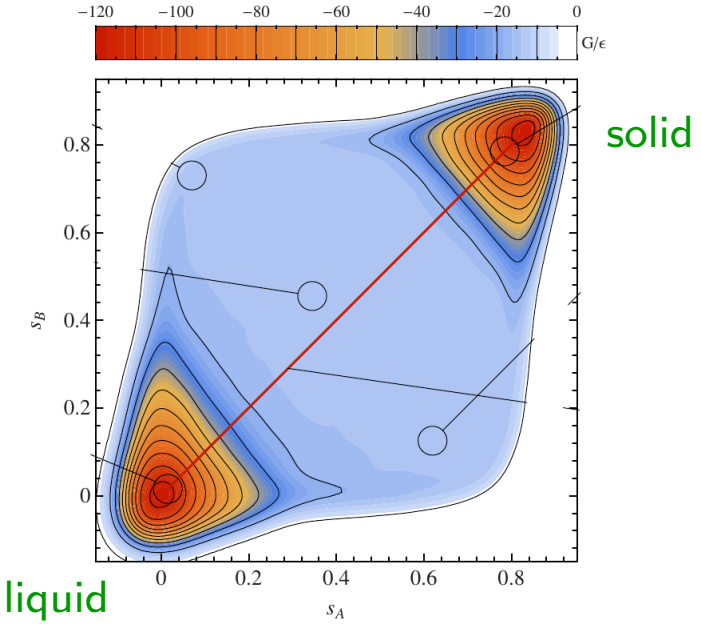
projection



$\gamma_{sl} = 0.30$

metadynamics

sampling



$\gamma_{sl} = 0.37$

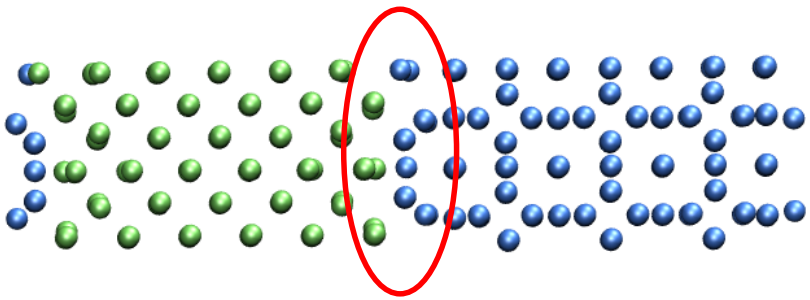
Angioletti-Uberti et al., PRB 81, 125416 (2010)

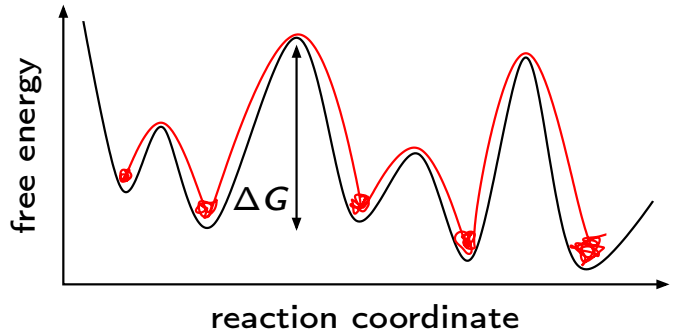
Interface free energies from the reweighted path ensemble

- use free energy to obtain γ_{sl}
- project free energy from reweighted (complete) path ensemble
- complete path ensemble
  - → project into arbitrary collective variable space
  - → extract properties: free energy, committor
  - → analyse reaction coordinates, mechanisms

Atomistic processes at solid-solid interfaces

Rare event problem





rare event techniques

- accelerated classical molecular dynamics
- stochastic trajectory, kinetic Monte Carlo
- metadynamics, umbrella sampling ($\rightarrow$ fix collective variable for sampling)
- transition path sampling

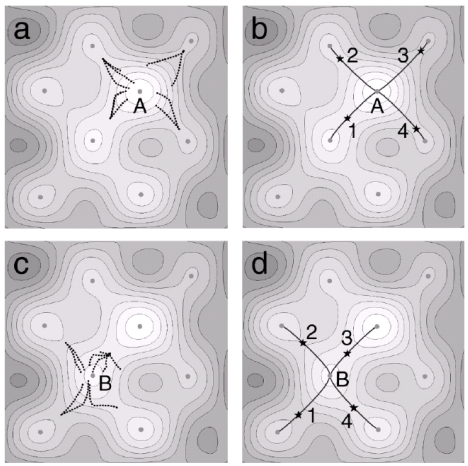
Adaptive kinetic Monte Carlo

Markov chain

- time evolution: $\frac{dP(j,t)}{dt} = -\sum_i p_{j\to i} P(j,t) + \sum_i p_{i\to j} P(i,t)$
- stable system states, transition probabilities/processes
- lattice, adaptive kMC

adaptive kMC

- find saddle points using minimum mode following method
- rate constants from harmonic TST: $k_i = \nu_{0,i} \exp(-\Delta E_i / k_\mathrm{B} T)$
- use determined process list for kMC move



G. Henkelman, H. Jónsson, JCP 115, 9657 (2001)

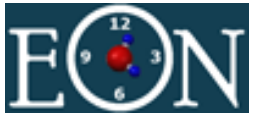
EON + BOPfox

challenges

- large system sizes, complex structures
- large number of force calls
- smooth PES

adaptive kMC

- with A. Harjunmaa (ICAMS),
  R. Terrell, G. Henkelman (UT Austin)
- improve saddle searches, kinetic data base



energies + forces

- with M. Ĉák, T. Hammerschmidt (ICAMS)
- development of BOPs for bcc TM

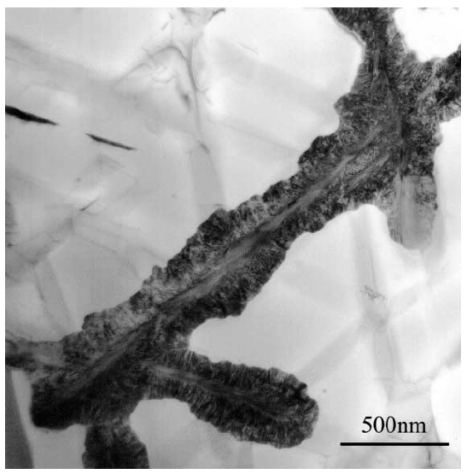
BOPfox

Interfaces between cubic and TCP phases

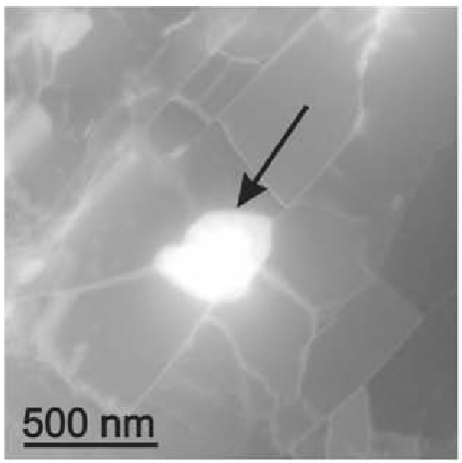
topologically close-packed phases

- complex crystal structure, Frank-Kasper polyhedra
- average coordinate: $\langle \mathrm{CN} \rangle = 13.3 - 13.5$

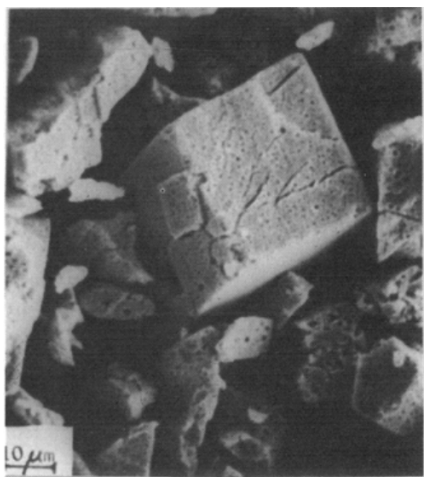
Ni-SX: fcc-σ [1]



steel: bcc-laves [2]



metastable β-W: bcc-A15 [3]

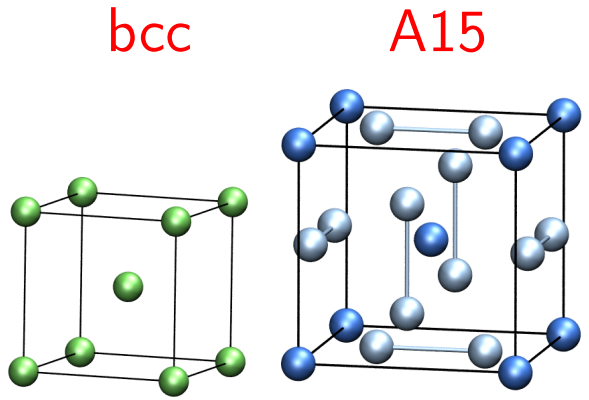


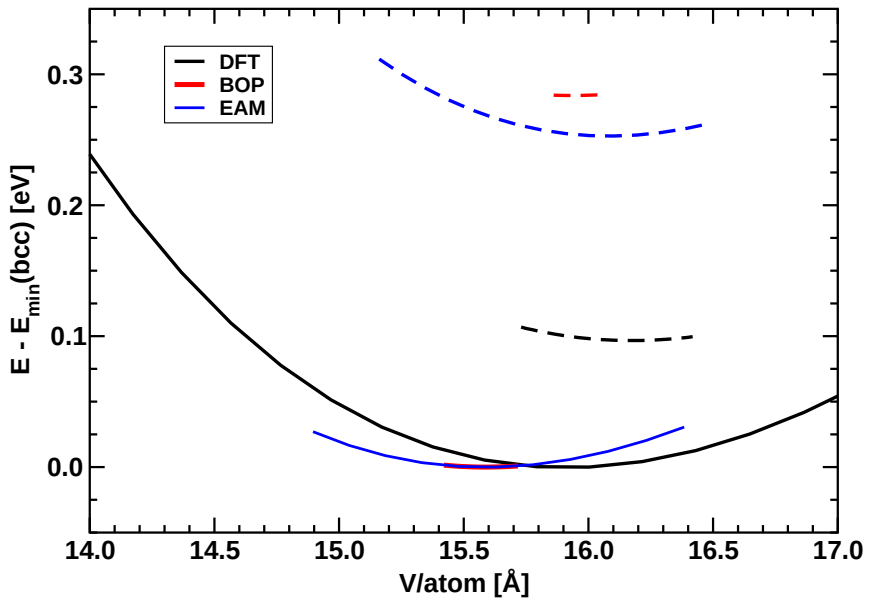
[1] Rae et al., Acta Mat. 49, 4113 (2001)
[2] Aghajani et al., Acta Mat. 57, 5093 (2009)
[3] Morcom et al., Met. Trans. 5, 155 (1974)

Testing potentials: stability of Mo bulk phases

molybdenum bulk properties

	DFT	BOP	EAM	Exp.
a_0(bcc) [Å]	3.17	3.15	3.15	3.15
a_0(A15) [Å]	5.06	5.03	5.05	–
$\Delta E_{\text{bcc-A15}}$ [meV]	97	284	253	–

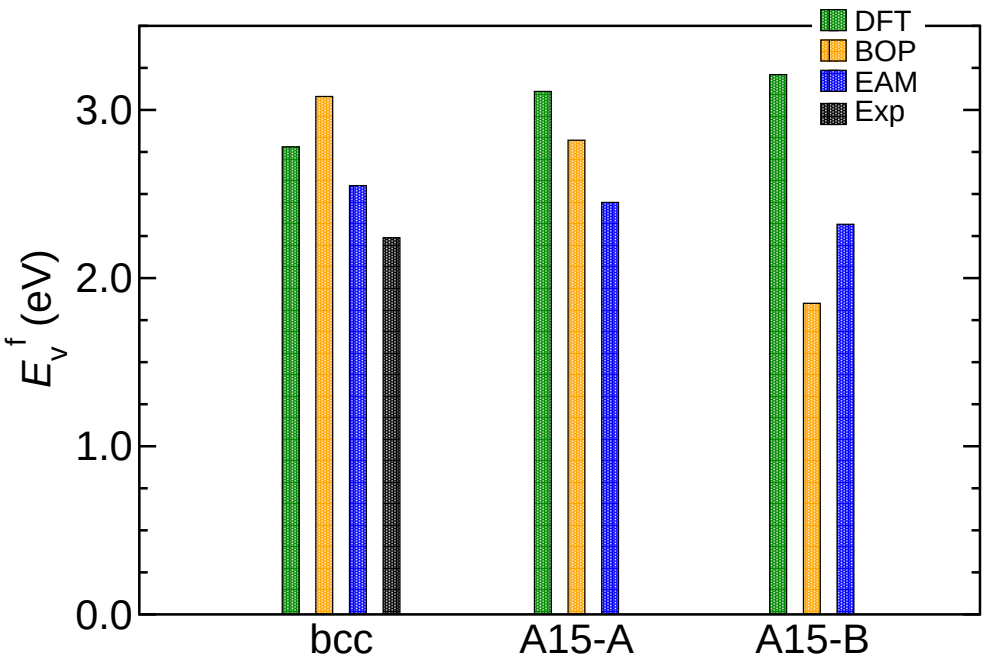




Testing potentials: vacancy formation energy Mo

- bcc: 1 inequivalent atom (14-fold)
- A15: A (12-fold), B (14-fold)

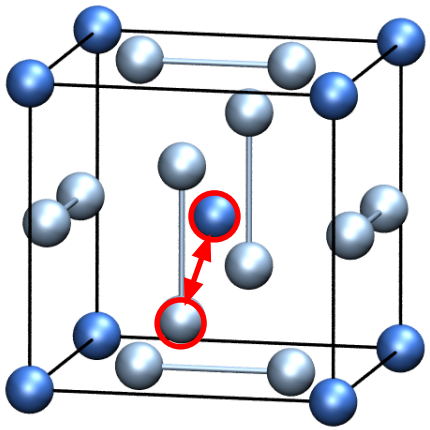
$$E_v^f = E_{\text{bulk}}(N-1) - \frac{N-1}{N} E_{\text{bulk}}(N)$$

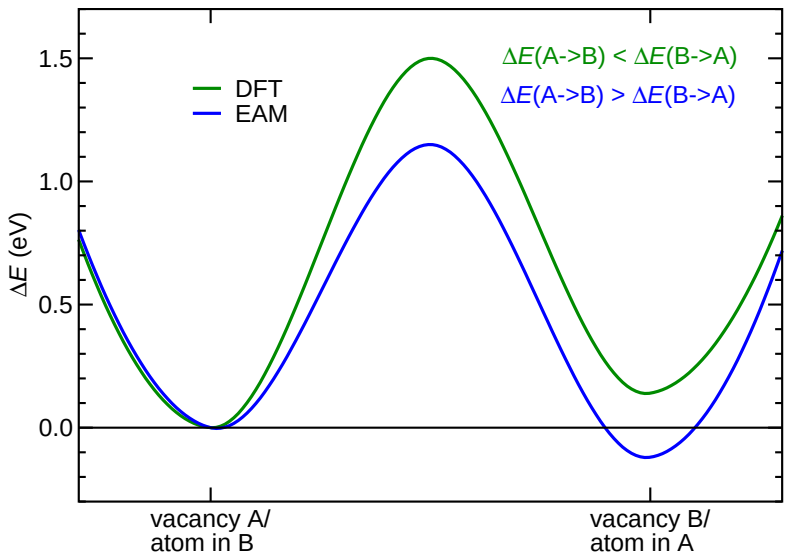


Testing potentials: diffusion barriers

A15 diffusion barriers (in eV)

	DFT	BOP	EAM
A→B	1.36	2.05	1.27
B→A	1.50	0.74	1.15



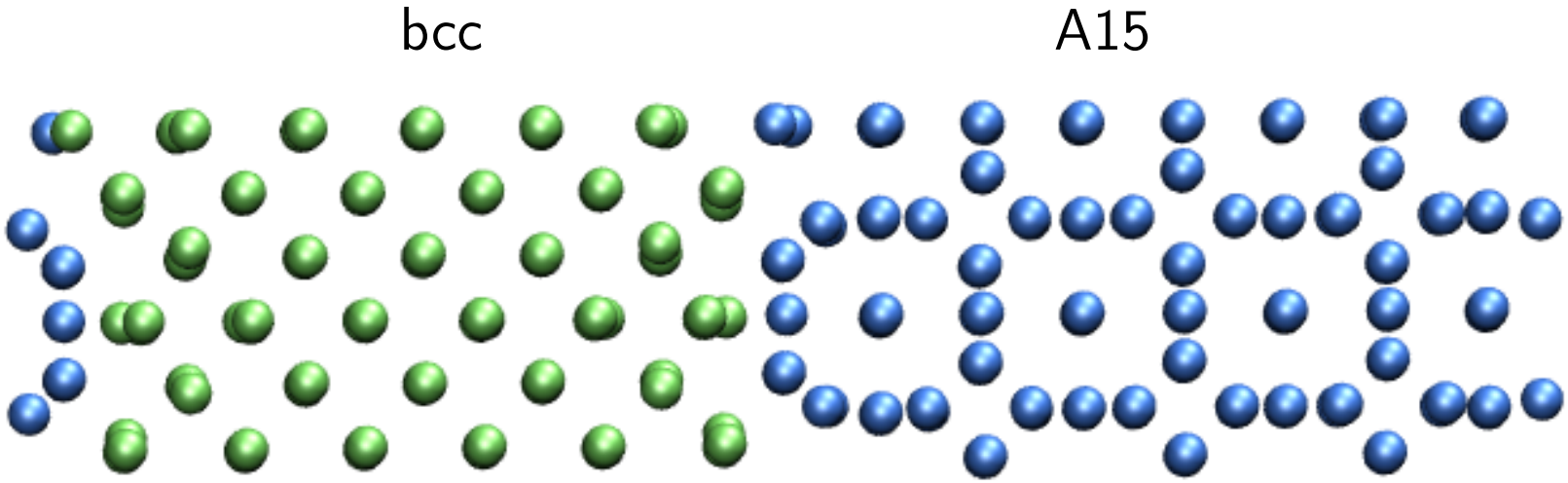


Need reliable potentials!

A15-bcc interface

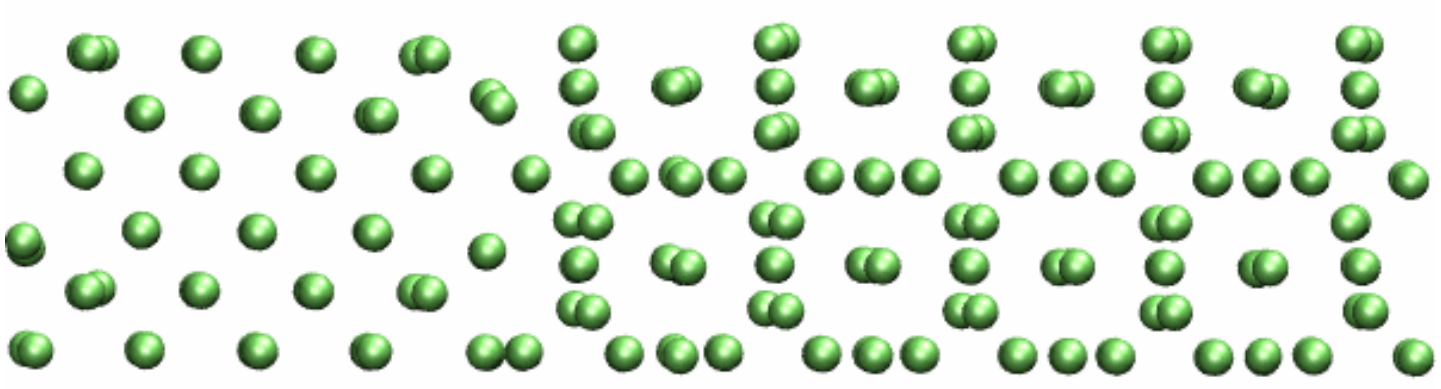
interface setup (T. Hammerschmidt)

- [100]-direction, minimise lattice mismatch, optimise volume
- remove high-energy atoms at interface

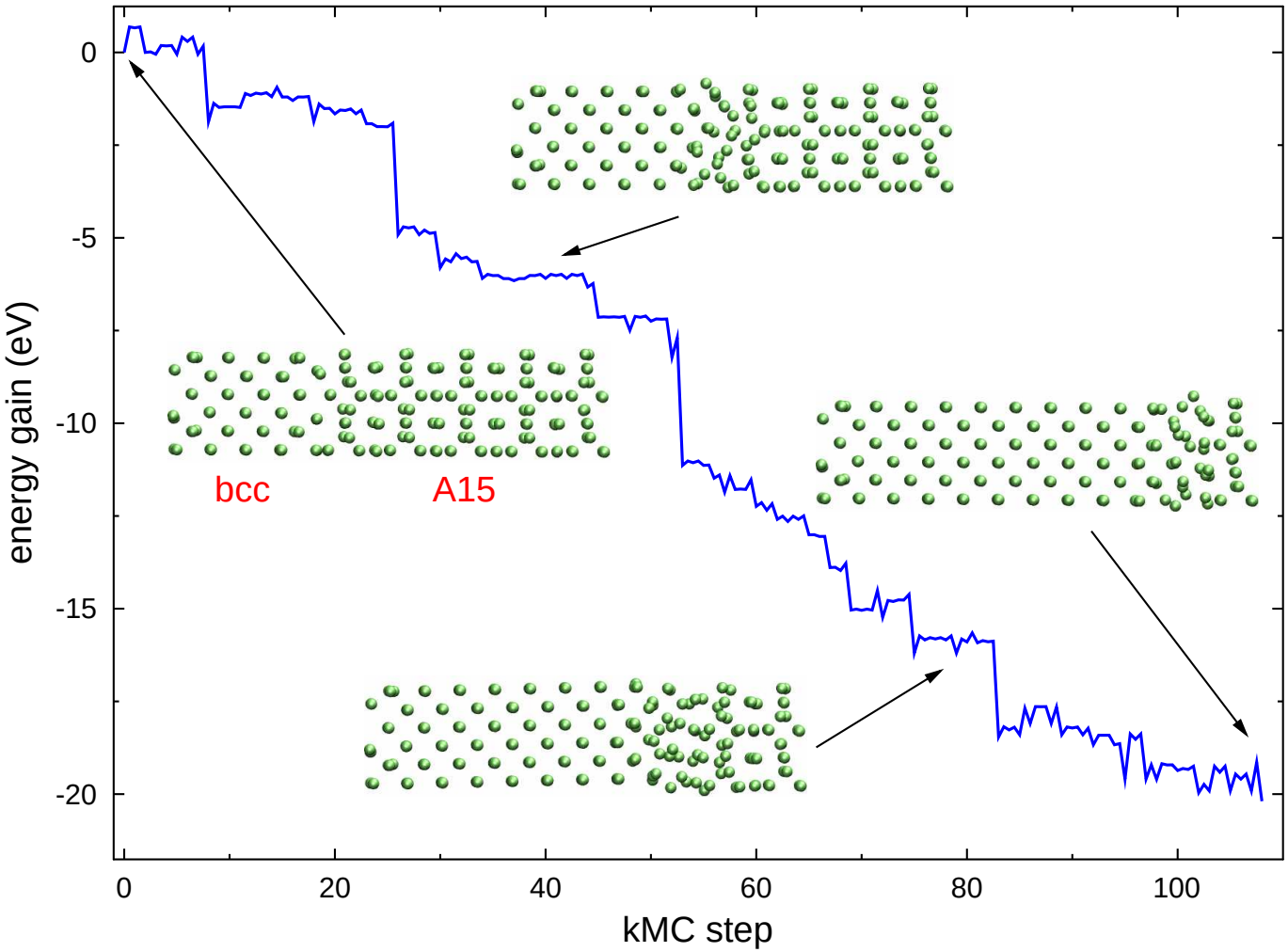


Molybdenum: bcc-A15 interface – adaptive kMC

- Finnis-Sinclair EAM
- one fixed interface
- transformation A15→bcc



Energy profile

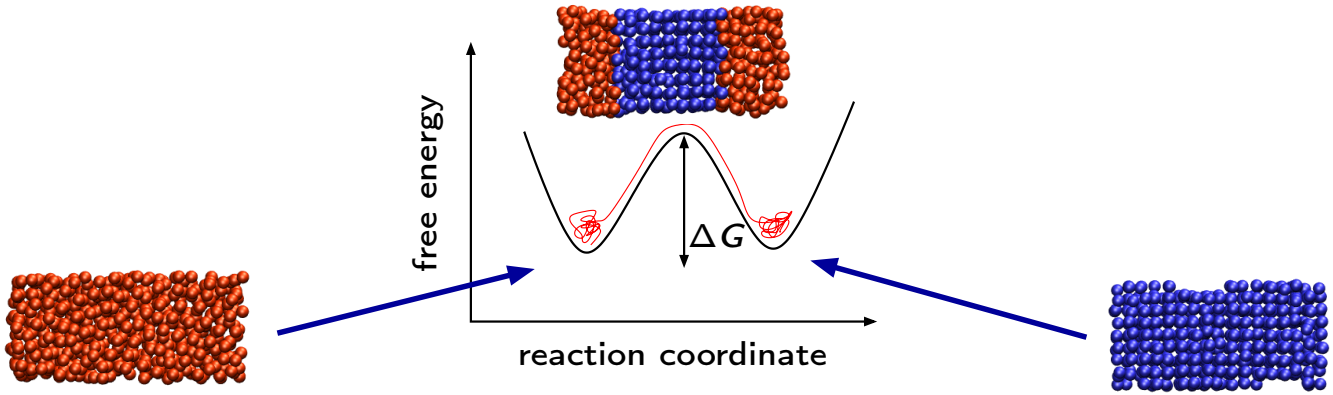


akMC for solid-solid phase transformation

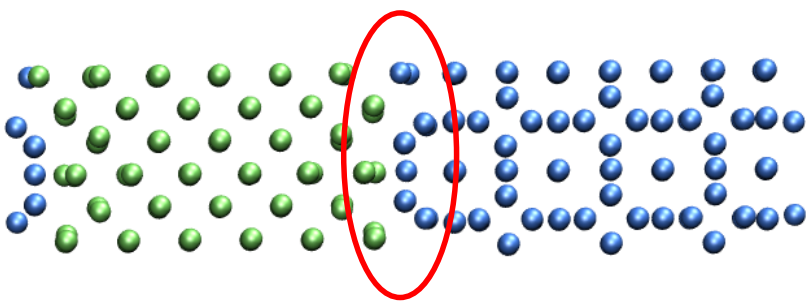
- interfaces between cubic/complex phases: growth of bcc Mo
- concerted multi-atom processes
- outlook:
  - → analysis/characterisation of growth processes, interface mobility
  - → influence of point/extended defects on growth
  - → larger system size, reliable potentials

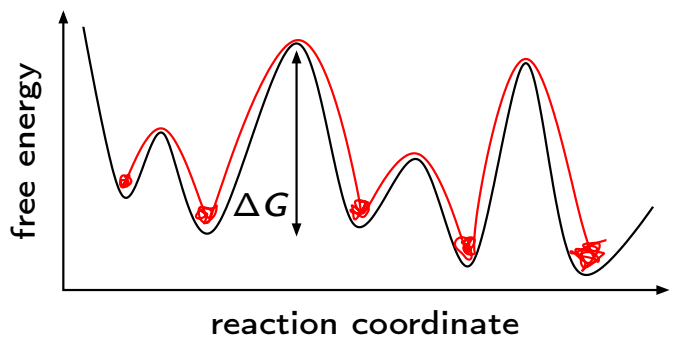
Summary

solid-liquid interface free energy



structural rearrangement at solid-solid interfaces





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