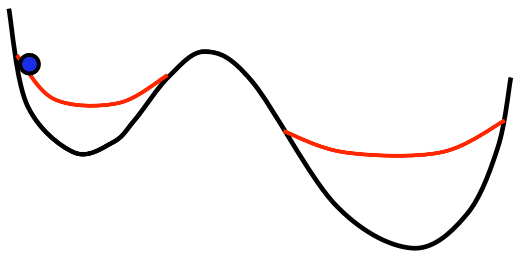
Hyperdynamics



A very brief introduction

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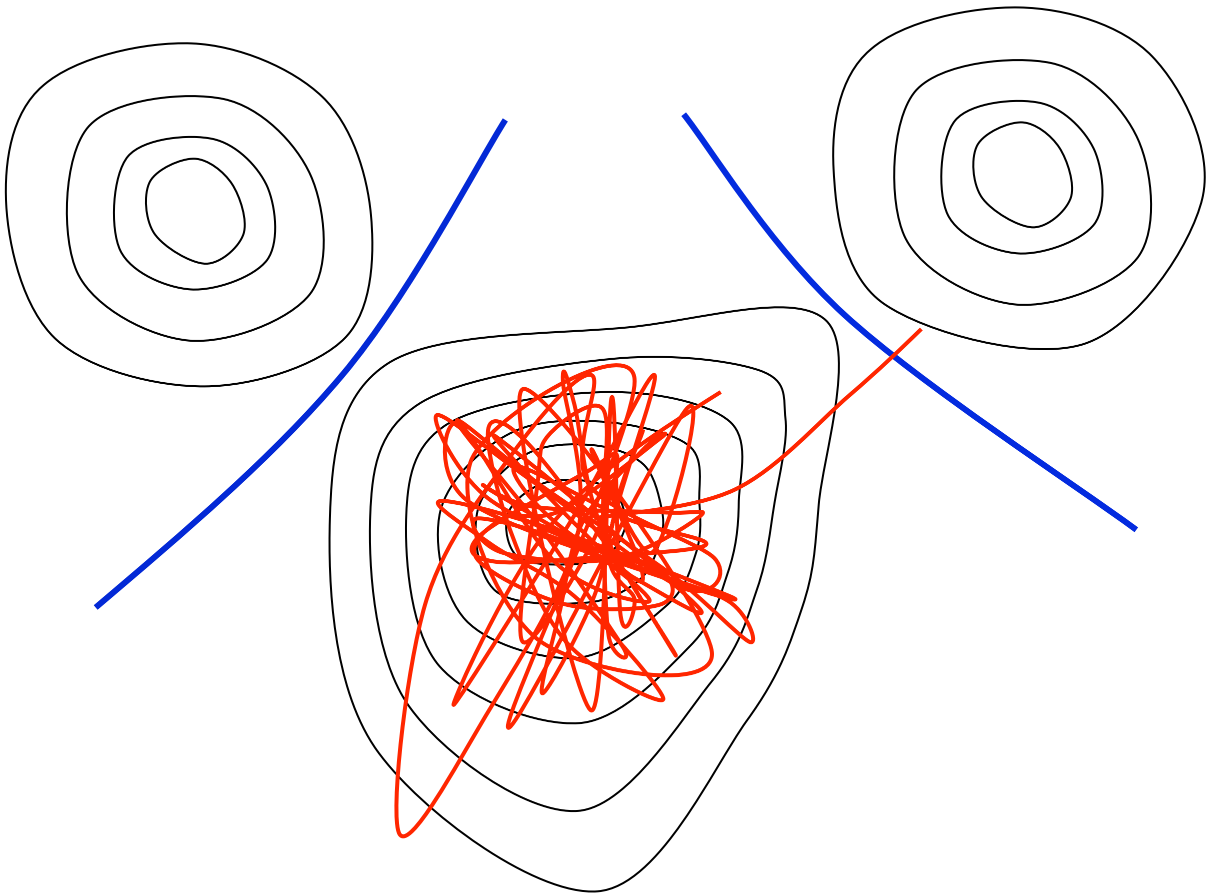
Work supported by
DOE/BES, LANL LDRD, DOE/ASCR, DOE/SciDAC

Infrequent-Event System



The system vibrates in 3-N dimensional basin many times before finding an escape path. In hyperdynamics, we partially fill in the basins with a bias potential to cause the trajectory to find an appropriate escape path more quickly.

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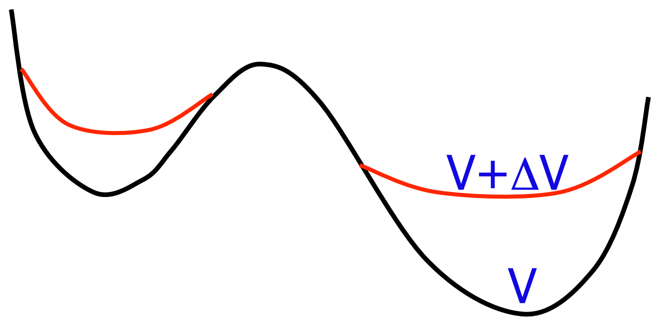
Hyperdynamics

Builds on umbrella-sampling techniques (e.g., Valleau 1970's)

Assumptions:

- infrequent events
- transition state theory (no recrossings)



Procedure:

- design bias potential ΔV (zero at dividing surfaces)
- run thermostatted trajectory on the biased surface ($V+\Delta V$)
- accumulate hypertime as

$$t_{hyper} = \Sigma \Delta t_{MD} \exp[\Delta V(R(t))/k_B T]$$

- time converges on correct value in long-time limit (w/ vanishing relative error)

AFV, J. Chem. Phys. 106, 4665 (1997)

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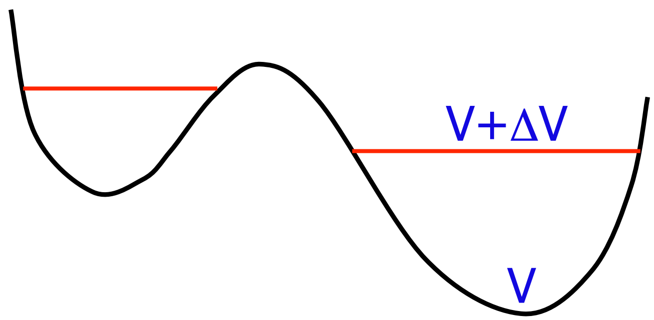
Hyperdynamics bias potential

An extremely simple form: flat bias potential



M. M. Steiner, P.-A. Genilloud, and J. W. Wilkins, Phys. Rev. B **57**, 10236 (1998).

- no more expensive than normal MD (negative overhead(!))
- very effective for low-dimensional systems
- diminishing boost factor for more than a few atoms.

Hyperdynamics - characteristics

Designing valid and effective bias potential is the key challenge.

Bias potential can be a function of

- the shape of the energy surface (AFV, 1997)
- the energy (Steiner, Genilloud and Wilkins, 1998)
- the geometry
    - bond lengths, Miron and Fichthorn, 2003, 2005
    - local strain, Hara and Li, 2010

Must be careful that bias is zero on all dividing surfaces or dynamics will be wrong.

When barriers are high relative to T, boost can be many orders of magnitude.

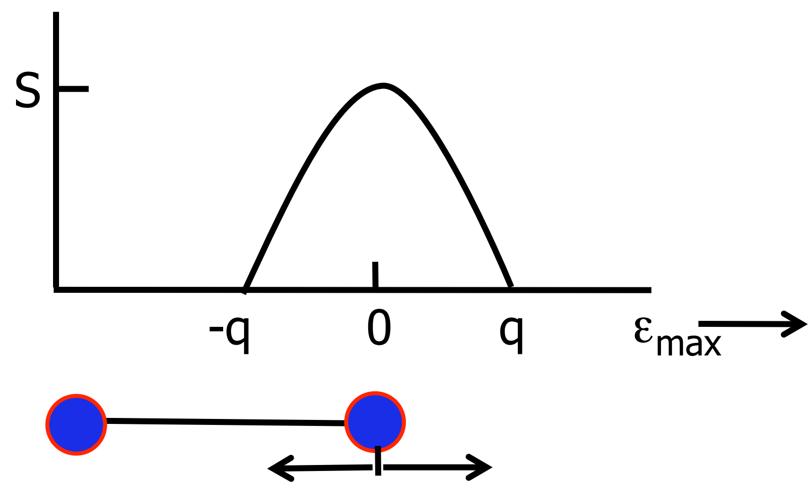
Simplified bond-boost bias potential

Based on Miron-Fichthorn 2003 form [R.A. Miron and K.A. Fichthorn, J. Chem. Phys. **119**, 6210 (2003)], but simplified.

Bias potential turns off when the relative distortion [$\varepsilon_{ij} = (r_{ij}-r_{ij}^{min})/r_{ij}^{min}$] of any bond exceeds a threshold value *q* (as in Miron-Fichthorn 2003).

Simplification: ΔV depends purely on coordinate (ε_{max}) of most-distorted bond. Only one bond at a time has any bias force.

$$\Delta V(\varepsilon_{max}) = S[1-(\varepsilon_{max}/q)^2]$$



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Simple bond-boost bias example

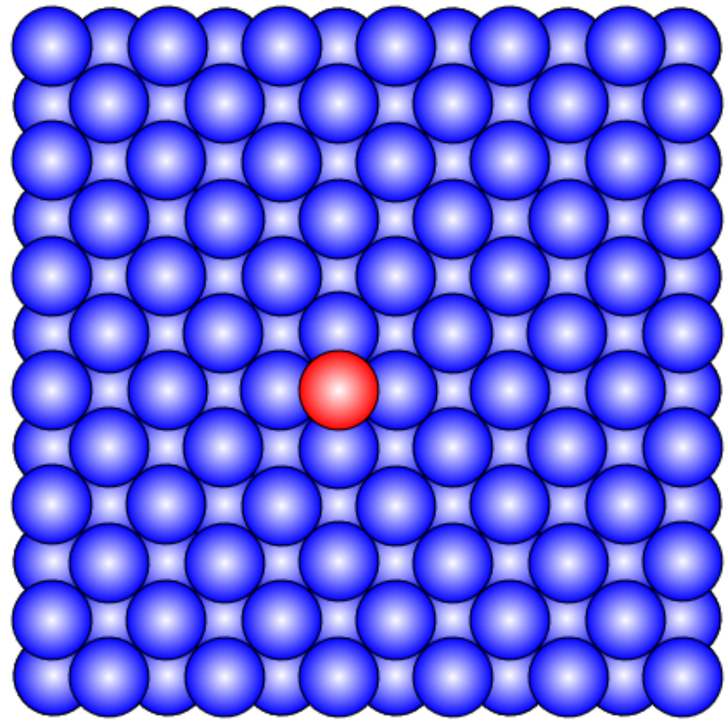
Simple bond-boost bias potential

Cu adatom on Cu(100) surface

Hop barrier = 0.53 eV

T(K)	hop time	boost factor (S=0.4 eV)
350 K	1.36 μs *	$1.1x10^3$
300 K	27 μs	$3.1x10^4$
200 K	0.8 s	$1.1x10^8$

*At T=350K, the hyperdynamics rate matches full harmonic TST ("Vineyard") rate within 5% error bars (743 events).



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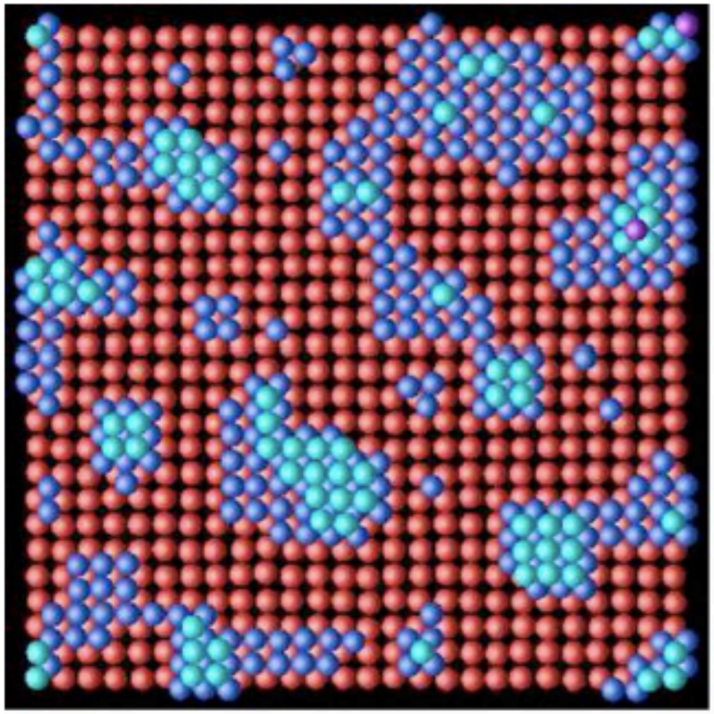
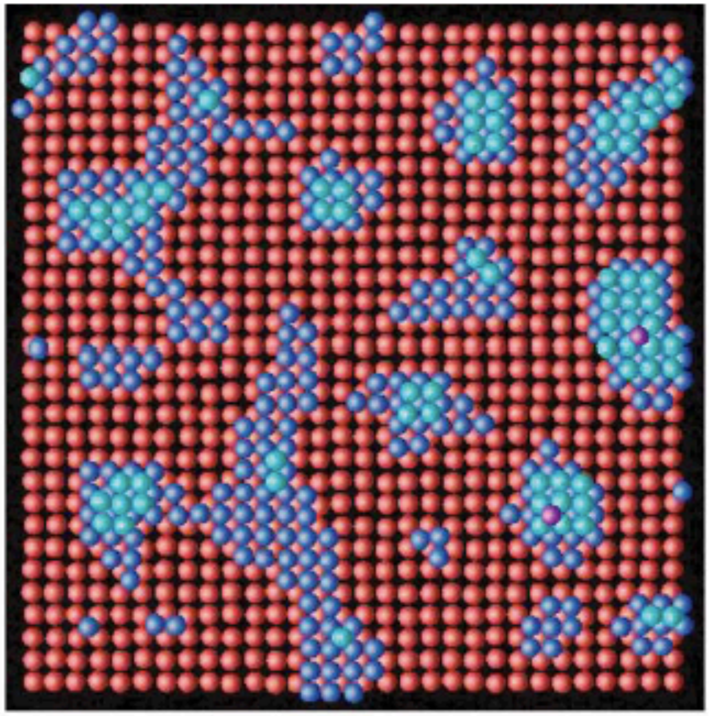
Hyperdynamics example from Kristen Fichthorn's group

Miron and Fichthorn Phys. Rev. B 72, 035415 (2005)

Co/Cu(001) growth at experimental deposition rates using bond-boost bias potential and bond-bridging for low barriers.



T=250K, t=0.54 s (0.1 ML/s)



T=310K, t=0.42 s (1.0 ML/s)

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