Atomistic simulations of rare events using the gentlest ascent dynamics

Amit Samanta

Applied and Computational Mathematics,
Princeton University, Princeton, USA.

Joint work with
Prof. Weinan E (Princeton), Xiang Zhou (Brown)

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Max Planck Institute for the Physics of Complex Systems
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A simple fact: Nature works on disparate time scales

A direct manifestation: In nature, dynamics often proceed in the form of **rare events**.

1. Focus : exploring a smooth energy surface for local minima, saddles starting from one initial point
2. Goal : set of dynamical equations that converge to saddle points

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    - follow minimum eigenmode close to saddle point - but can easily become unstable (degenerate eigenvalues)
    - how to move out of basin of attraction - need better sampling techniques
    - no global convergence

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    - n $=$ 4 atoms, 6 saddle points[1]
    - n $=$ 10 atoms, $>$ $160,000$ saddle points[1]

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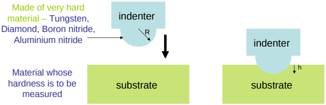
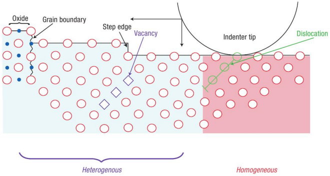
Many transition events : Nanoindentation



Measured quantities:- indentation load (P), indentation depth (h)

Important Parameters:- indentation rate, indenter tip radius (R), elastic modulus, temperature



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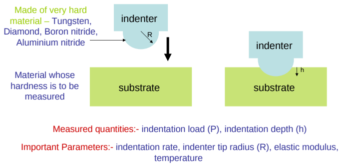

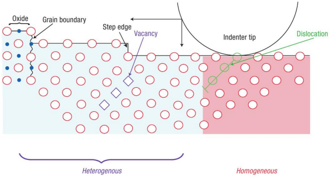

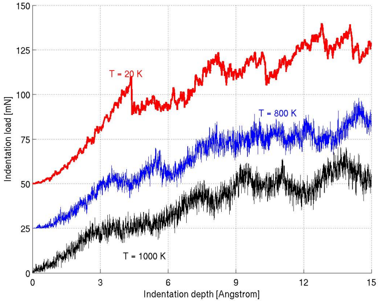

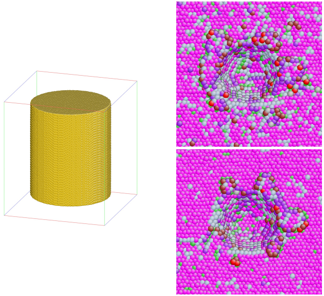

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Gentlest Ascent Dynamics

- Idea: $\mathbf{F} = -\nabla V(\mathbf{x})\,, \qquad \mathbb{H} = \nabla^2 V(\mathbf{x})$
  - move along direction **n**, minimize along other dimensions
  - $\tilde{\mathbf{F}} = \mathbf{F}_{\perp} - \mathbf{F}_{||}, \qquad \mathbf{F}_{||} = (\mathbf{F}, \mathbf{n})\,\mathbf{n}, \qquad \mathbf{F}_{\perp} = \mathbf{F} - \mathbf{F}_{||}$

W. E and X. Zhou, *Nonlinearity* (2011)
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- Equations of motion:

$$\dot{\mathbf{x}} = \mathbf{F}(\mathbf{x}) - 2(\mathbf{F}, \mathbf{n})\,\mathbf{n}$$

$$\gamma\dot{\mathbf{n}} = -\mathbb{H}\mathbf{n} + (\mathbf{n}, \mathbb{H}\mathbf{n})\,\mathbf{n}$$

Lemma:The stable fixed points of this dynamics are the index-1 saddle points of V . (Local minima of V are saddle points of GAD)

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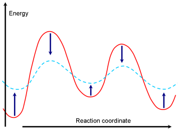
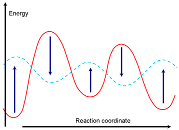


shallow wells



change in stability

- simple, amendable to mathematical analysis, can be extended to higher index saddles, non-gradient systems, efficient numerical schemes

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Convergence to One Saddle Point

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2-dimensional example : $V(\mathbf{x}, \mathbf{y}) = \sin(\pi\mathbf{x})\sin(\pi\mathbf{y})$

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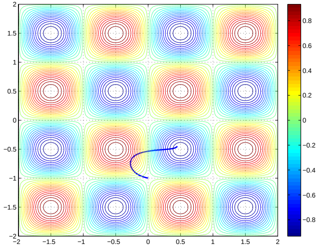

- randomly initialized direction vector
- time step important
- guess direction determines convergence

Configuration Space Density Distribution

$$\dot{\mathbf{x}} = \mathbf{F}(\mathbf{x}) - 2(\mathbf{F}, \mathbf{n})\mathbf{n} + \sigma\dot{\mathbf{w}}$$
$$\gamma\dot{\mathbf{n}} = -\mathbb{H}\mathbf{n} + (\mathbf{n}, \mathbb{H}\mathbf{n})\mathbf{n}$$

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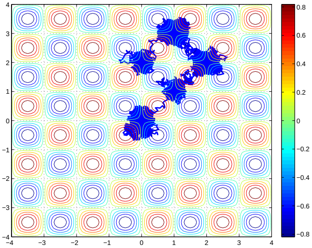

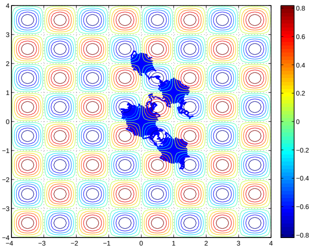

randomly initialized direction vector

System spends considerable amount of time near saddle points.

Variants: MD-GAD

$$\dot{\mathbf{x}} = \mathbf{v}$$

$$\dot{\mathbf{v}} = \mathbf{F} - 2(\mathbf{F}, \mathbf{n})\,\mathbf{n}$$

$$\gamma\dot{\mathbf{n}} = -\mathbb{H}\mathbf{n} + (\mathbf{n}, \mathbb{H}\mathbf{n})\,\mathbf{n}$$

incorporate thermostat, barostat

A. Samanta and W. E, *J Chem Phys* (2012)

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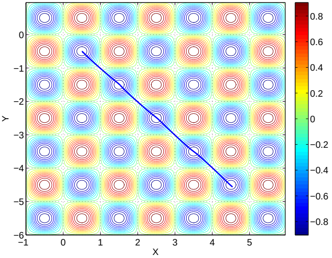

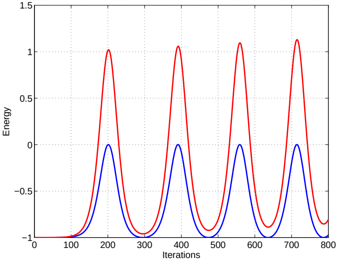

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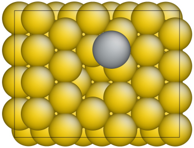
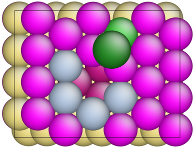
A. Samanta and W. E, *J Chem Phys* (2012)

Ad-atom diffusion on (111) surface of Cu



ad-atom on Cu surface



coordination number coloring

Simulation details :

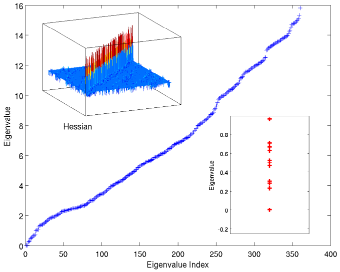
1. Copper thin-film, 120 atoms, (111) free surface on top
2. periodic boundary conditions along other directions
3. interatomic potential - Embedded Atom Model (EAM)
   - $E = \sum_{\langle i,j \rangle} E_{pair}(\mathbf{r}_{ij}) + \sum_i E_{embed}(\rho_i)$
   - Elastic constants, lattice parameter, cohesive energy, stacking fault energy, etc. used for fitting

Y. Mishin, et al., *Phys. Rev. B* (2001)
A. Samanta and W. E, *J Chem Phys* (2012)

Ad-atom diffusion on (111) surface of Cu : initialization problem

How to initialize direction vector for high dimensional PES?

- random vector - less informed
- eigen vectors of Hessian - expensive
- select important degrees of freedom - permute them to obtain guess directions



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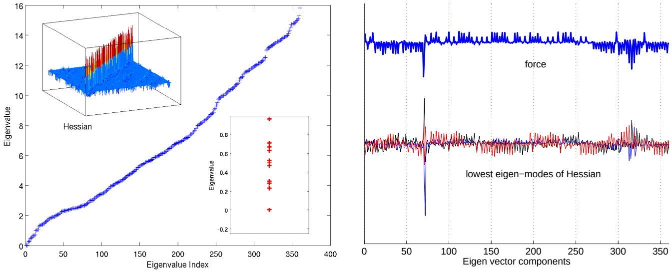

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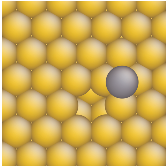
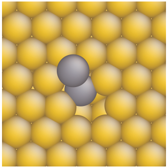
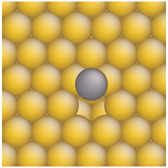
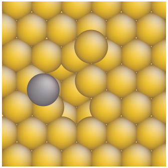
Ad-atom diffusion on (111) surface of Cu : collection of saddle points









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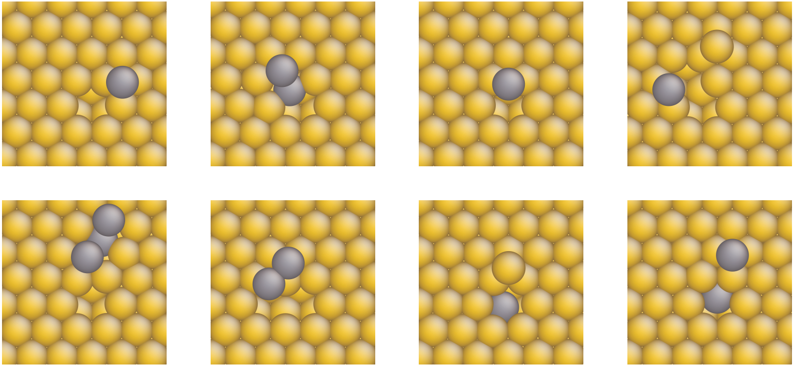
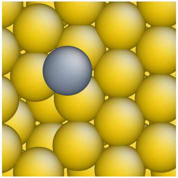


Atoms involved in transition events are colored in grey

Cu thin-film 120 atoms, EAM potential (Mishin et al.)

Selectively initialized direction vector

Ad-atom diffusion on (111) surface of Cu : MD-GAD



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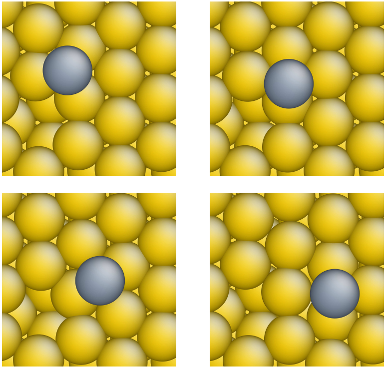


Copper sample, 120 atoms, 6 (111) layers

Embedded Atom Model potential

Selectively initialized direction vector

A. Samanta and W. E, *J Chem Phys* (2012)

Variants: finding high index saddles

Auxiliary variable = a k-dimensional subspace spanned by vectors $\{\mathbf{n}_1, \mathbf{n}_2, \cdots, \mathbf{n}_k\}$. $N = (\mathbf{n}_1, \cdots, \mathbf{n}_k)$

$$\dot{\mathbf{x}} = -\nabla V(\mathbf{x}) + 2\sum_j (\nabla V(\mathbf{x}), \mathbf{n}_j)\, \mathbf{n}_j$$

$$\dot{N} = -\nabla^2 V(\mathbf{x})\, N + N\Lambda$$

Λ is a Lagrange multiplier matrix for the constraint $N^T N = I$.

Lemma

The stable fixed points of this dynamics are the index-k saddle points of V

A. Samanta and W. E, *J Chem Phys* (2012)

Variants: Quasi-Newtonian scheme

$$\dot{\mathbf{x}} = \alpha \mathbf{H}^{-1}\mathcal{P}\mathbf{F}, \qquad \mathcal{P} = \left(\mathbf{I} - \nu \mathbf{n}\mathbf{n}^{\mathrm{T}}\right)$$

$$\dot{\mathbf{n}} = \mathbf{H}^{-1}\mathbf{n} - \Lambda\mathbf{n}, \qquad \mathbf{n}^{\mathrm{T}}\mathbf{n} = 1$$

Lemma

If $\alpha = -\mathrm{sign}\left(\lambda_1\right)$ and $0 < \nu < 1$, then, the stable fixed points of this dynamics are the index-1 saddle points of V

- modify Hessian to overcome singularities : $\mathbf{H} + \beta_0 \mathbf{F}\mathbf{F}^{\mathrm{T}}$
- Update Hessian using Sherman-Morrison, Davidon-Fletcher-Powell schemes

Variants: Quasi-Newtonian scheme

$$\mathbf{p}_k = \bar{\mathbf{H}}_k^{-1}\mathcal{P}_k\mathbf{F}_k, \qquad \mathcal{P}_k = \left(\mathbf{I} - \nu\mathbf{n}_k\mathbf{n}_k^{\mathrm{T}}\right)$$

$$\mathbf{x}_{k+1} = \mathbf{x}_k + \alpha_k\mathbf{p}_k$$

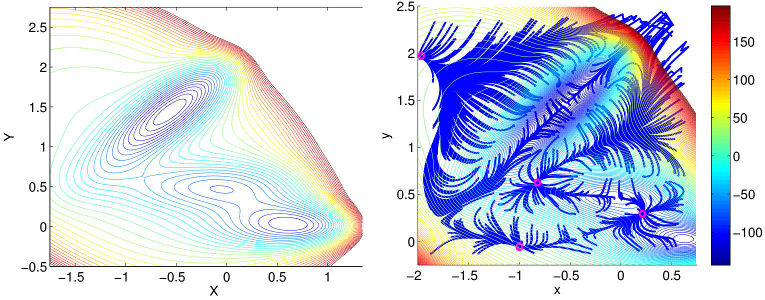
$$\mathbf{n}_k^* = \bar{\mathbf{H}}_{k+1}^{-1}\mathbf{n}_k, \qquad \mathbf{n}_{k+1} = \mathbf{n}^*/\|\mathbf{n}^*\|$$

$$\lambda_{k+1}^{-1} = \mathbf{n}_{k+1}\bar{\mathbf{H}}_{k+1}^{-1}\mathbf{n}_{k+1},$$

$$\alpha_{k+1} = -\mathrm{sign}\left(\lambda_{k+1}\right)$$

- Accurate Hessian : quadratic rate of convergence
- Approximate Hessian : superlinear rate of convergence
- Adaptive time step can yield superlinear convergence in GAD

Convergence problem : Muller potential



- degenerate eigenvalues
- failure to converge to relevant saddle point
- one possible solution : rank-1 update $\mathbf{H} + \beta_0 \mathbf{F}\mathbf{F}^{\mathrm{T}}$

Conclusions

Exploring high dimensional configuration space is an issue of general interest.

1. Finding saddles, local minima
   - use MD-GAD, Stochastic GAD, Deterministic GAD
2. Global optimization
   - Couple with simulated annealing, parallel tempering
3. Model reduction
   - Phase field model - information about saddle configuration
4. Mapping out topology of energy surface

GAD and its variants will help us to do these.

- local convergence
- sampling of initial direction vectors
- efficient numerical scheme

Thankyou for your time!

Questions?