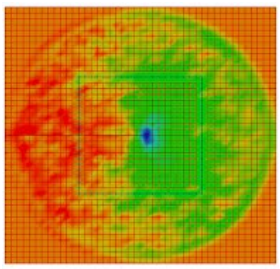
SAND2013-9652C

October 2013-January 2014

ESP900: Atomistic/Molecular Simulation:

Lecture 6: Molecular Statics



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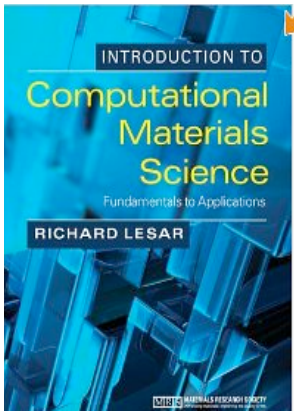
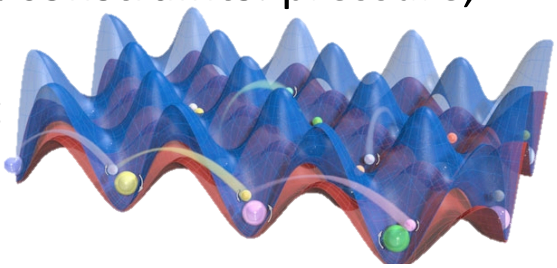
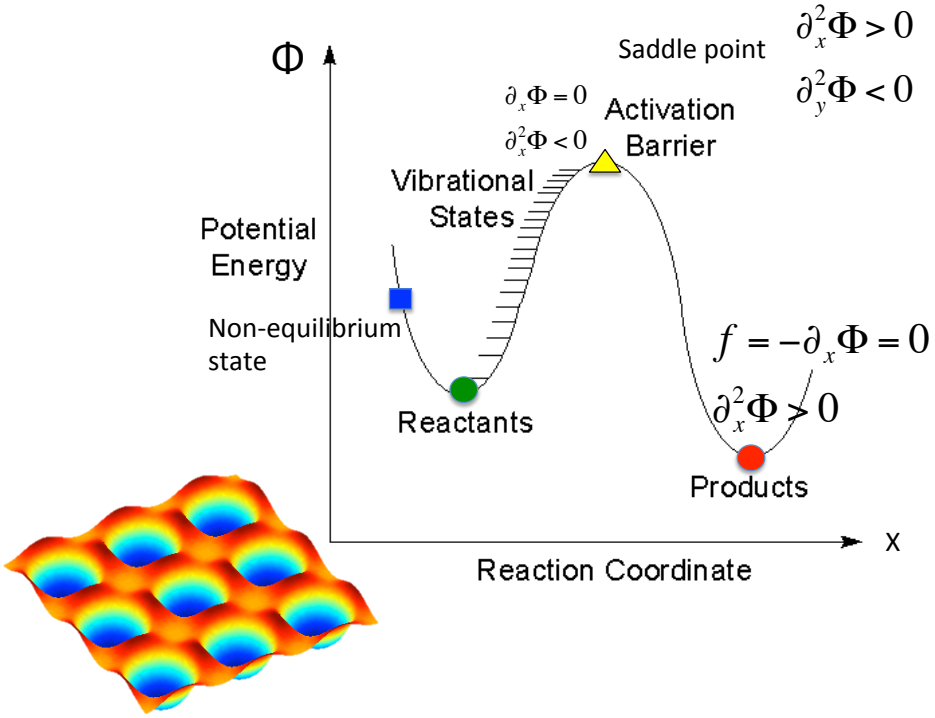


Exploring the potential energy surface

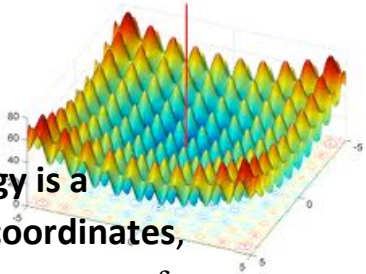
- **Energy minimization** $E = \Phi(x) + K(v)$
- **Fundamentals**: minima, saddle-points, search directions, line-searches
- **Local techniques:** steepest descent, conjugate gradients, Newton's method
- **Global techniques**: simulated annealing
- **Boundary conditions & constraints**: pressure, contact
- **Finding reaction paths**: nudged elastic band



Basics



Energy minimization

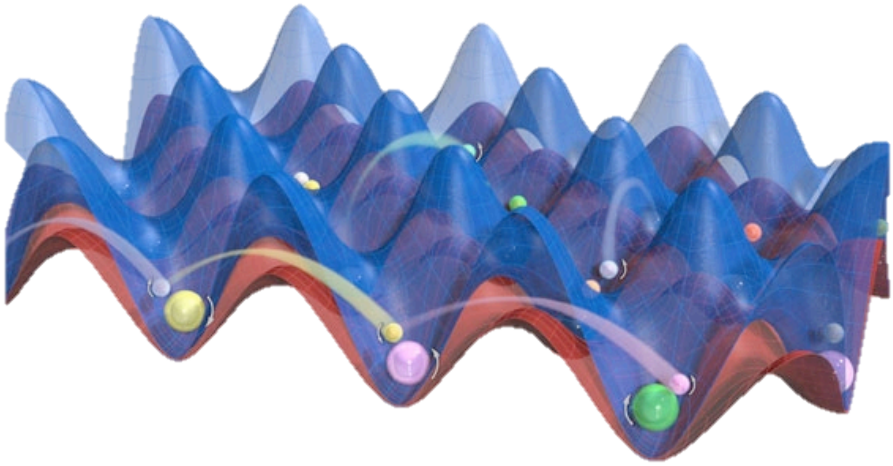


- For most systems, the total **potential energy is a complex, multi-dimensional function of the coordinates,** $\Phi(\{\mathbf{x}^\alpha\})$, and can be visualized as a potential energy surface.
- In the absence of molecular motion/ at the **zero temperature** limit, we expect atoms to occupy **positions of minimum energy** on the PE surface
  - **Global** energy minimum – the lowest energy positions on the PE surface
  - **Local** energy minima – low energy positions accessible from the current configuration

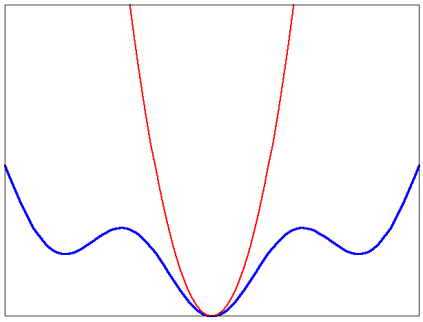
Finding minimum energy configurations lead to properties of the simulated material, e.g. **elastic constants, stacking fault energies, instability mechanisms**

Example: surface hopping

The energy surface mimics the actual surface structure i.e. high energy above surface atoms and wells in-between. Given kinetic energy (aka temperature) a test particle/adatom will diffuse across a surface.



Energy minimization



A Taylor series expansion, i.e. linear or quadratic approximation, is the start of most solution methods:

$$\Phi(y) = \Phi(x) + \partial_{\mathbf{x}}\Phi \cdot (y-x) + \frac{1}{2}(y-x)\cdot \partial_{\mathbf{x}}^2\Phi \cdot (y-x) + \ldots$$

Gradient of the PE is the ***force*** $\mathbf{f}_\alpha = -\mathbf{g}_\alpha = -\partial_{\mathbf{x}^\alpha}\Phi = 0$

Hessian of the PE is the ***dynamical matrix*** (vibration/phonon modes)

$$\mathbf{D} = \partial^2_{x^\alpha x^\beta}\Phi > 0$$

1st order/gradient-based methods

Steepest descent

Atoms are moved in the direction of their net force i.e. the ***search direction*** **s**

$$\mathbf{x}_{k+1}^{\alpha} = \mathbf{x}_{k}^{\alpha} + \lambda_k \mathbf{s}_{k}^{\alpha} \quad \text{where} \quad \mathbf{s}_{k}^{\alpha} = -\frac{\mathbf{g}_{k}^{\alpha}}{\left|\mathbf{g}_{k}^{\alpha}\right|} \quad \text{and} \quad \mathbf{g}_{k}^{\alpha} = \frac{\partial \Phi}{\partial \mathbf{x}_{k}^{\alpha}}$$

The step size λ_k is determined from a ***line search*** i.e. a 1D optimization using exact tangents or a secant method sometimes with limits to the step size (Wolfe conditions)

$$\lambda = -\upsilon \frac{\mathbf{g}_k^T \mathbf{s}_k}{\mathbf{h}_k^T \mathbf{s}_k - \mathbf{g}_k^T \mathbf{s}_k} \quad \text{where} \quad \mathbf{h}_k = \left.\frac{\partial \Phi}{\partial \mathbf{x}_k}\right|_{\mathbf{x}_k + \upsilon \mathbf{s}_k}$$

Conjugate Gradients

The steepest descent method is generally robust but not optimal on some energy surfaces, e.g. long, narrow valleys.

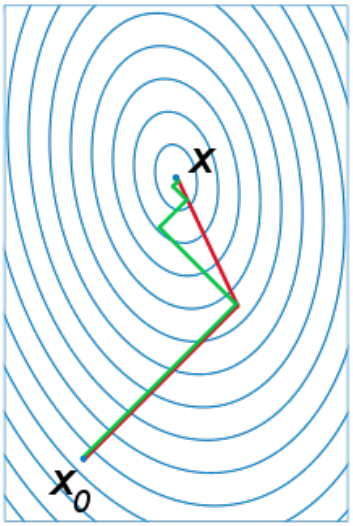
CG is an optimal method where the atoms are moved in a direction *conjugate* to the previous directions with respect to local dynamical matrix.

$$\mathbf{s}_k = -\mathbf{g}_k + \gamma_k \mathbf{s}_{k-1}$$

Since the problem is non-linear the orthogonality coefficient can be chosen in various ways

Fletcher-Reeves vs. Polak-Ribiere

$$\gamma_k = \mathbf{g}_k^T \mathbf{g}_k \big/ \mathbf{g}_{k-1}^T \mathbf{g}_{k-1} \qquad \gamma_k = \left(\mathbf{g}_k - \mathbf{g}_{k-1}\right)^T \mathbf{g}_k \big/ \mathbf{g}_{k-1}^T \mathbf{g}_{k-1}$$



Red CG, Green SD

The line search uses the same algorithms as in SD $\mathbf{x}_{k+1} = \mathbf{x}_k + \lambda_k \mathbf{s}_k$

2nd order/Newton's method

If 2nd derivatives of the potential energy are available analytically or numerically through finite differences, the quadratic approximation

$$\Phi(\mathbf{x}) = \Phi(\mathbf{x}_k) + (\mathbf{x}-\mathbf{x}_k)^T \mathbf{g}_k + \frac{1}{2}(\mathbf{x}-\mathbf{x}_k)^T \mathbf{D}_k \cdot (\mathbf{x}-\mathbf{x}_k)$$

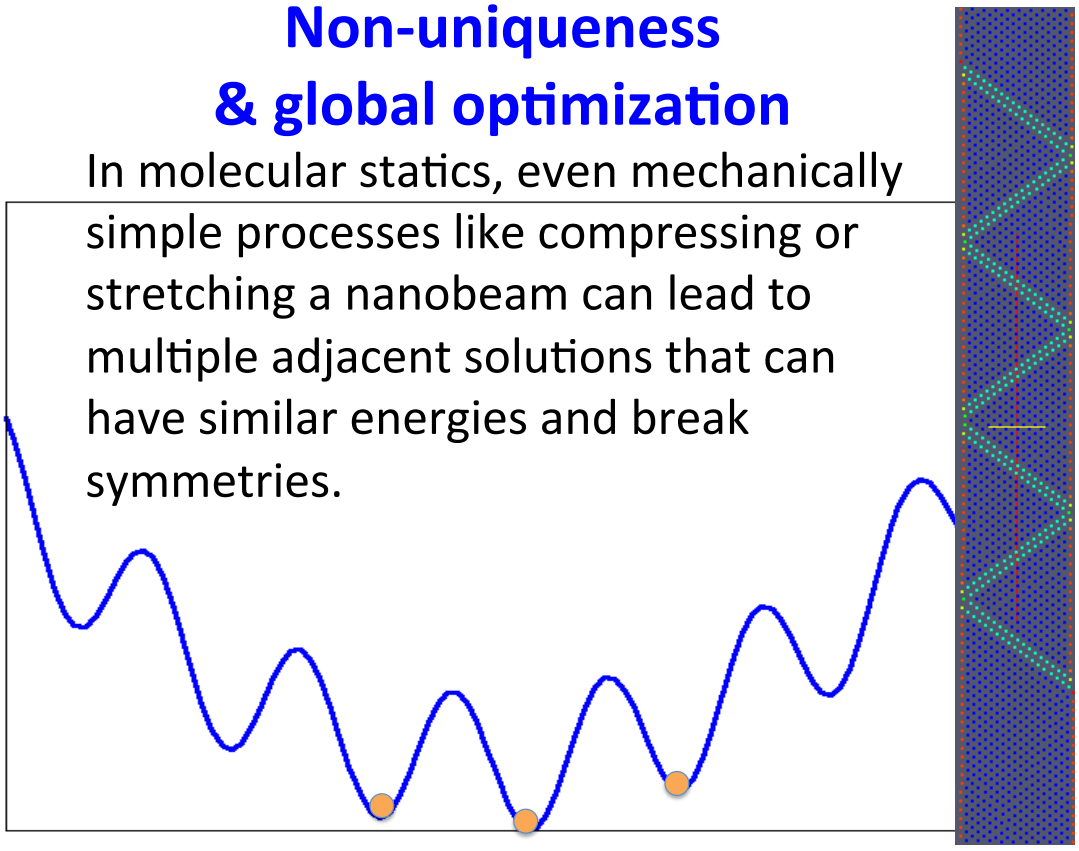
leads to a 2nd order update that converges faster but is more costly than CG

$$\mathbf{x}_{k+1} = \mathbf{x}_k - \mathbf{D}_k^{-1}\mathbf{g}_k$$

- If the PE is not smooth or the Hessian is inexact the convergence won't be quadratic.
- A line search can be employed but the quadratic model determines an optimal step size
- Sometimes CG is used to solve the incremental linear system

Non-uniqueness & global optimization

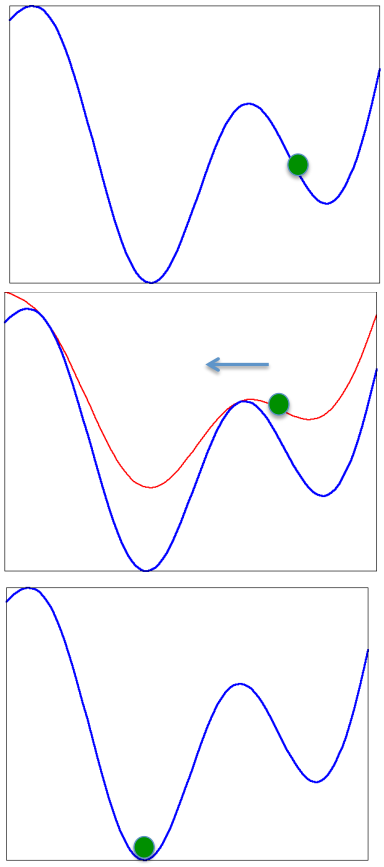
In molecular statics, even mechanically simple processes like compressing or stretching a nanobeam can lead to multiple adjacent solutions that can have similar energies and break symmetries.



Simulated Annealing

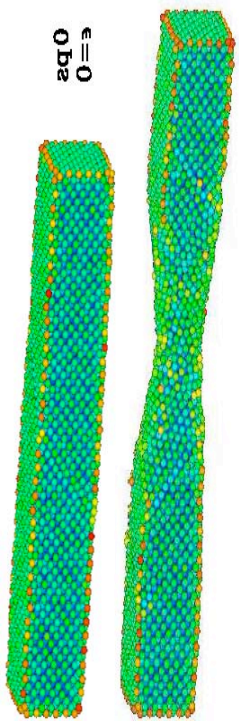
To escape a local minima:

- "**Heat**" via dynamics or random moves
- **Continue** till in a lower energy well
- **Quench** via local, potential energy minimization
- **Repeat** (generally you never know if you are at the global minimum or if a unique one exists)



Boundary conditions (mechanical)

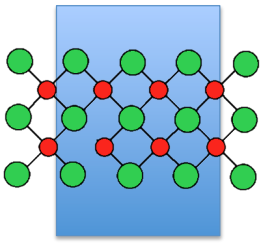
- **Free**/"shrink wrapped" – atoms move unconstrained through space. Usually used only in specific scenarios and systems…
  - Nanoparticles, molecules
  - Free surfaces (e.g. indentation problems)
  - Small volumes of fluids
- **Fixed** – atoms in a region are held fixed in space or given prescribed velocities/motions. This can often be effective for inducing mechanical loading on an atomic system. (However, it can introduce artificial thermal boundary resistance in dynamic systems)
- **Periodic**- typically used to approach the thermodynamic (large system) limit faster in dynamic systems but can be used to promote symmetry in loading/deformation



Constraints

Constraints g(x) can be effected by adding a Lagrange multiplier term to the PE

$$\phi = \Phi(x) + \frac{1}{2}\lambda g(x)$$



Or a penalty term λ=ε g(x)

For instance , a zero pressure constraint can be effect by a rescaling of the simulation box (LAMMPS "box/relax") since p = p(x) = p(FX) where g = p-p(x) = 0

External loading

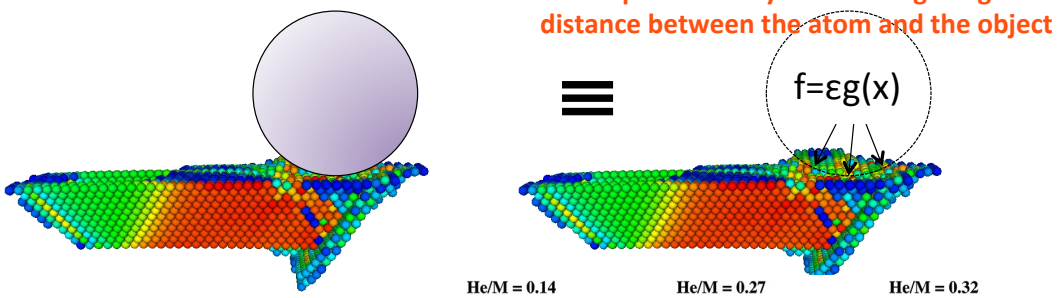
For an interaction between an atomic system contacting an indenter for example, we can use external. penalty forces to represent the object rather than simulating it directly

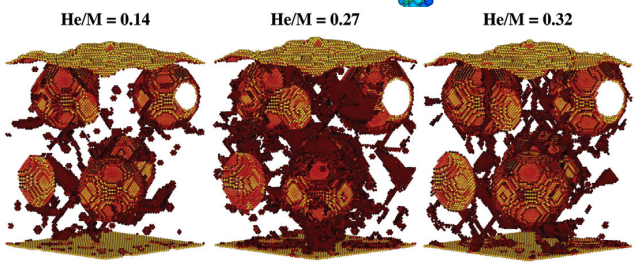
$$\phi = \Phi(x) + \frac{1}{2}\varepsilon g(x)^2$$

with

$$g(x) \geq 0$$

The impenetrability constraint g is signed distance between the atom and the object

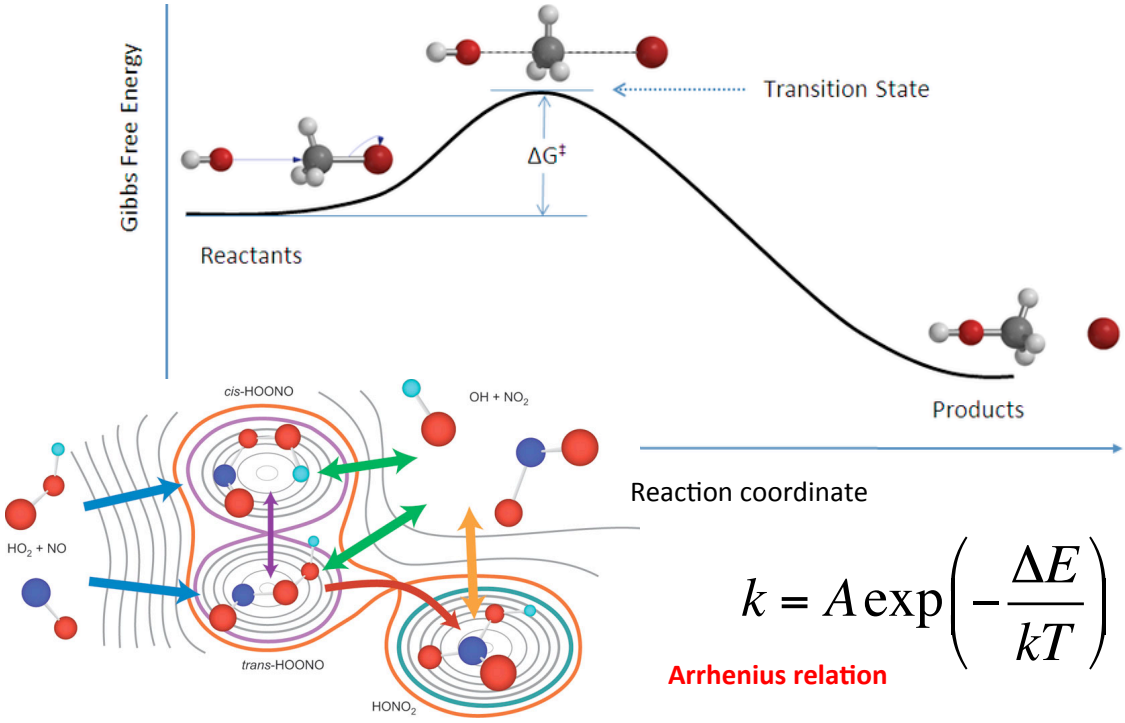




Simulating gas bubble expansion in a metal

Transition state theory

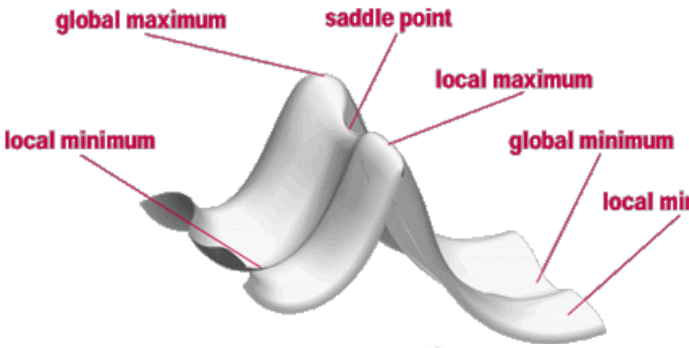
Other details of the PE surface beyond the local energy minima are useful, in fact, the barriers between adjacent minima are tied to transitions



$$k = A\exp\left(-\frac{\Delta E}{kT}\right)$$

Arrhenius relation

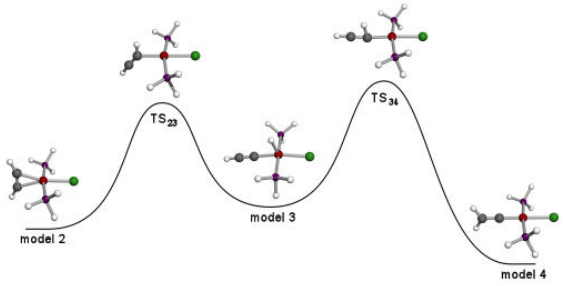
Transition states



Transition states are the configurations at the saddle points.

$$\det(\mathbf{D} - \lambda\mathbf{I}) = 0$$

$$\lambda_1 < 0 \quad \text{and} \quad \lambda_i > 0 \quad i > 1$$



A **saddle point** is a point on the PE surface where there is a minimum in all directions except one.

The **minimum energy path** (MEP) is the lowest energy path between two adjacent local minima separated by a saddle point.

Nudged elastic band

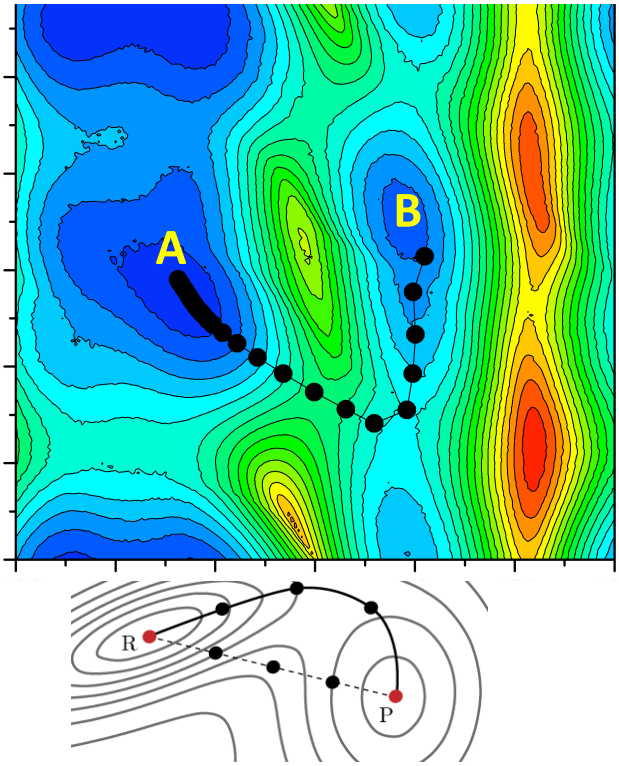
Nudged elastic band (NEB) is a method used to find points along the MEP, including the saddle point given two neighboring minima A and B.

A discrete number of configurations are created along the linear interpolation of A and B.

Then images are moved according to:

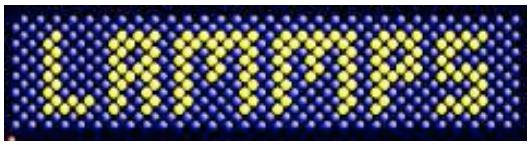
- the force acting on them perpendicular to the path
- an artificial spring force keeping the images spaced along the MEP.

The highest energy image gives a good estimate of the transition state.



Variations of NEB

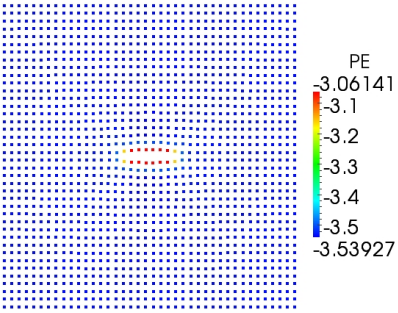
- **Original** – the total 'force' on each intermediate image is calculated by combining a tangential spring force and the normal projection of the true force along the path. Iteratively minimizing these image forces produces a MEP. The saddle point is determined by scanning the MEP for its maximum.
- **Improved tangent estimate** – Henkelman and Jónsson show that the original NEB method is *prone to the occurrence of kinks and an instability* in the elastic band if the number of images is sufficiently large. They developed modifications to the tangent vectors and spring forces to smooth the MEP.
- **Climbing image NEB** – as the configuration images are equally spaced, there is *no guarantee that the interpolation estimate for the saddle point has converged*. Henkelman et al. suggest modifications to the NEB whereby images can climb along the MEP to better home-in on the location of the saddle point, thereby improving the interpolation made to estimate it.

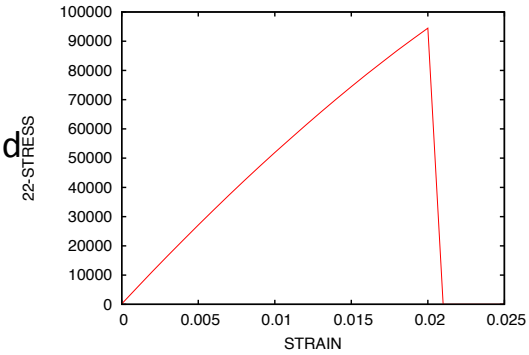


"Homework"

- Two choices:
  - Crack (materials science)
  - Carbon nanotube (molecules)
- Use a sequence of energy minimizations to extract the material response e.g. force vs. stretch or stress vs. strain
- Visualize the sequence of configuration, e.g.

dump2ensight.py crack.dmp
And then launch **paraview** and load *crack.case* **OR**
sed -i 's/^1 /C /g' cnt.xyz
And then launch **jmol** and load *cnt.xyz*

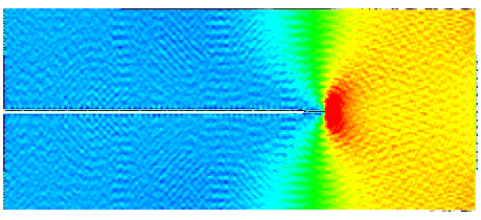




INPUT-Crack

```
boundary  p p p
atom_style      atomic
variable a equal 3.6150
lattice fcc $a origin 0.25 0.25 0.25
region    SYSTEM    block -10 10 -10 10 0 3
region    UPPER     block -10 10   0 10 0 3
region    LOWER     block -10  0 -10 10 0 3
create_box  1 SYSTEM
create_atoms  1 region SYSTEM
mass    1 63.55
group    internal region SYSTEM
group    UPPER region UPPER
group    LOWER region LOWER
pair_style  eam
pair_coeff  * * Cu_u3.eam
region  ABOVECRACK block -2.01 2.01  0 8 INF INF
units lattice
group   ABOVECRACK region ABOVECRACK
region  BELOWCRACK block -2.01 2.01 -8 0 INF INF
units lattice
group   BELOWCRACK region BELOWCRACK
neigh_modify  delay 1000000
neigh_modify  exclude group ABOVECRACK
BELOWCRACK
```

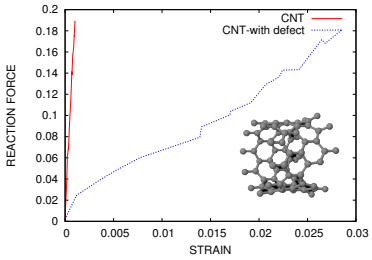
```
compute U all displace/atom
compute PE all pe/atom
dump CONFIG all custom 1000000 crack.dmp id
type x y z c_PE c_U[1] c_U[2] c_U[3]

variable L equal 20*$a
variable n equal 20
variable i loop $n
variable s equal 0.01*$L/$n
variable S equal pyy
label loop_i
  variable strain equal ($i-1)*$s
  change_box all y delta 0 $s remap units lattice
  minimize  0.0 1.e-10 100000 1000000
  print ">>> step $i strain ${strain} stress $S"
next i
jump SELF loop_i
```

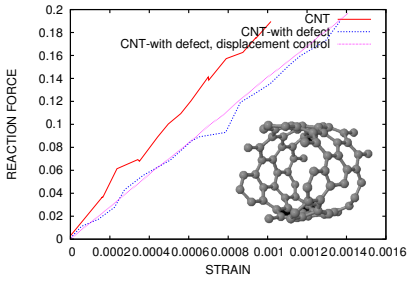


INPUT-CNT

```
boundary  s s f
read_data  cnt.data
lattice       diamond  3.6
pair_style  airebo 3.0
pair_coeff  * * ./CH.airebo C
mass          *  12.01

variable zhi equal zhi
variable zTip equal ${zhi}-4.0
variable zlo equal zlo
variable zLO equal ${zlo}+10

region  TIP block INF INF INF INF ${zTip} INF
units box
group TIP region TIP

region  FIXED block INF INF INF INF INF $
{zLO}  units box
group FIXED region FIXED

fix FIX FIXED setforce 0 0 0
compute CM TIP com
```

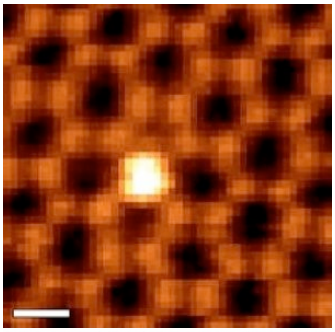
```
min_modify line quadratic
min_style cg
variable L0 equal c_CM[3]
variable n equal 40
variable i loop $n
variable s equal 0.025
label loop_i
  variable f equal ($i-1)*$s
  fix F TIP addforce 0 0 $f
  fix_modify F energy yes
  minimize  0.0 1.e-10 100000 1000000
  if "$i==1" then "variable L equal ${L0}"
  variable strain equal c_CM[3]/$L-1
  variable r equal f_FIX[3]
  print ">>> step $i strain ${strain} reaction $r"
  unfix F
next i
jump SELF loop_i
```

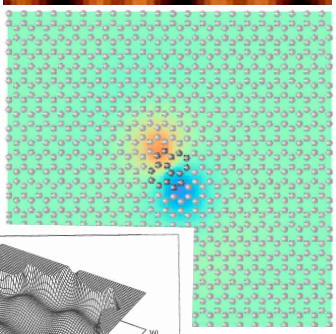


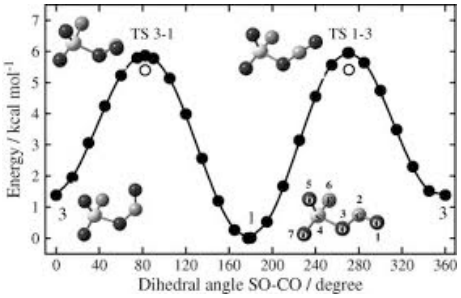


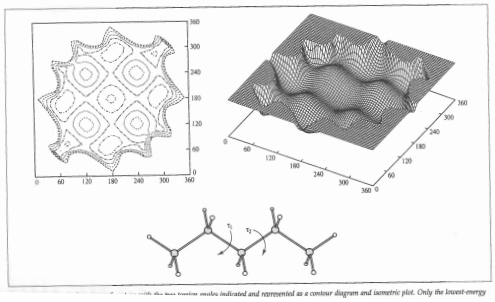
BONUS

- Change the loading increment, do you get the same response?
- Change the convergence tolerances, do you get the same response
- Convert the CNT input to displacement control, is the response different/more stable?
- Does it matter where the defect is in the CNT?
- Create a point defect in a periodic Si or C system, calculate the defect energy i.e. the difference in energy between a perfect system and the same system minus one atom. See the differences in energy and structure when a Stillinger-Weber vs Tersoff potential is used
- Calculate the energy surface for a simple molecule e.g. C_2H_6, as a function of rotation of one or more bonds









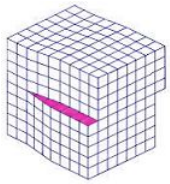
Further reading

Jonathan Richard Shewchuk, “An Introduction to the Conjugate Gradient Method Without the Agonizing Pain”, 1994

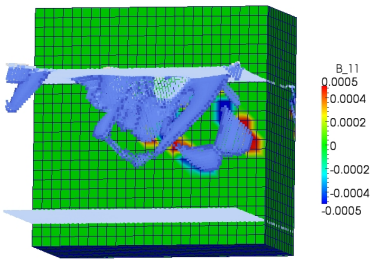
http://www.cs.cmu.edu/~jrs/jrspapers.html#cg

This article discusses first-order gradient methods in greater detail including :

- The quadratic origins of first-order methods
- How eigenvalues and eigenvectors fit in
- Stopping and Restarting the CG algorithm
- Preconditioning
- Canned algorithms
- Proofs



Lecture 7



Week 6: **Molecular Statics**

- Boundary conditions
- Energy minimization, e.g. the conjugate gradient algorithm
- Energy surface exploration, e.g. Nudged Elastic Band, transition states

Homework : Minimization of a point defect.

Week 7: **Analyzing Inhomogeneous Systems**

- Identification and visualization of defects and structures
- Metrics, e.g. radial distribution function, common neighbor analysis, centrosymmetry
- Available tools
- Homework: Calculation of centrosymmetry and slip vector around a defect

Reading Suggestions for Lec. 7

- Chapter 4 & 5 of Rapaport
- Chapter 2 & 8 Buehler
- http://en.wikipedia.org/wiki/Radial_distribution_function
- http://en.wikipedia.org/wiki/Molecular_dynamics
- http://lammps.sandia.gov/