1.021, 3.021, 10.333, 22.00 Introduction to Modeling and Simulation
Spring 2011

Part I – Continuum and particle methods

How to model chemical interactions

Lecture 5

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Content overview

I. Particle and continuum methods

Lectures 1-13

1. Atoms, molecules, chemistry
2. Continuum modeling approaches and solution approaches
3. Statistical mechanics
4. Molecular dynamics, Monte Carlo
5. Visualization and data analysis
6. Mechanical properties – application: how things fail (and how to prevent it)
7. Multi-scale modeling paradigm
8. Biological systems (simulation in biophysics) – how proteins work and how to model them

II. Quantum mechanical methods

Lectures 14-26

1. It's A Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. The Many-Body Problem: From Many-Body to Single-Particle
4. Quantum modeling of materials
5. From Atoms to Solids
6. Basic properties of materials
7. Advanced properties of materials
8. What else can we do?

Overview: Material covered so far…

- **Lecture 1: Broad introduction to IM/S**

- **Lecture 2**: **Introduction to atomistic and continuum modeling** (multi-scale modeling paradigm, difference between continuum and atomistic approach, case study: diffusion)

- **Lecture 3**: **Basic statistical mechanics – property calculation I** (property calculation: microscopic states vs. macroscopic properties, ensembles, probability density and partition function)

- **Lecture 4**: **Property calculation II** (advanced property calculation, introduction to chemical interactions, Monte Carlo method)

- **Lecture 5: How to model chemical interactions**

Lecture 5: How to model chemical interactions

Outline:

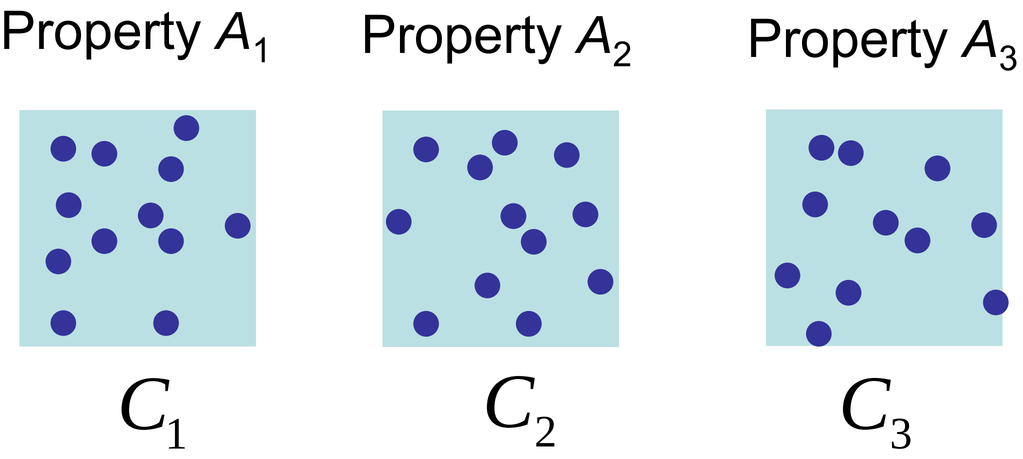
1. Monte-Carlo (MC) approach: Metropolis-Hastings algorithm
2. How to model chemical interactions
    - 2.1 Pair potentials
    - 2.2 How to model metals: Multi-body potentials

Goals of today's lecture:

- Get to know basic methods to model chemical bonds (starting with simple "pair potentials")
- Learn how to identify parameters for models of chemical bonds (for pair potentials)
- Limitations of pair potentials – and other, alternative methods

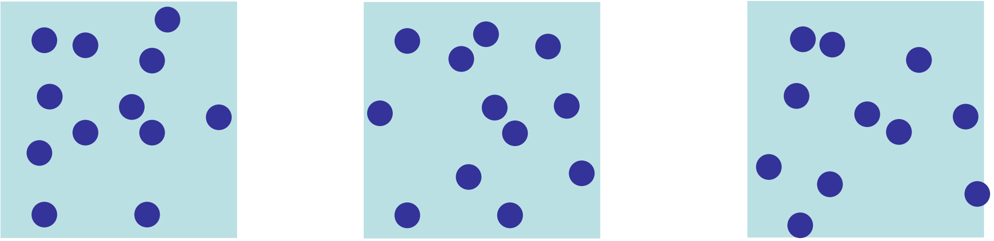
1. Monte-Carlo (MC) approach: Metropolis-Hastings algorithm

Averaging over the ensemble



$$A_{\text{macro}} \cancel{\neq} \frac{1}{3}\left(A_1 + A_2 + A_3\right)$$

Averaging over the ensemble



Property A_1 Property A_2 Property A_3

C_1 C_2 C_3

$$A_{\text{macro}} \neq \frac{1}{3}\left(A_1 + A_2 + A_3\right)$$

Instead, we must average with proper weights that represent the probability of a system in a particular microscopic state!

(I.e., not all microscopic states are equal)

$$A_{\text{macro}} = \rho_1 A_1 + \rho_2 A_2 + \rho_3 A_3 =$$

$$\rho_1(r_1, p_1)A_1(r_1, p_1) + \rho_2(r_2, p_2)A_2(r_2, p_2) + \rho_3(r_3, p_3)A_3(r_3, p_3)$$

$\uparrow$

Probability to find system in state C_1

How to solve…

$$< A > = \int_p \int_r A(p,r)\underset{\uparrow}{\rho}(p,r)\,dr\,dp$$

Probability density distribution

E.g.: $T(p) = \frac{1}{3}\frac{1}{Nk_B}\sum_{i=1}^{N}\frac{m_i^2\vec{v}_i^2}{m_i} = A(p)$

Virtually impossible to carry out analytically

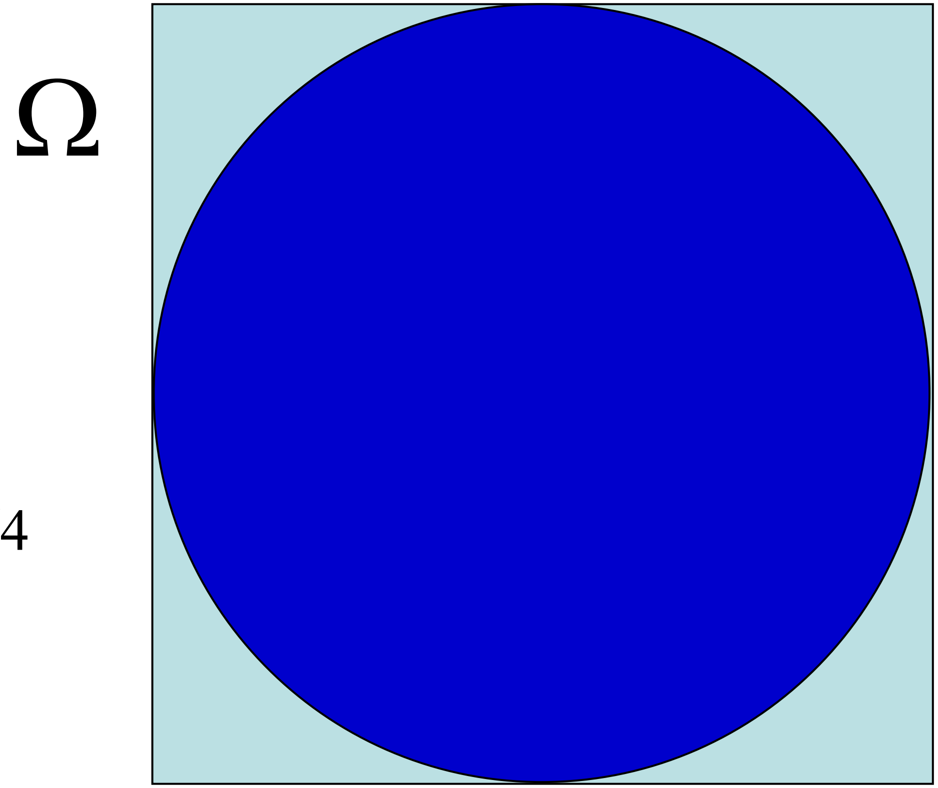
Must know all possible configurations

Therefore: Require numerical simulation

Molecular dynamics OR Monte Carlo

Monte Carlo scheme

Method to carry out integration over "domain"



$d = 1$

Want:

$$A = \int_{\Omega} f(\vec{x})\, d\Omega$$

E.g.: Area of circle (=π/4 exact solution)

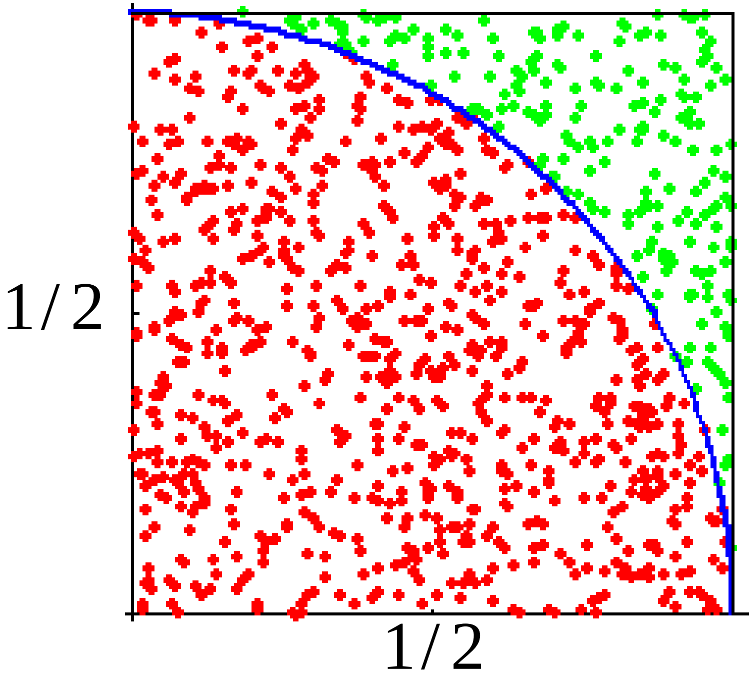
$$f(\vec{x}) = \begin{cases} 1 & \text{inside} \\ 0 & \text{outside} \end{cases}$$

$$A_C = \frac{\pi d^2}{4} \qquad A_C = \frac{\pi}{4}$$

$$\pi = 4A_C$$

Monte Carlo scheme for integration

- **Step 1**: Pick random point $\vec{x}_i$ in Ω
- **Step 2**: Accept/reject point based on criterion (e.g. if inside or outside of circle and if in area not yet counted)
- **Step 3**: If accepted, add $f(\vec{x}_i) = 1$ to the total sum



Courtesy of John H. Mathews. Used with permission.

$$A_C = \int_\Omega f(\vec{x}) d\Omega \qquad A_C = \frac{\pi}{16}$$

$$\Updownarrow$$

$$\boxed{A_C = \frac{1}{N_A} \sum_i f(\vec{x}_i)}$$

N_A: Attempts made

How to apply to ensemble average?

- Similar method can be used to apply to integrate the ensemble average

$$< A >= \int_p \int_r A(p,r)\rho(p,r)drdp$$

$$\rho(p,r) = \frac{1}{Q}\exp\left[-\frac{H(p,r)}{k_B T}\right]$$

“discrete”

$$< A >= \sum_{i=1}^{N_A} \frac{A\exp\left(-H(r_A,p_A)/\left(k_B T\right)\right)}{\sum_{i=1}^{N_A}\exp\left(-H(r_A,p_A)/\left(k_B T\right)\right)}$$

Computationally inefficient: If states are created “randomly” that have low probability….

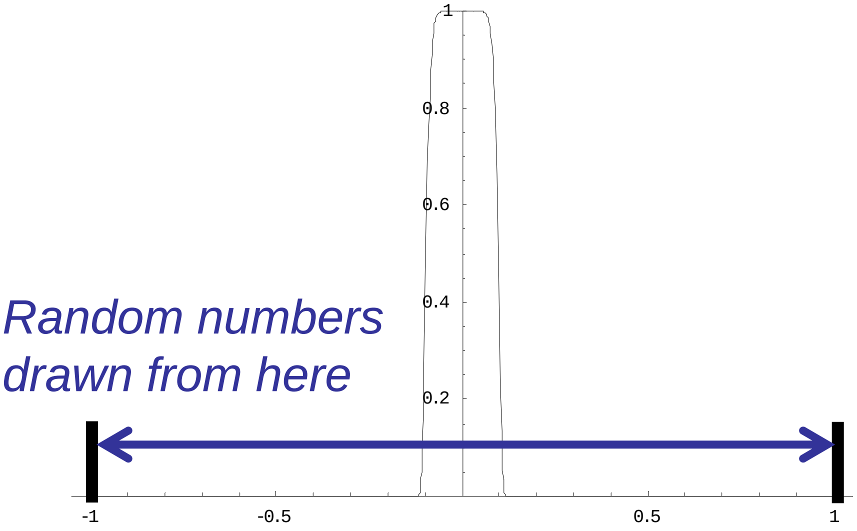
- To be computationally more effective, need more complex iteration scheme (replace “*random sampling*” by “*importance sampling*”)

Challenge: sampling specific types of distributions

- We want to
  - Integrate a sharply-peaked function
  - Use Monte Carlo with uniformly-distributed random numbers (e.g. here from -1 to 1)

$$f(x) = \exp\left(-(100x)^{12}\right)$$

$$A = \int_{-1}^{1} f(x)dx$$

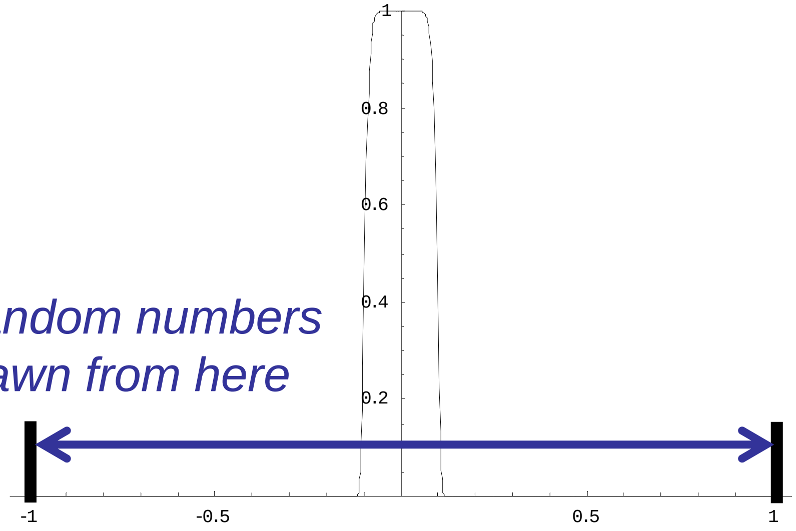


Challenge: sampling specific types of distributions

- We want to
  - Integrate a sharply-peaked function
  - Use Monte Carlo with uniformly-distributed random numbers (e.g. here from -1 to 1)
- What happens?
  - Very few points contribute to the integral (~9%)
  - Poor computational efficiency/convergence
- Solution: use a different distribution of random numbers to sample "*importance sampling*"

$$f(x) = \exp\left(-(100x)^{12}\right)$$

$$A = \int_{-1}^{1} f(x)dx$$



Random numbers drawn from here

Importance sampling

- **Core concept:** Picking states with a biased probability: Importance sampling (sampling the “correct” way…)

$$< A >= \int_p \int_r A(p,r)\rho(p,r)\,dr\,dp \qquad \rho(p,r) = \frac{1}{Q}\exp\left[-\frac{H(p,r)}{k_B T}\right]$$

Importance sampling

- **Core concept:** Picking states with a biased probability: Importance sampling (sampling the “correct” way…)

$$< A >= \int_p \int_r A(p,r)\rho(p,r)drdp \qquad \rho(p,r) = \frac{1}{Q}\exp\left[-\frac{H(p,r)}{k_B T}\right]$$

Notice: Probability (and thus importance) related to energy of state

Importance sampling: Metropolis algorithm

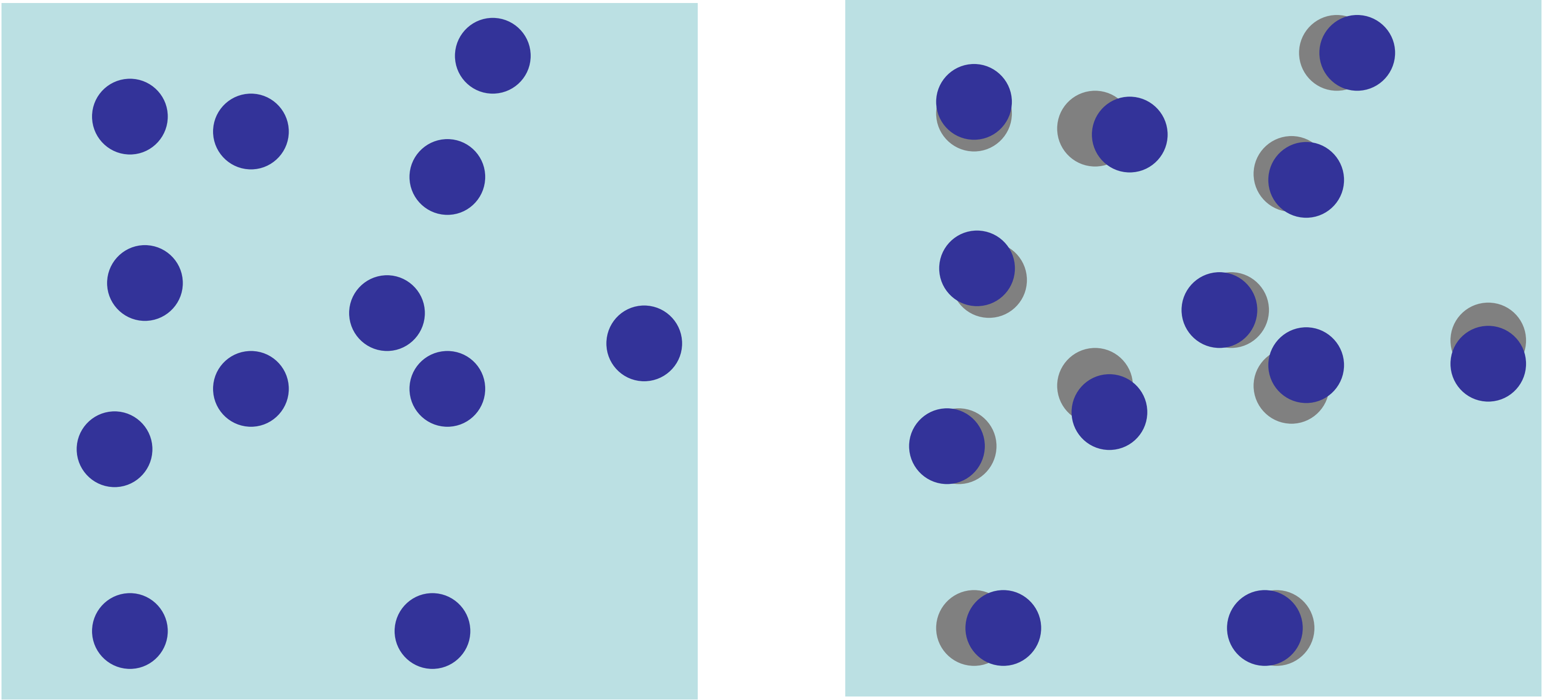
- Leads to an appropriate “chain” of states, visiting each state with **correct probability**

- Concept:
  - Pick random initial state
  - Move to trial states
  - Accept trial state with certain probability (based on knowledge about behavior of system, *i.e*., energy states)

Original reference: *J. Chem. Phys.* **21**,1087, 1953

Metropolis-Hastings Algorithm

Concept: Generate set of random microscopic configurations
Accept or reject with certain scheme



State A

State B

Random move to new state B

Metropolis-Hastings Algorithm: *NVT*

Have: State A (initial state) + energy function $H(A)$

Step 1: Generate new state B (random move)

Metropolis-Hastings Algorithm: *NVT*

Have: State A **(initial state) + energy function** $H(A)$

Step 1: **Generate new state** B **(random move)**

Step 2: **if** $H(B)<H(A)$ **then** $a = 1$

else

Draw random number $0 < p < 1$

a = true[1]/false[0]
for acceptance

"Downhill" moves
always accepted

Metropolis-Hastings Algorithm: *NVT*

Have: State A (initial state) + energy function $H(A)$

```
Step 1:  Generate new state $B$ (random move)
Step 2:  if $H(B)<H(A)$ then $\boxed{a = 1}$
         else
             Draw random number $0 < p < 1$
             if $p < \exp\left[-\frac{H(B)-H(A)}{k_B T}\right]$ $\boxed{a = 1}$
             else
                 $\boxed{a = 0}$
             endif
```

a = true[1]/false[0]
for acceptance

"Downhill" moves always accepted, uphill moves with finite ("thermal") probability

a=variable either 0 or 1

Metropolis-Hastings Algorithm: *NVT*

```
Have: State $A$ (initial state) + energy function $H(A)$

Step 1:  Generate new state $B$ (random move)

Step 2:  if $H(B)<H(A)$ then $a = 1$
         else
                Draw random number $0 < p < 1$
                if $p < \exp\left[-\frac{H(B)-H(A)}{k_B T}\right]$  $a = 1$
                else
                        $a = 0$
                endif
         endif

Step 3:  if $a = 1$ then accept state $B$
         endif
```

a = true[1]/false[0]
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a=variable either 0 or 1
(used to detect acceptance
of state B when a=1)

Metropolis-Hastings Algorithm: *NVT*

```
Have: State $A$ (initial state) + energy function $H(A)$
repeat $N_A$ times
    Step 1: Generate new state $B$ (random move)
    Step 2: if $H(B)<H(A)$ then $a = 1$
            else
                Draw random number $0 < p < 1$
                if $p < \exp\left[-\frac{H(B)-H(A)}{k_B T}\right]$ $a = 1$
                else
                    $a = 0$
                endif
            endif
    Step 3: if $a = 1$ then accept state $B$
            endif
```

a = true[1]/false[0]
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a=variable either 0 or 1
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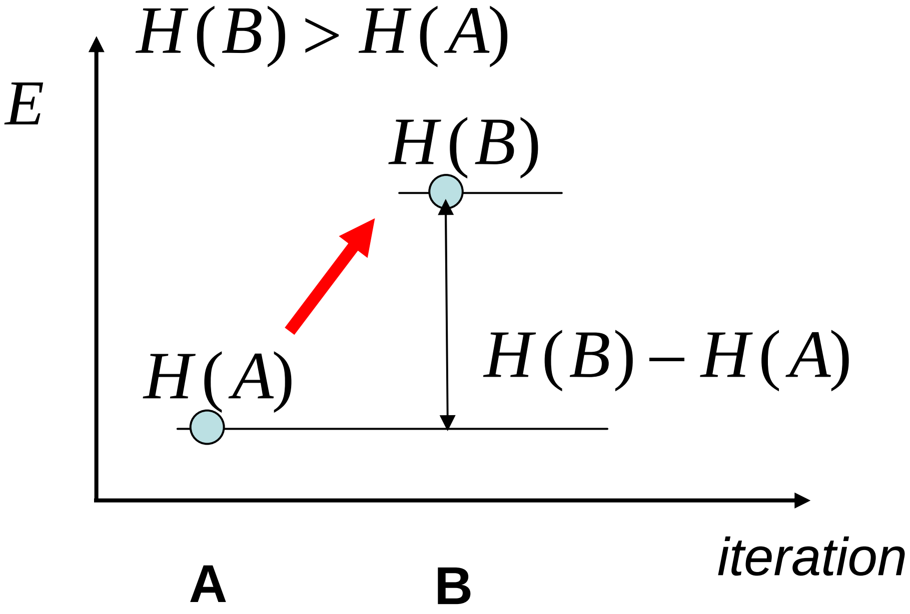
$$< A >= \frac{1}{N_A} \sum_{i=1..N_A} A(i)$$

Arrhenius law - explanation

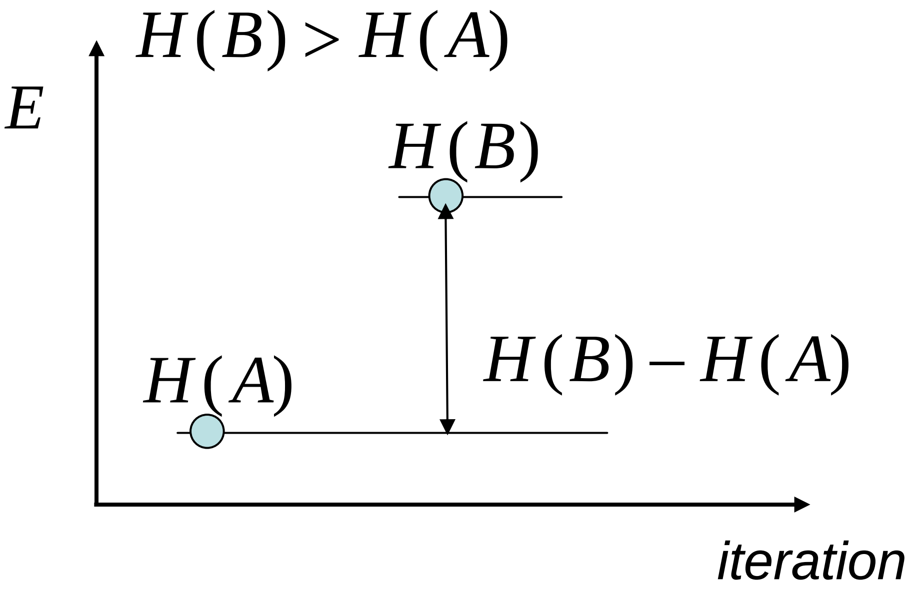


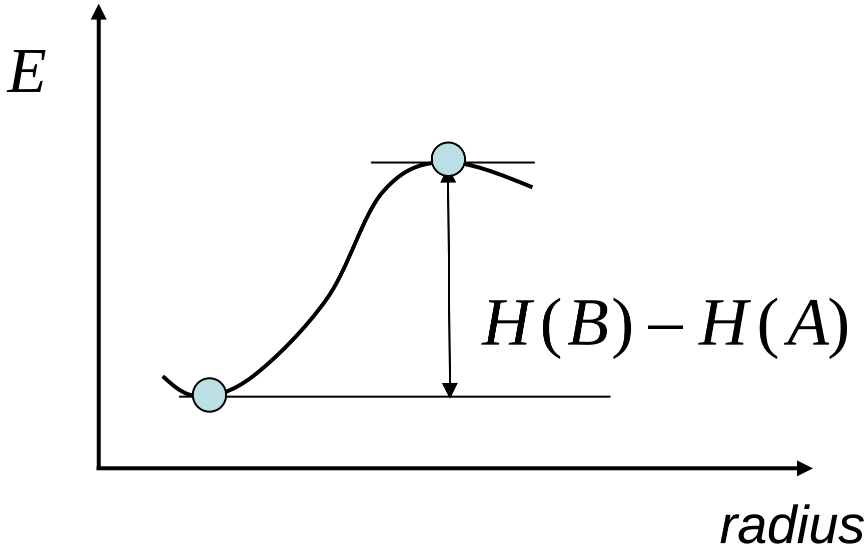
Consider two states, A and B

State B *has higher energy than state* A

Otherwise accepted anyway!

Arrhenius law - explanation





Energy difference between
states A and B
("uphill")

Probability of success of overcoming the barrier at temperature T

$$\exp\left[-\frac{H(B)-H(A)}{k_B T}\right]$$

Arrhenius law - explanation

Probability
of success
of overcoming the
barrier

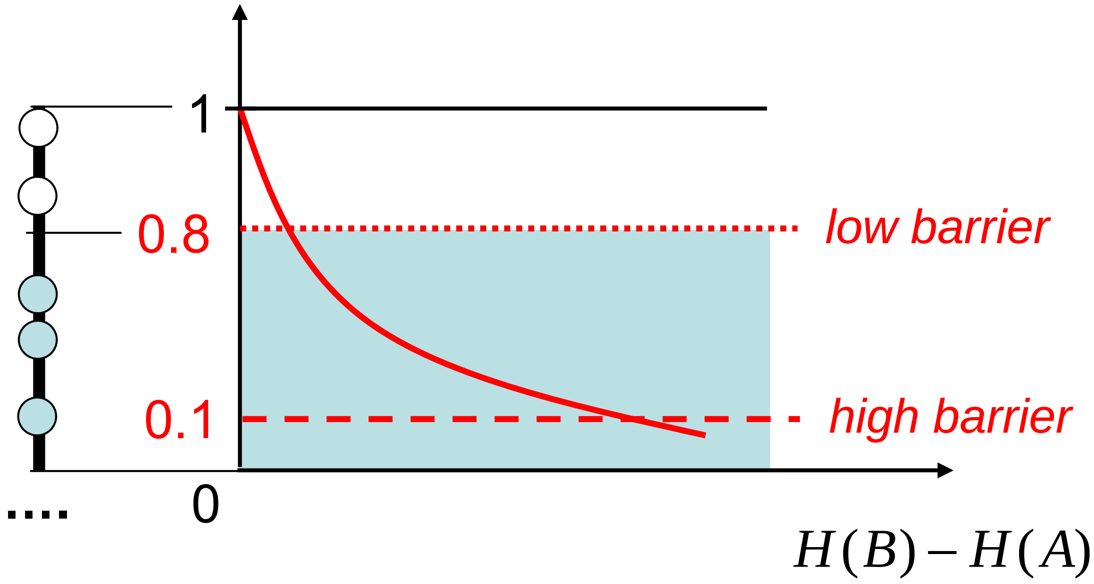
$$\exp\left[-\frac{H(B)-H(A)}{k_B T}\right]$$

Random number $0 < p < 1$
(equal probability to draw any number between 0 and 1)

Acceptance if:

$$p < \exp\left[-\frac{H(B)-H(A)}{k_B T}\right]$$

E.g. when $\exp(..) = 0.8$ most choices for p will be below, that is, higher chance for acceptance



Play "1D darts"

Summary: Metropolis-Hastings Algorithm

```
Have: State $A$ (initial state) + energy function $H(A)$

repeat $N_A$ times
    Step 1:  Generate new state $B$ (random move)
    Step 2:  if $H(B)<H(A)$ then $a = 1$
             else
                 Draw random number $0 < p < 1$
                 if $p < \exp\left[-\frac{H(B)-H(A)}{k_B T}\right]$ $a = 1$
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a=variable either 0 or 1
(used to detect acceptance
of state B when a=1)

$$< A >= \frac{1}{N_A} \sum_{i=1..N_A} A(i)$$

Summary: MC scheme

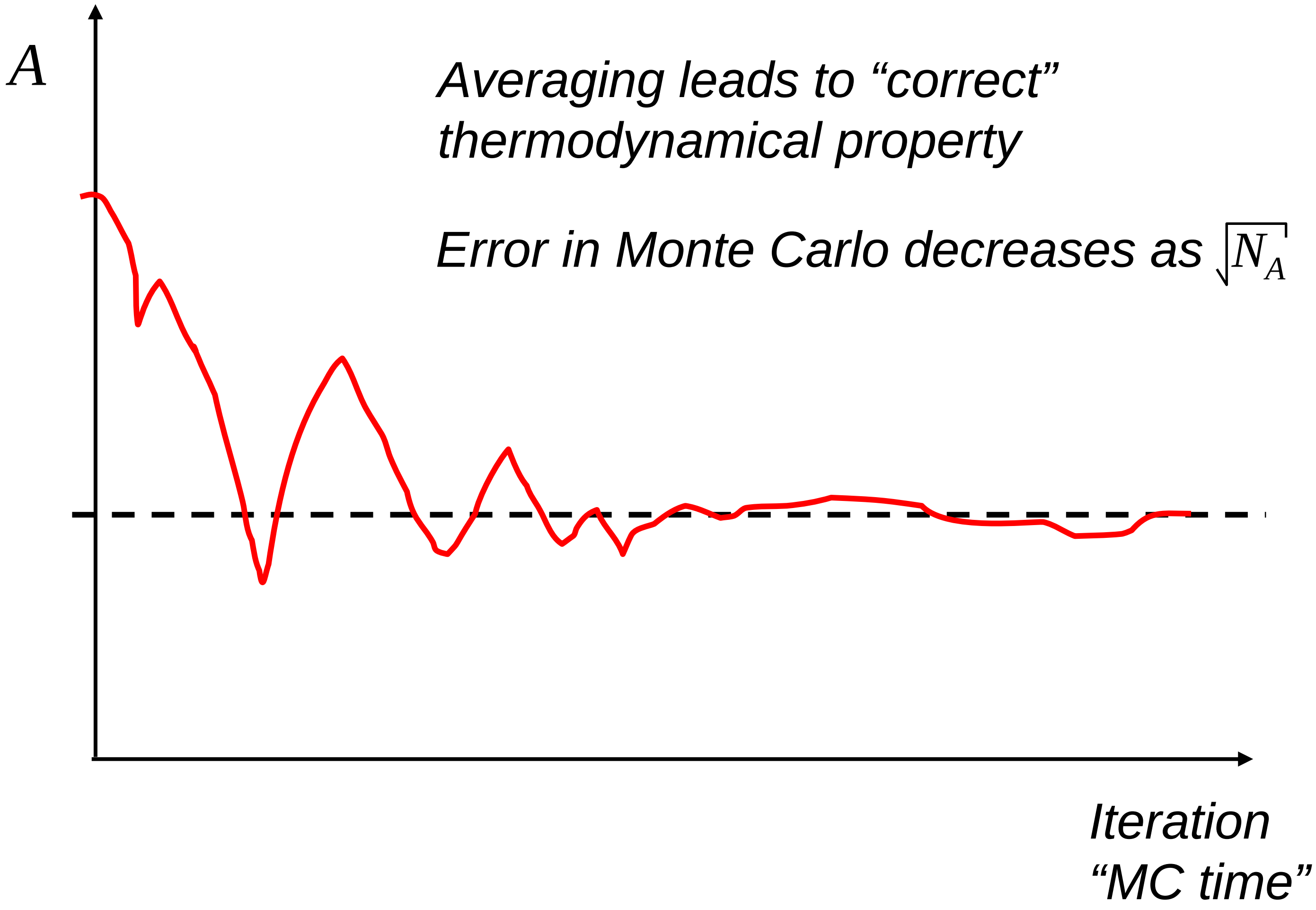
Have achieved:

$$< A >= \int\limits_p \int\limits_r A(p,r)\rho(p,r)drdp \quad \longleftrightarrow \quad \boxed{< A > \frac{1}{N_A} \sum_{i=1..N_A} A_i}$$

Note:

- Do not need forces between atoms (for accelerations)
- Only valid for equilibrium processes

Property calculation with MC: example



Averaging leads to “correct” thermodynamical property

Error in Monte Carlo decreases as $\sqrt{N_A}$

Complex moves

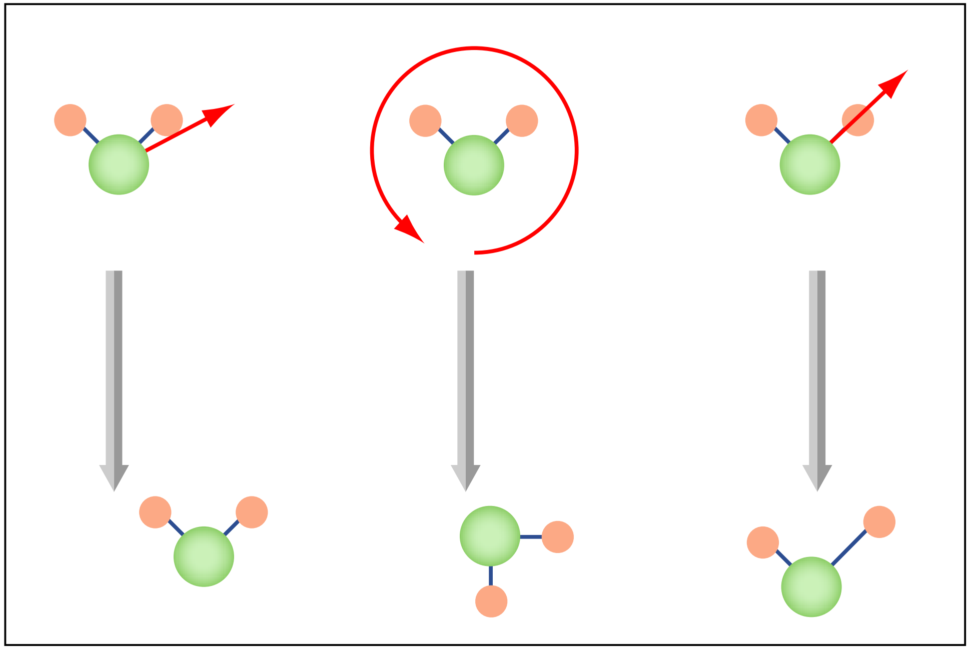
- Move sets can be adapted for other cases, e.g. not just move of particles but also **rotations of side chains** (=rotamers), **torsions**, etc.

  E.g. application in protein folding problem when we'd like to determine the 3D folded structure of a protein in thermal equilibrium

After: R.J. Sadus

Possible Monte Carlo moves

- Trial moves
  - Rigid body translation
  - Rigid body rotation
  - Internal conformational changes (soft vs. stiff modes)
  - Titration/electronic states
  - …
- Questions:
  - How “big” a move should we take?
  - Move one particle or many?



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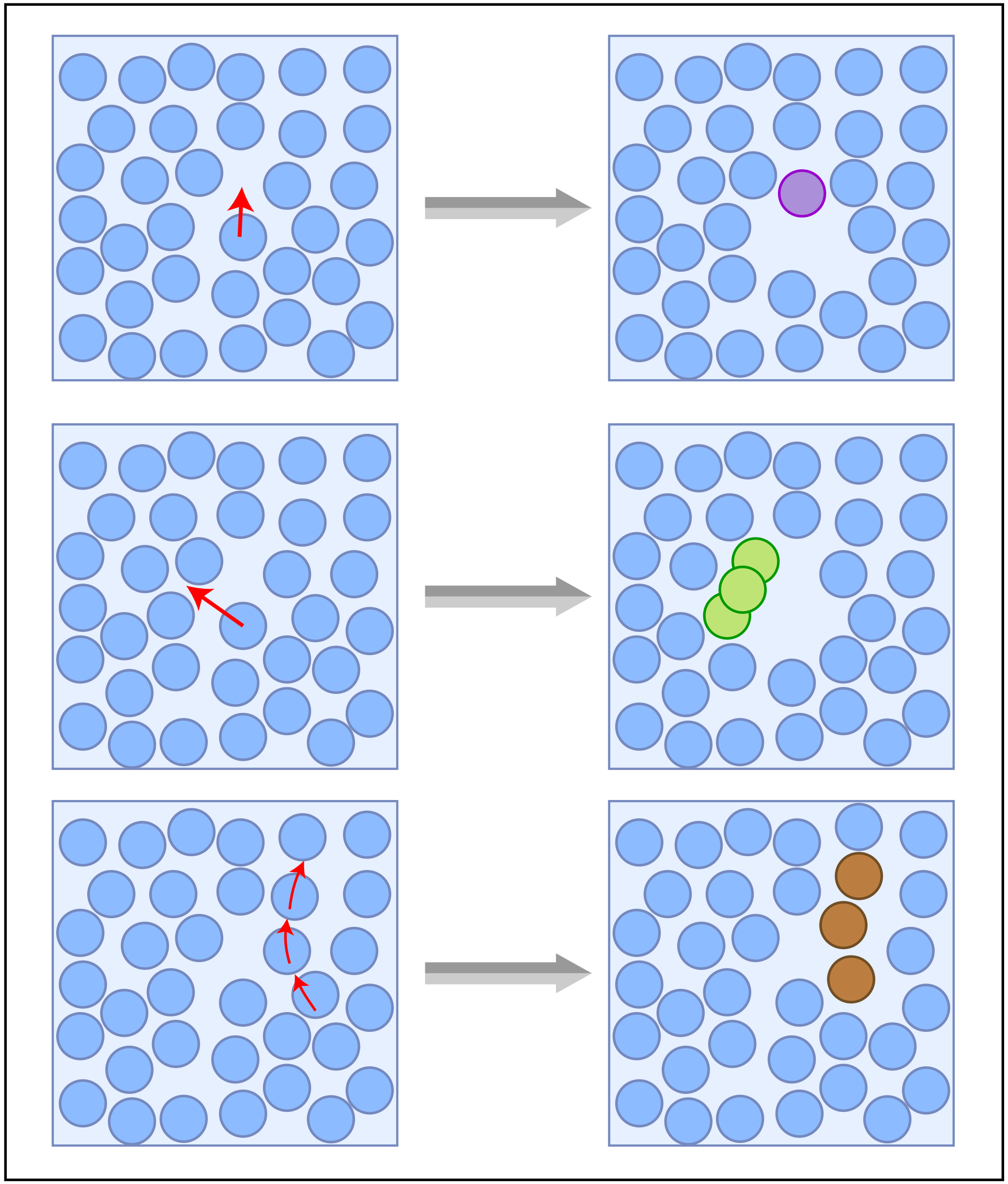
Monte Carlo moves

- How "big" a move should we take?
  - **Smaller moves**: better acceptance rate, slower sampling
  - **Bigger moves**: faster sampling, poorer acceptance rate
- Move one particle or many?
  - Possible to achieve more efficient sampling with *correct* multi-particle moves
  - One-particle moves must choose particles at random



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2. How to model chemical interactions

Atomic interactions – different types of chemical bonds

- **Primary bonds (“strong”)**
  - Ionic (ceramics, quartz, feldspar - **rocks**)
  - Covalent (**silicon**)
  - Metallic (copper, nickel, **gold**, silver)
    (high melting point, 1000-5,000K)

- **Secondary bonds (“weak”)**
  - Van der Waals (**wax**, low melting point)
  - Hydrogen bonds (proteins, **spider silk**)
    (melting point 100-500K)

Atomic interactions – different types of chemical bonds

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  - Hydrogen bonds (proteins, **spider silk**)
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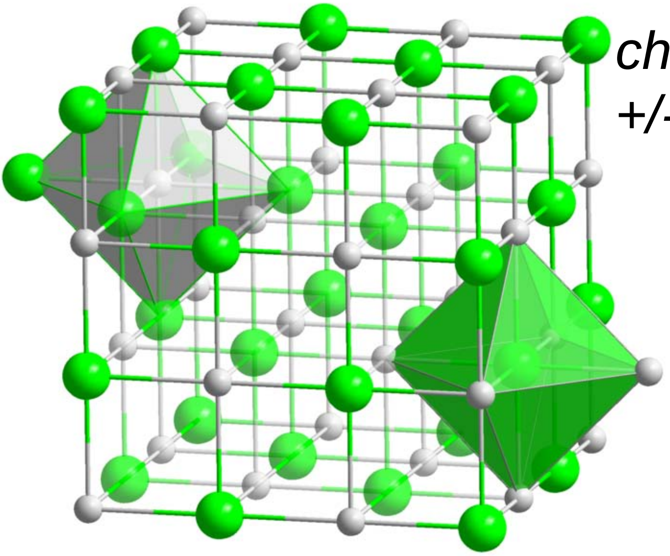
- Ionic: Non-directional (point charges interacting)
- Covalent: Directional (bond angles, torsions matter)
- Metallic: Non-directional (electron gas concept)

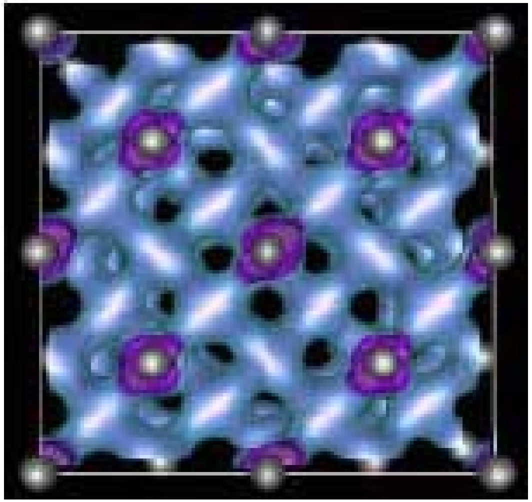
Difference of material properties originates from different atomic interactions

Types of bonding (illustrations)



charge +/-

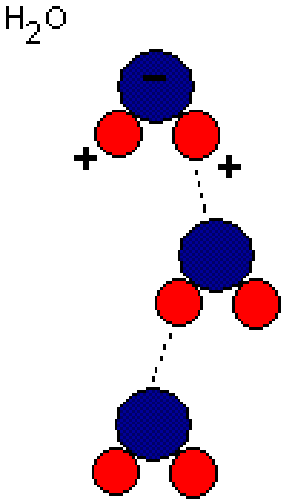
Ionic bonding



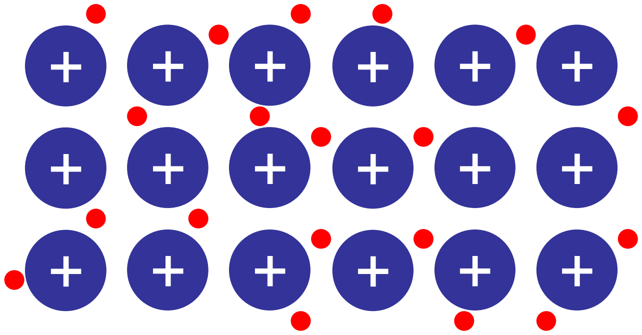
electron density (localized!)

Covalent bonding

Hydrogen bonding



donor/ acceptor



Metallic bonding

Wax

Courtesy of Ruth Ruane, http://www.whitewitch.ie. Used with permission.

Soft, deformable, does not break under deformation

Rocks

Image courtesy of Wikimedia Commons.

Quite brittle (breaks e.g. during earthquake)

Rocks and sand on Mars

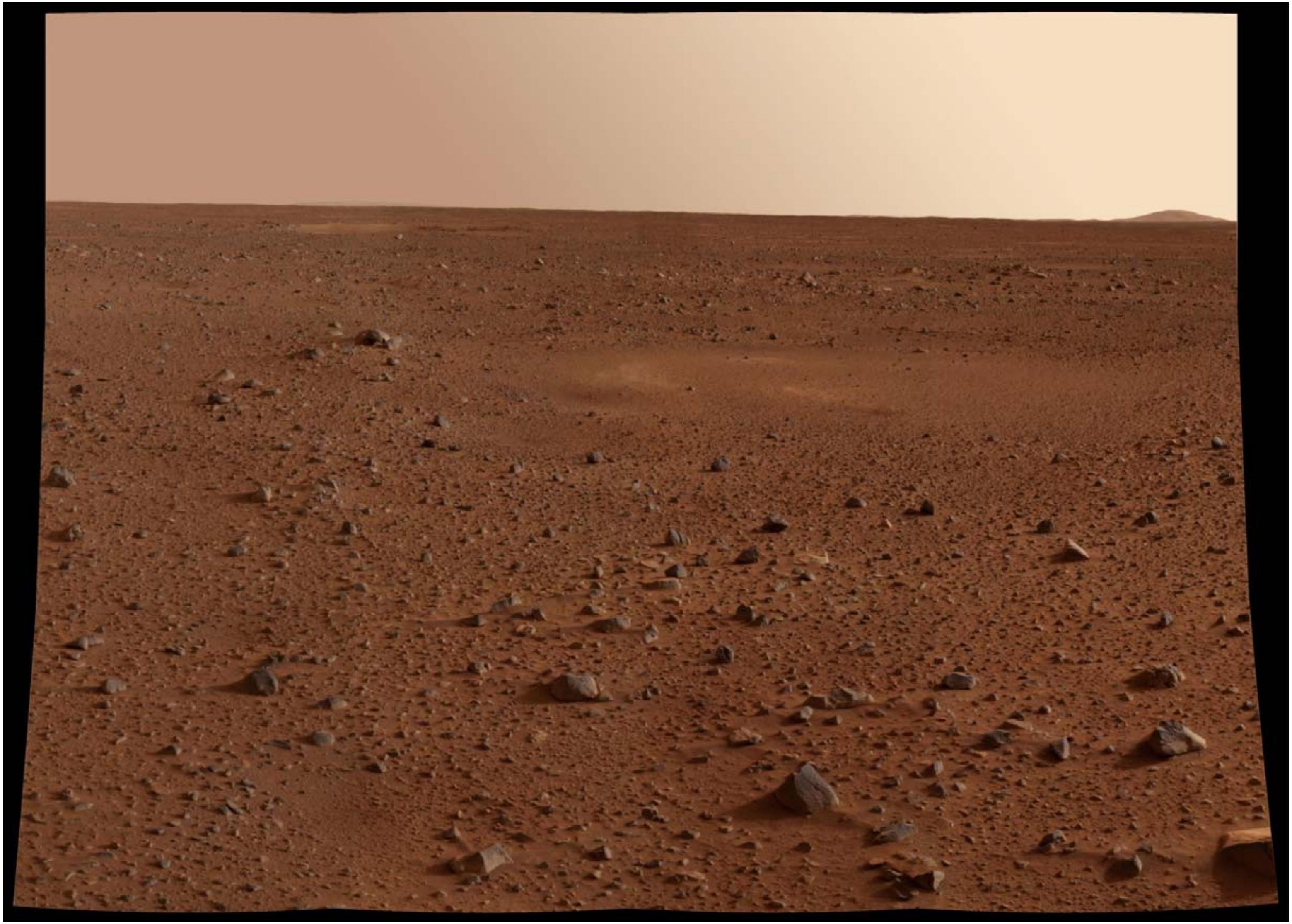


Image courtesy of NASA.

What are the properties and composition of extraterrestrial rocks?

Gold

Image courtesy of Wikimedia Commons.

Very “soft” metal, deformable, high density

Silicon

Image courtesy of NASA.

Rather brittle – shatters into many pieces if dropped

Spider web

Image courtesy of U.S. Fish and Wildlife Service.

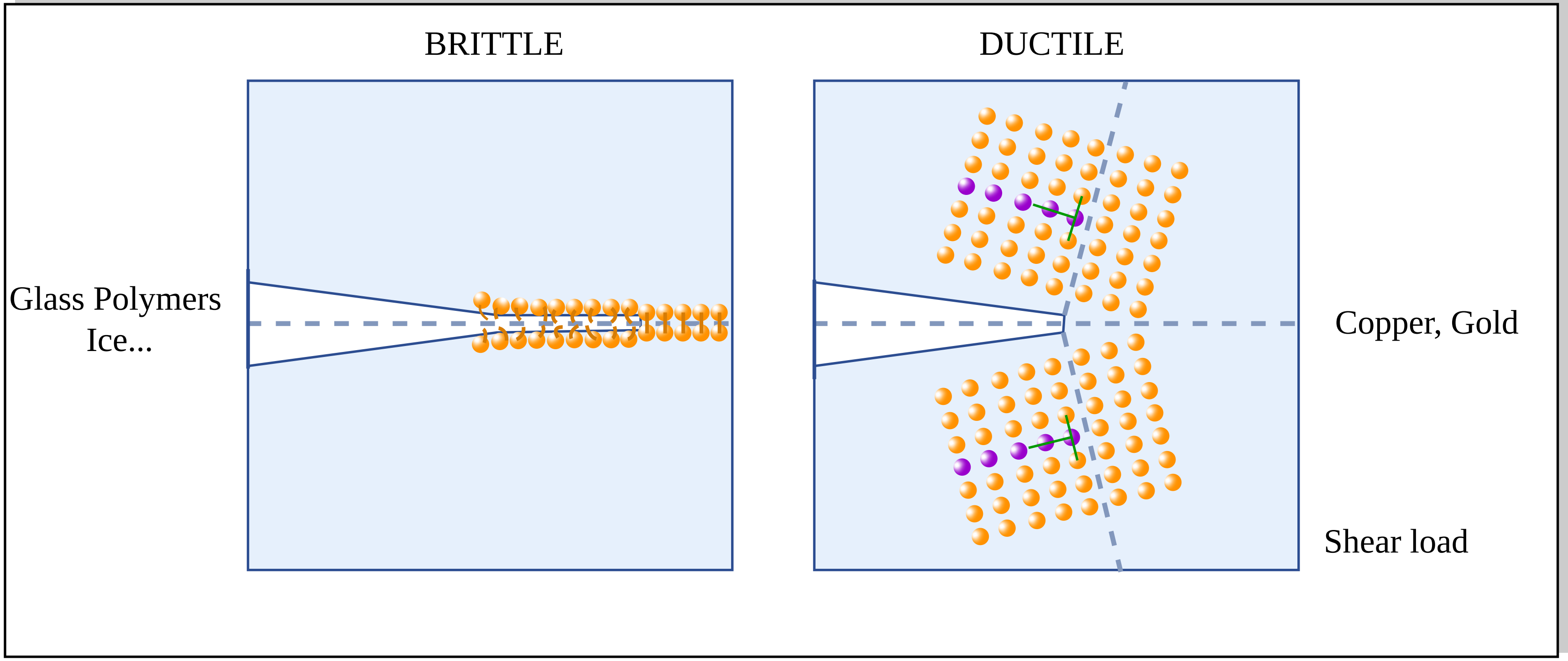
Very extensible, deformation, yet very strong (similar to steel)

Tree’s leaf

Image courtesy of Wikimedia Commons.

Very deformable under bending (wind loads), but breaks easily under tear

Particularly intriguing…brittle or ductile?



BRITTLE

DUCTILE

Glass Polymers
Ice...

Copper, Gold

Shear load

Image by MIT OpenCourseWare.

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Outline

- Goal: model chemical bonds with the objective to enable force calculation (see lecture 2, basic MD algorithm) or energy calculation (see lecture 4/5, MC)

- **Two-step approach**:

  1. Define energy landscape, *i.e.* defines how distance between particles controls the energy stored in the bond

  2. Then take derivatives to obtain forces, to be used in the MD algorithm

“Modeling and simulation” paradigm:

- First, develop mathematical expressions (modeling)
- Second, use model in numerical solution (simulation, =MD)

Models for atomic interactions

- Define interatomic potentials that describe the energy of a set of atoms as a function of their coordinates r:

$$U_{total} = U_{total}(r)$$

Depends on position of all other atoms

$$r = \left\{ \vec{r}_j \right\} \quad j = 1..N$$

Models for atomic interactions

- Define interatomic potentials that describe the energy of a set of atoms as a function of their coordinates r:

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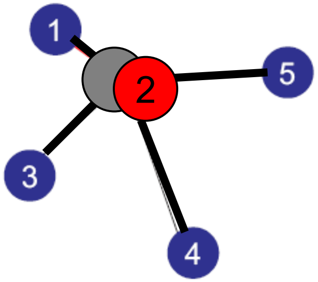


$$\boxed{\vec{F}_i = -\nabla_{\vec{r}_i} U_{total}(r)} \quad i = 1..N$$

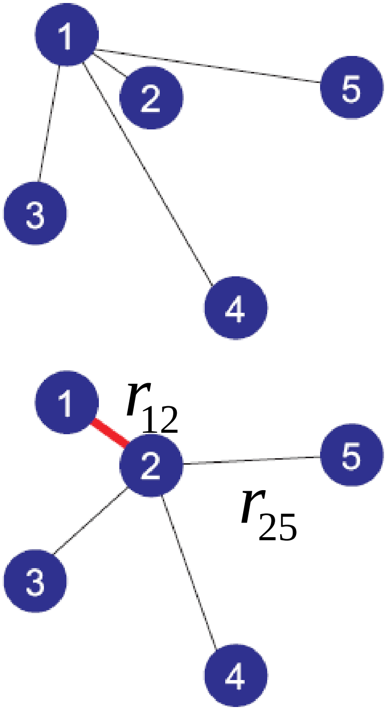
$$\nabla_{\vec{r}_i} = \left(\frac{\partial}{\partial r_{1,i}}, \frac{\partial}{\partial r_{2,i}}, \frac{\partial}{\partial r_{3,i}} \right)$$

Change of potential energy due to change of position of particle i ("gradient")

2.1 Pair potentials

Pair potentials: energy calculation

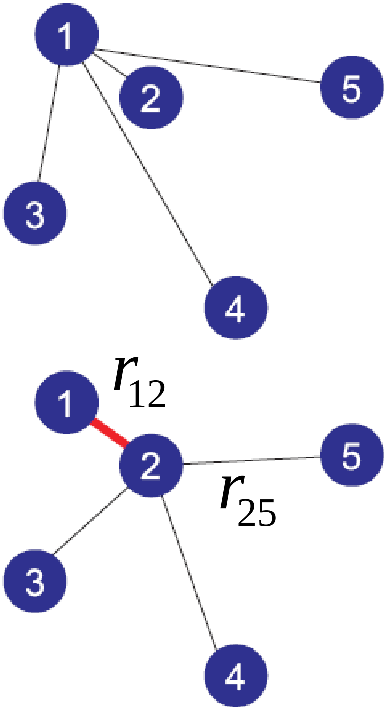
Simple approximation: Total energy is sum over the energy of all pairs of atoms in the system



$r_{ij} =$ distance between particles i and j

Pair potentials: energy calculation

Simple approximation: Total energy is sum over the energy of all pairs of atoms in the system



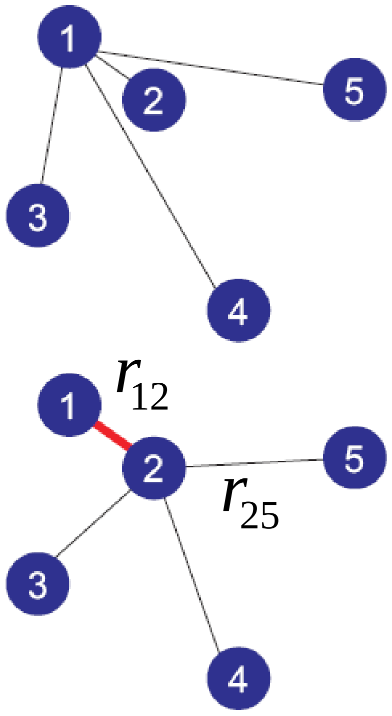
$r_{ij} =$ distance between particles i and j

$$\downarrow$$

$\phi(r_{ij})$ Pair wise interaction potential energy for each bond

Pair potentials: energy calculation

Simple approximation: Total energy is sum over the energy of all pairs of atoms in the system



r_{ij} = distance between particles i and j

$$\downarrow$$

$\phi(r_{ij})$ Pair wise interaction potential energy for each bond

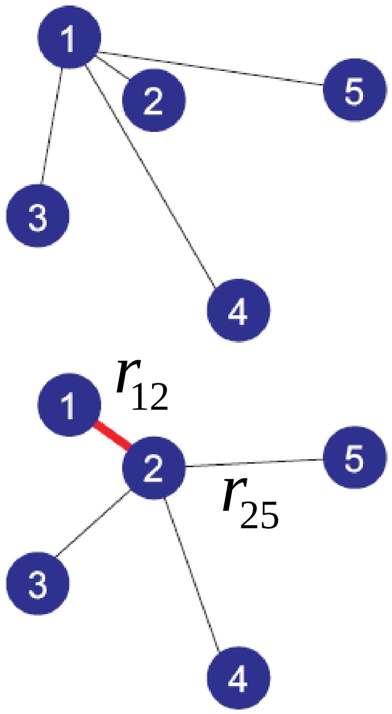
Energy of atom i $U_i = \sum_{j=1}^{N} \phi(r_{ij})$

Overview - pair potentials: total energy calculation

Simple approximation: Total energy is sum over the energy of all pairs of atoms in the system

Pair wise interaction potential

$$\phi(r_{ij})$$



Pair wise summation of bond energies

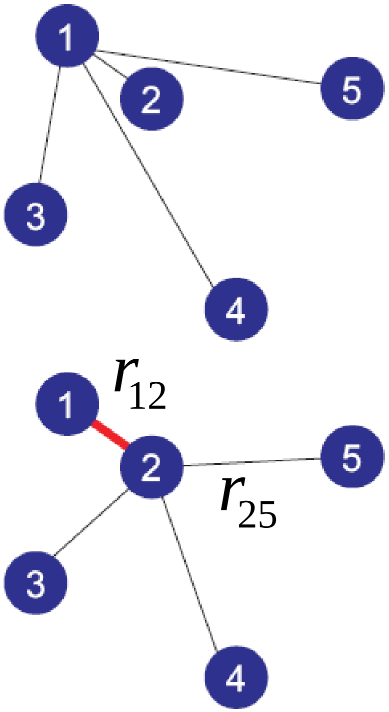
Energy of atom *i* $$U_i = \sum_{j=1}^{N} \phi(r_{ij})$$

avoid double counting

$$U_{total} = \frac{1}{2} \sum_{i=1, i \neq j}^{N} \overbrace{\sum_{j=1}^{N} \phi(r_{ij})}$$

r_{ij} = distance between particles *i* and *j*

Example: calculation of total energy



two "loops" over pairs of all particles

$$U_{total} = \tfrac{1}{2} \sum_{i=1, i \neq j}^{N} \sum_{j=1}^{N} \phi(r_{ij})$$

with $\phi_{ij} = \phi(r_{ij})$

$$U_{total} = \frac{1}{2}\left(\phi_{12} + \phi_{13} + \phi_{14} + \phi_{1N} \ldots + \phi_{21} + \phi_{23} + \ldots + \phi_{2N} + \ldots + \phi_{N-1,N}\right)$$

Interatomic pair potentials: examples

$$\phi(r_{ij}) = D\exp\left(-2\alpha(r_{ij}-r_0)\right) - 2D\exp\left(-\alpha(r_{ij}-r_0)\right)$$

Morse potential

$$\phi(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

Lennard-Jones 12:6 potential
(excellent model for noble Gases, Ar, Ne, Xe..)

$$\phi(r_{ij}) = A\exp\left(-\frac{r_{ij}}{\sigma}\right) - C\left(\frac{\sigma}{r_{ij}}\right)^{6}$$

Buckingham potential

$$\phi(r_{ij}) = a_0 + \frac{1}{2}k(r_{ij}-r_0)^2$$

Harmonic approximation
(no bond breaking)

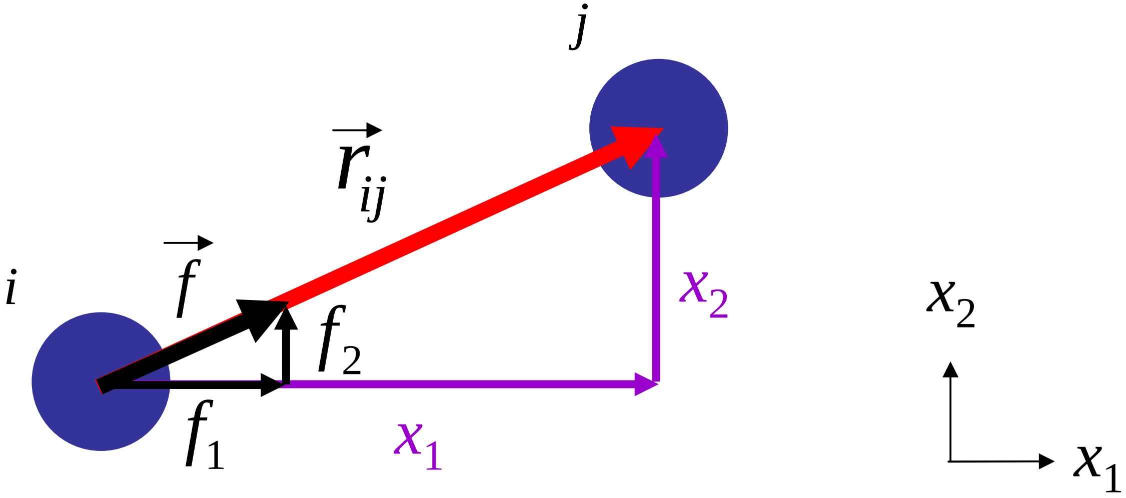
How to use a pair potential, e.g. LJ

Force calculation – pair potential

Forces on particles can be calculated by taking derivatives from the potential function & by considering all pairs of atoms

Start with **force magnitude (STEP 1):** Negative derivative of potential energy with respect to atomic distance

$$F = -\frac{\mathrm{d}\,\phi(r)}{\mathrm{d}\,r}\Big|_{r=r_{ij}} = -\frac{\mathrm{d}\,\phi(r_{ij})}{\mathrm{d}\,r_{ij}} = -\phi'(r_{ij})$$



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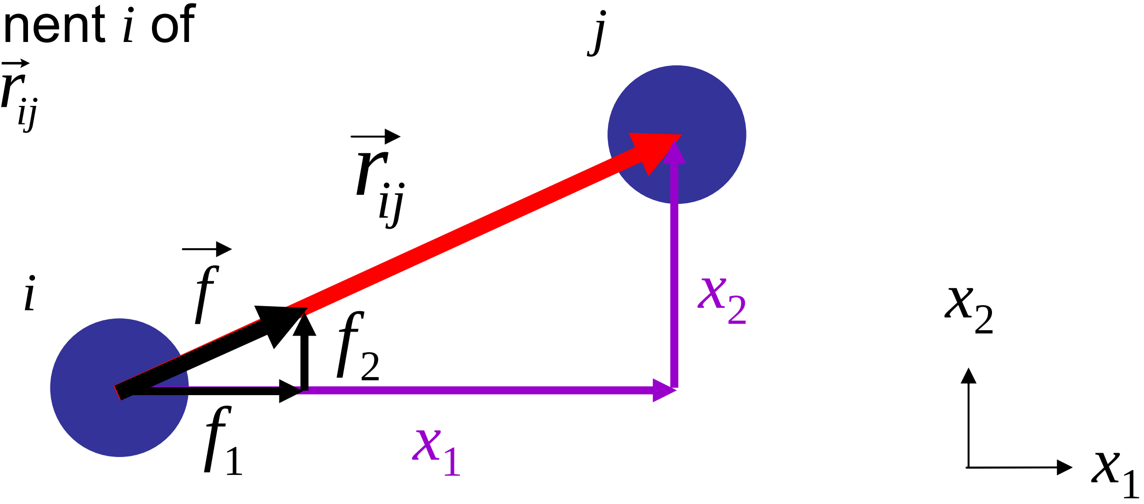
Calculate **force vector (STEP 2)**:

Component i of vector $\vec{r}_{ij}$

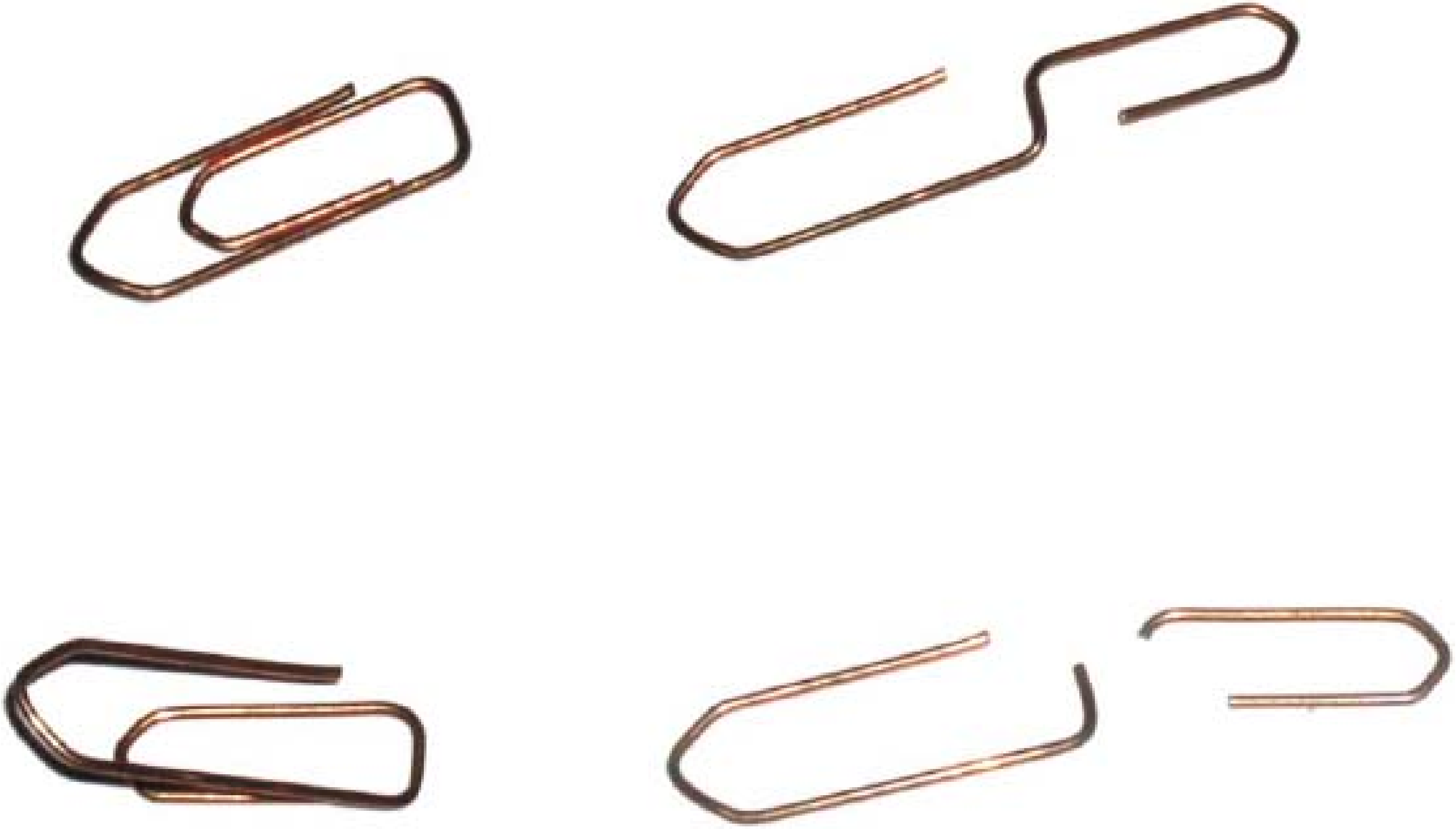
$$f_i = F\frac{x_i}{r_{ij}} \qquad \vec{f} = f_i \vec{e}_i$$

$$r_{ij} = \left|\vec{r}_{ij}\right|$$

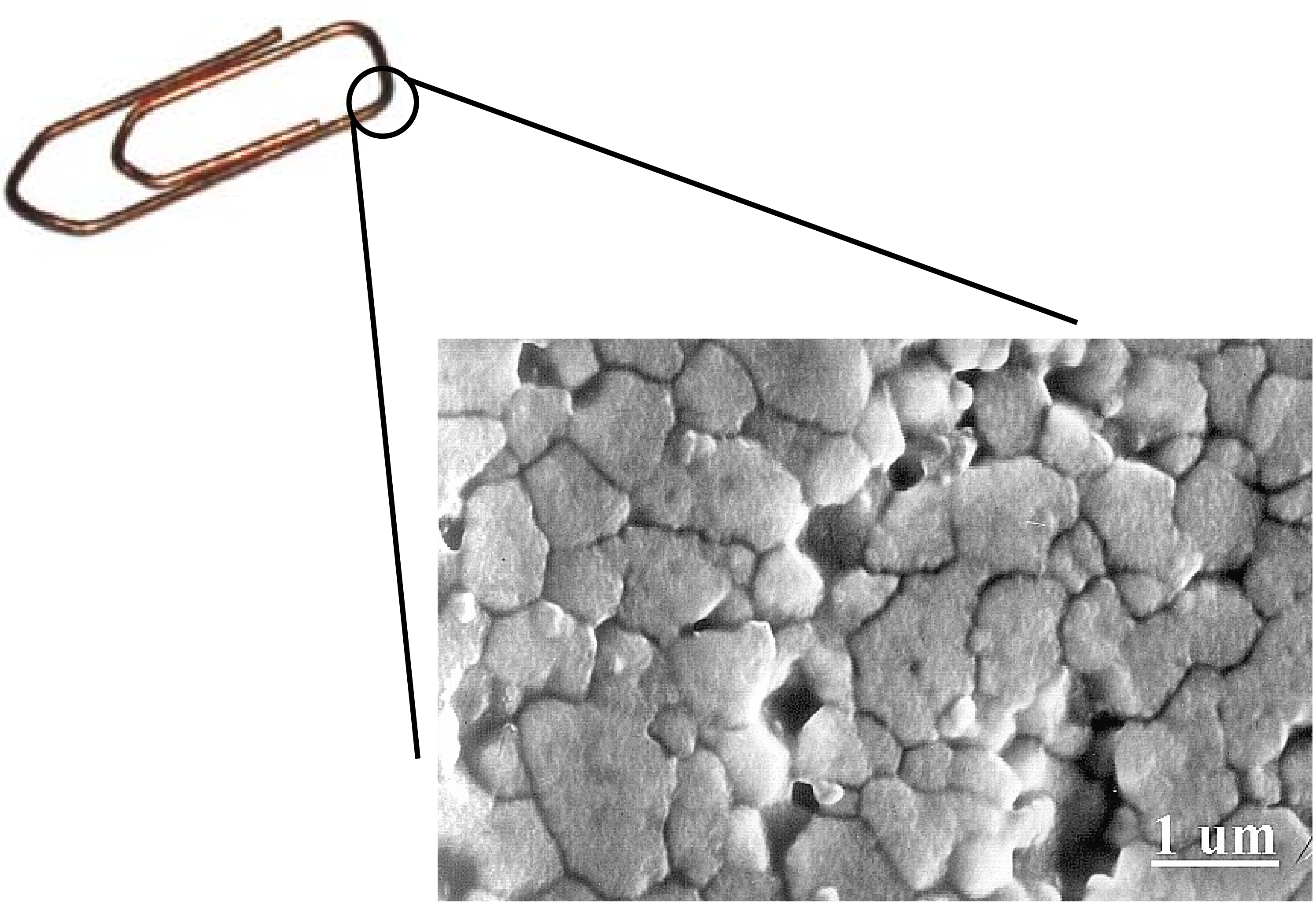


What can we do with this potential?

Bending a copper wire until it breaks



A closer look



Courtesy of Goran Drazic. Used with permission.

http://www2.ijs.si/~goran/sd96/e6sem1y.gif

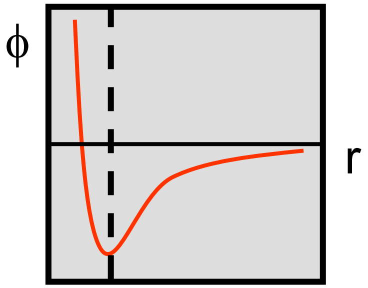
Case study: plasticity in a micrometer crystal of copper

Simulation details

- 1,000,000,000 atoms (0.3 micrometer side length)

- 12:6 Lennard-Jones ductile material, for copper

- Visualization using energy filtering method (only show high energy atoms)



Generic features of atomic bonding: „repulsion vs. attraction“

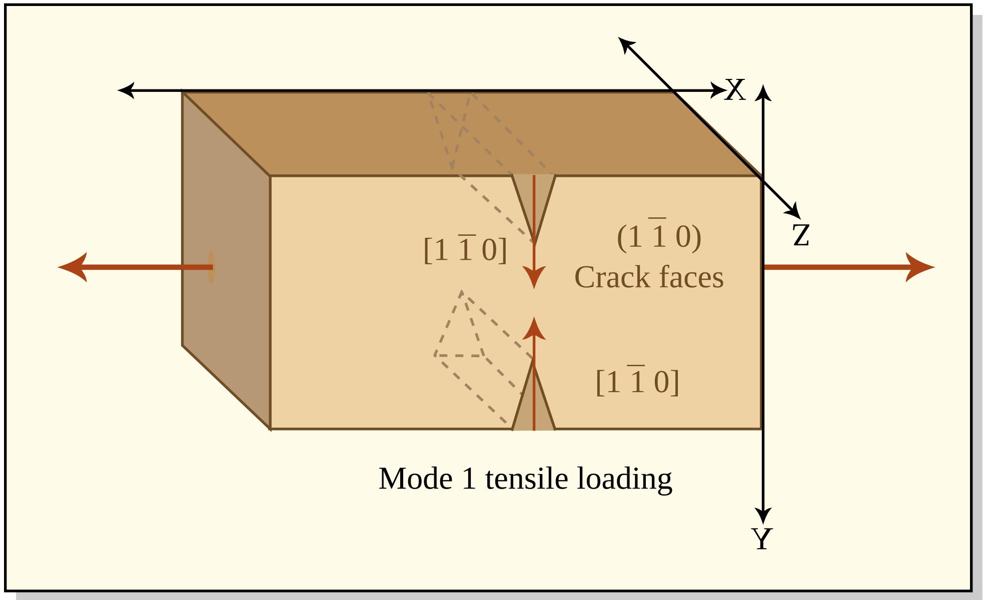


Image by MIT OpenCourseWare. After Buehler, et al., 2005.

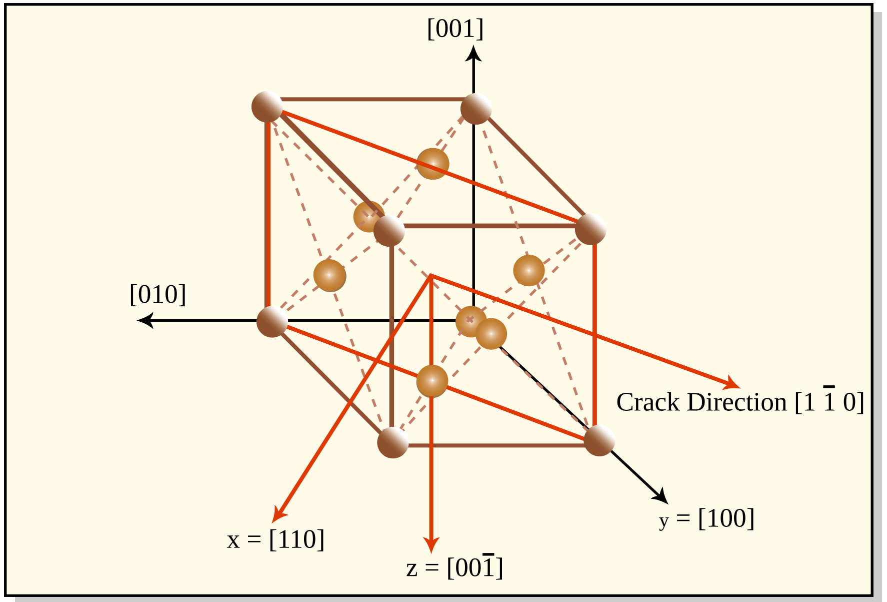


Image by MIT OpenCourseWare. After Buehler, et al., 2005.

A simulation with 1,000,000,000 particles
Lennard-Jones - copper

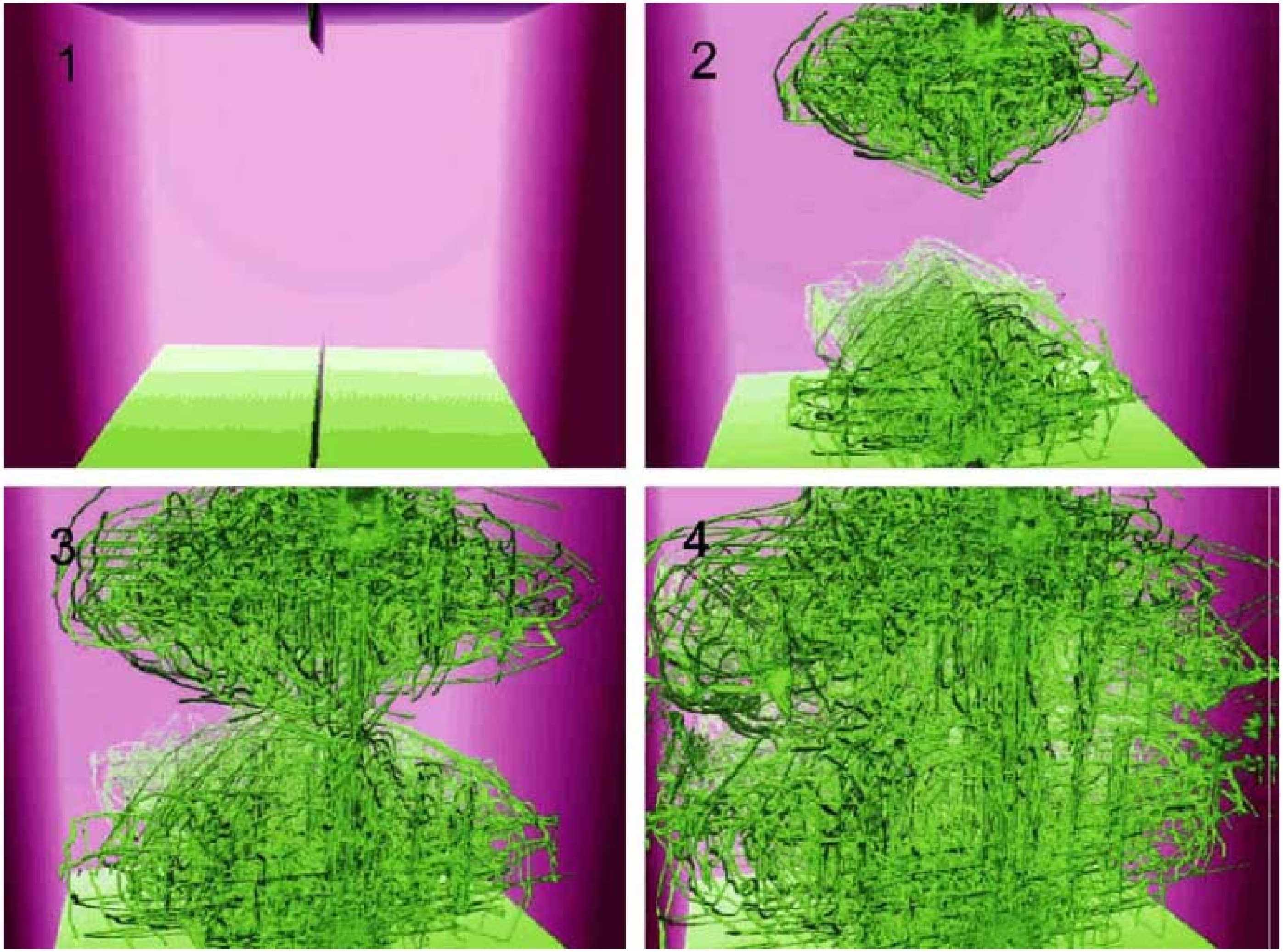
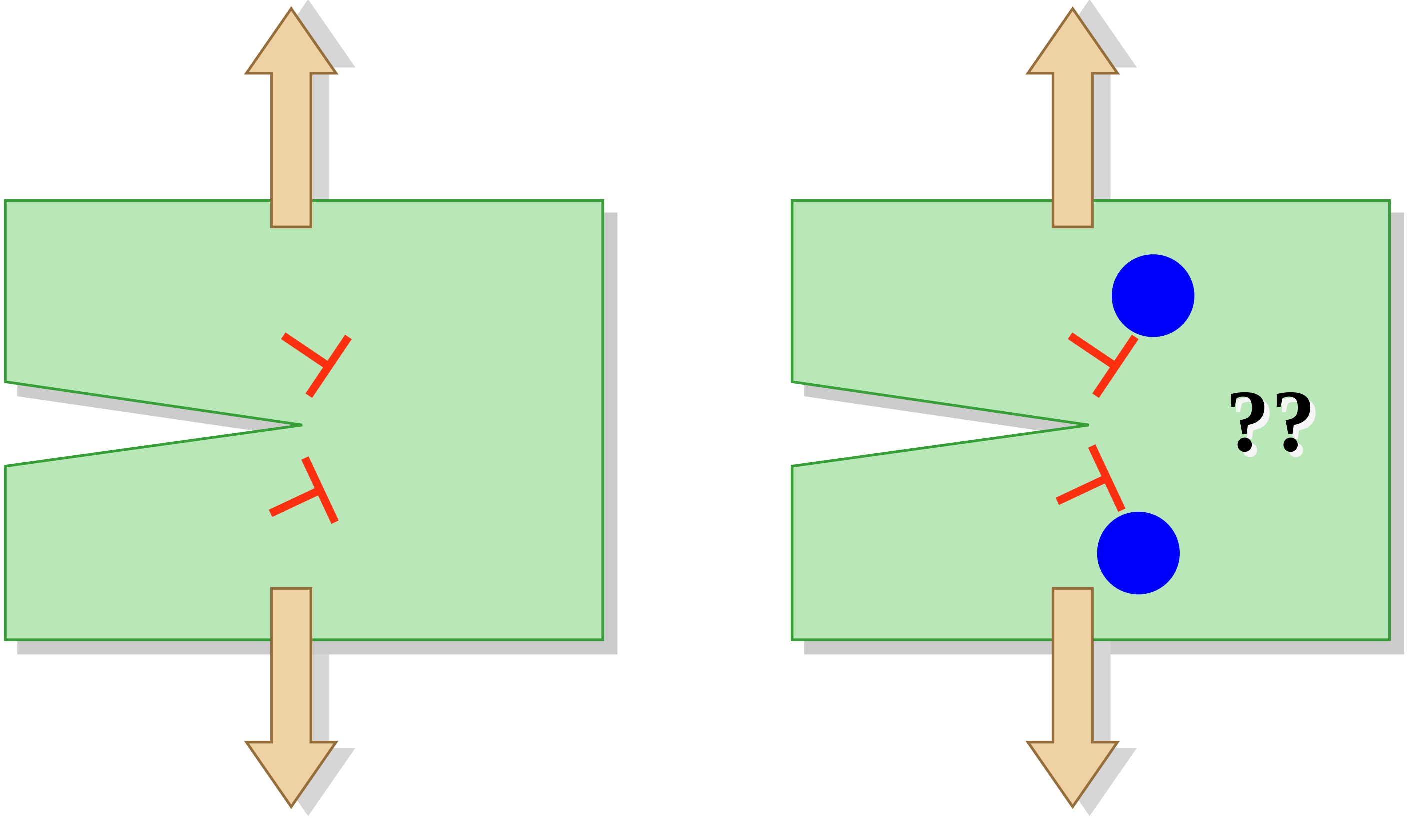


Fig. 1 c from Buehler, M., et al. "The Dynamical Complexity of Work-Hardening: A Large-Scale Molecular Dynamics Simulation." *Acta Mech Sinica* 21 (2005): 103-11.

Strengthening mechanisms



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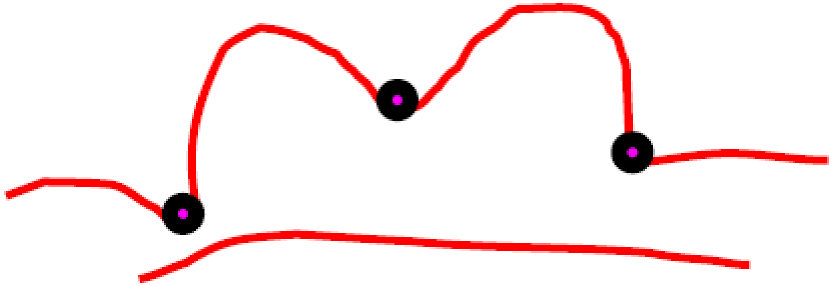


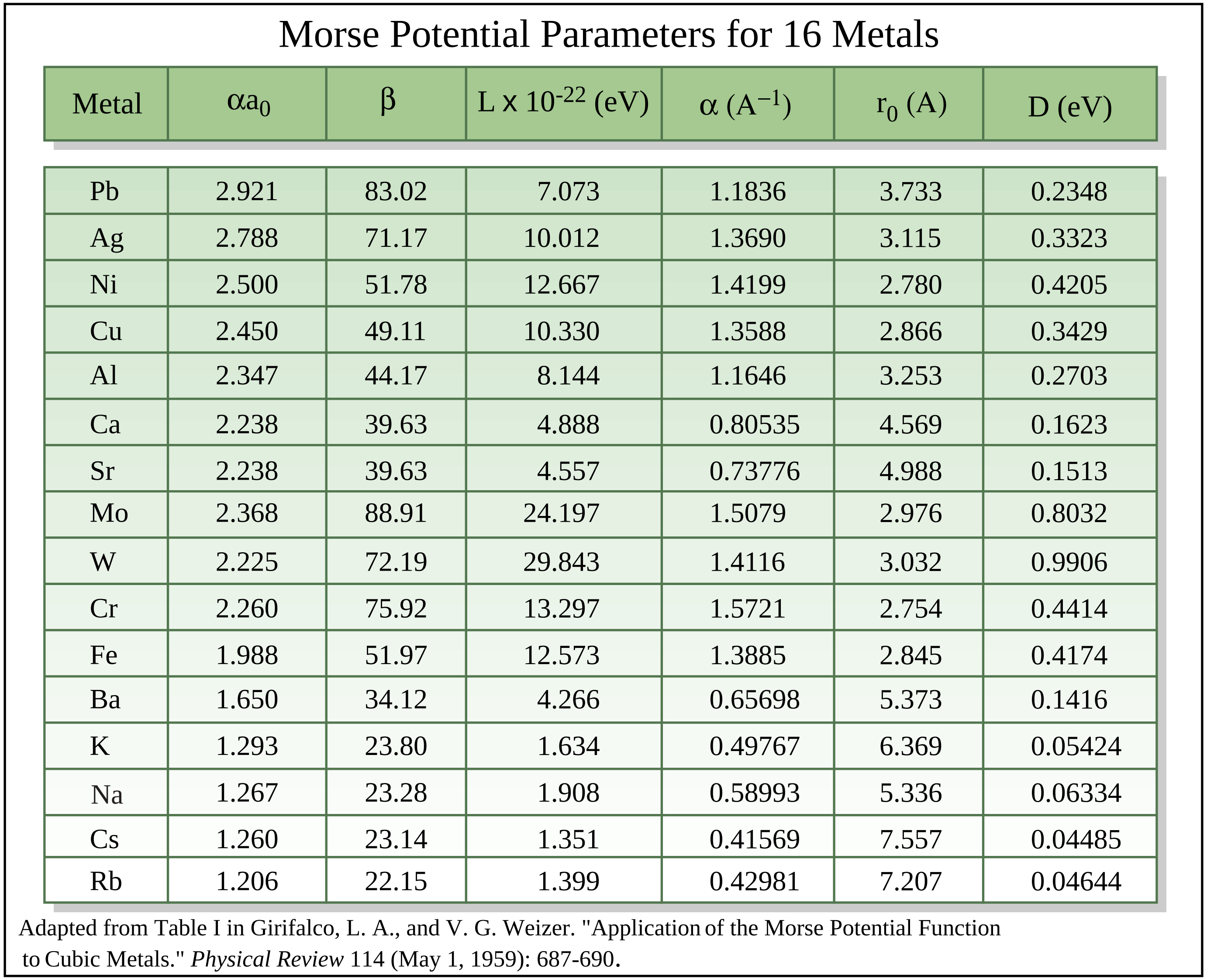
Strengthening caused by hindering dislocation motion

If too difficult, ductile modes break down and material becomes brittle

Parameters for Morse potential

(for reference)

Morse potential parameters for various metals



Morse Potential Parameters for 16 Metals

Metal	αa_0	β	$L \times 10^{-22}$ (eV)	α (A^{-1})	r_0 (A)	D (eV)
Pb	2.921	83.02	7.073	1.1836	3.733	0.2348
Ag	2.788	71.17	10.012	1.3690	3.115	0.3323
Ni	2.500	51.78	12.667	1.4199	2.780	0.4205
Cu	2.450	49.11	10.330	1.3588	2.866	0.3429
Al	2.347	44.17	8.144	1.1646	3.253	0.2703
Ca	2.238	39.63	4.888	0.80535	4.569	0.1623
Sr	2.238	39.63	4.557	0.73776	4.988	0.1513
Mo	2.368	88.91	24.197	1.5079	2.976	0.8032
W	2.225	72.19	29.843	1.4116	3.032	0.9906
Cr	2.260	75.92	13.297	1.5721	2.754	0.4414
Fe	1.988	51.97	12.573	1.3885	2.845	0.4174
Ba	1.650	34.12	4.266	0.65698	5.373	0.1416
K	1.293	23.80	1.634	0.49767	6.369	0.05424
Na	1.267	23.28	1.908	0.58993	5.336	0.06334
Cs	1.260	23.14	1.351	0.41569	7.557	0.04485
Rb	1.206	22.15	1.399	0.42981	7.207	0.04644

Adapted from Table I in Girifalco, L. A., and V. G. Weizer. "Application of the Morse Potential Function to Cubic Metals." *Physical Review* 114 (May 1, 1959): 687-690.

Image by MIT OpenCourseWare.

$$\phi(r_{ij}) = D\exp\left(-2\alpha(r_{ij}-r_0)\right) - 2D\exp\left(-\alpha(r_{ij}-r_0)\right)$$

Morse potential: application example (nanowire)

Source: Komanduri, R., et al. "Molecular Dynamics (MD) Simulation of Uniaxial Tension of Some Single-Crystal Cubic Metals at Nanolevel." *International Journal of Mechanical Sciences* 43, no. 10 (2001): 2237-60.

Further Morse potential parameters:

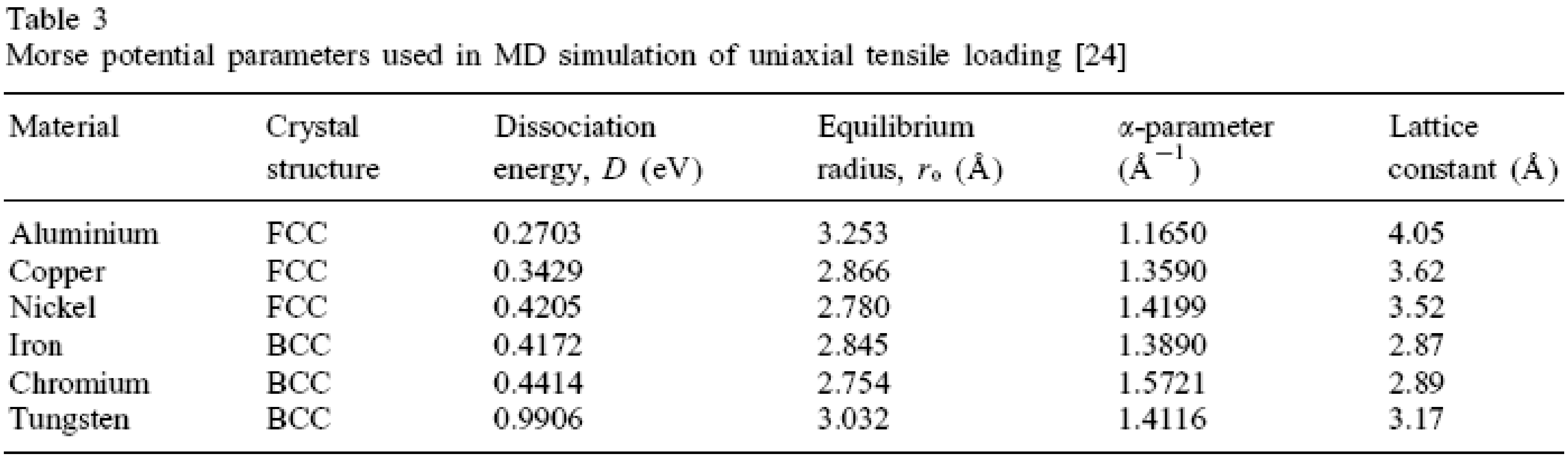


Table 3
Morse potential parameters used in MD simulation of uniaxial tensile loading [24]

Material	Crystal structure	Dissociation energy, D (eV)	Equilibrium radius, r_o (Å)	α-parameter (Å^{-1})	Lattice constant (Å)
Aluminium	FCC	0.2703	3.253	1.1650	4.05
Copper	FCC	0.3429	2.866	1.3590	3.62
Nickel	FCC	0.4205	2.780	1.4199	3.52
Iron	BCC	0.4172	2.845	1.3890	2.87
Chromium	BCC	0.4414	2.754	1.5721	2.89
Tungsten	BCC	0.9906	3.032	1.4116	3.17

Courtesy of Elsevier, Inc., http://www.sciencedirect.com. Used with permission.

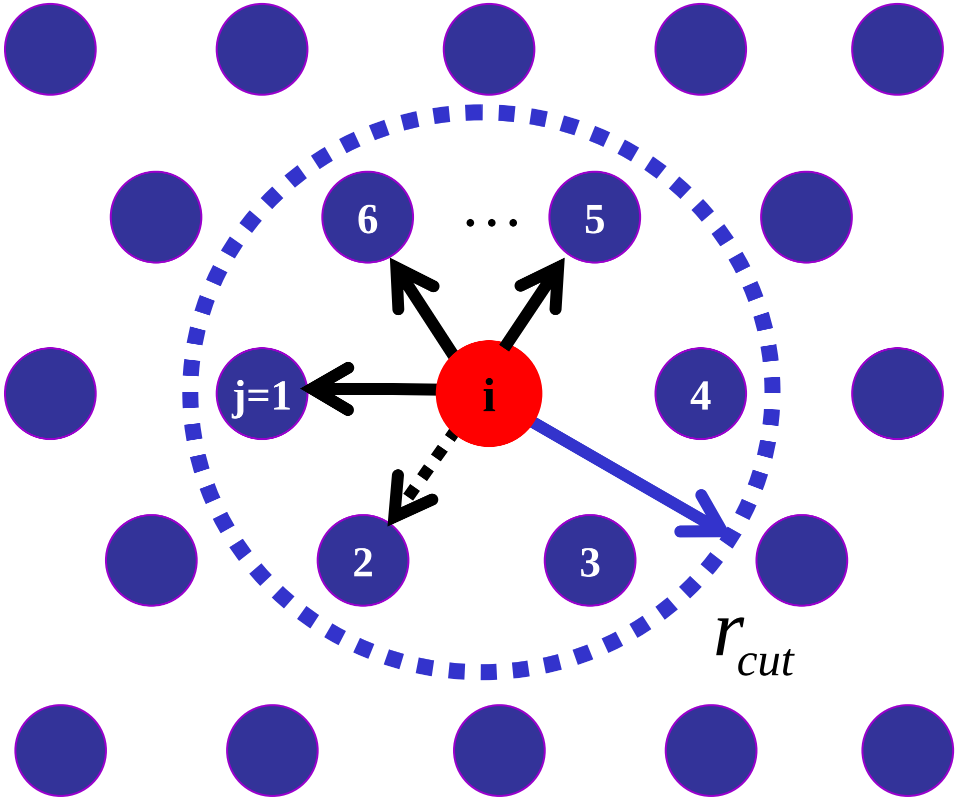
Cutoff-radius: saving time

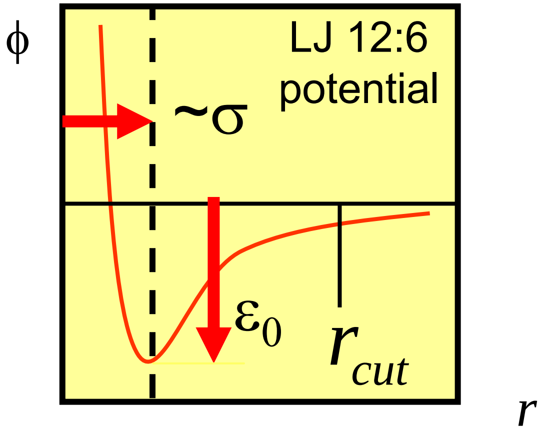
Cutoff radius

$$U_i = \sum_{j=1}^{N} \phi(r_{ij})$$

$$\Big\downarrow$$

$$U_i = \sum_{j=1..N_{neigh}} \phi(r_{ij})$$





Cutoff radius = considering interactions only to a certain distance
Basis: Force contribution negligible (slope)

Derivative of LJ potential ~ force

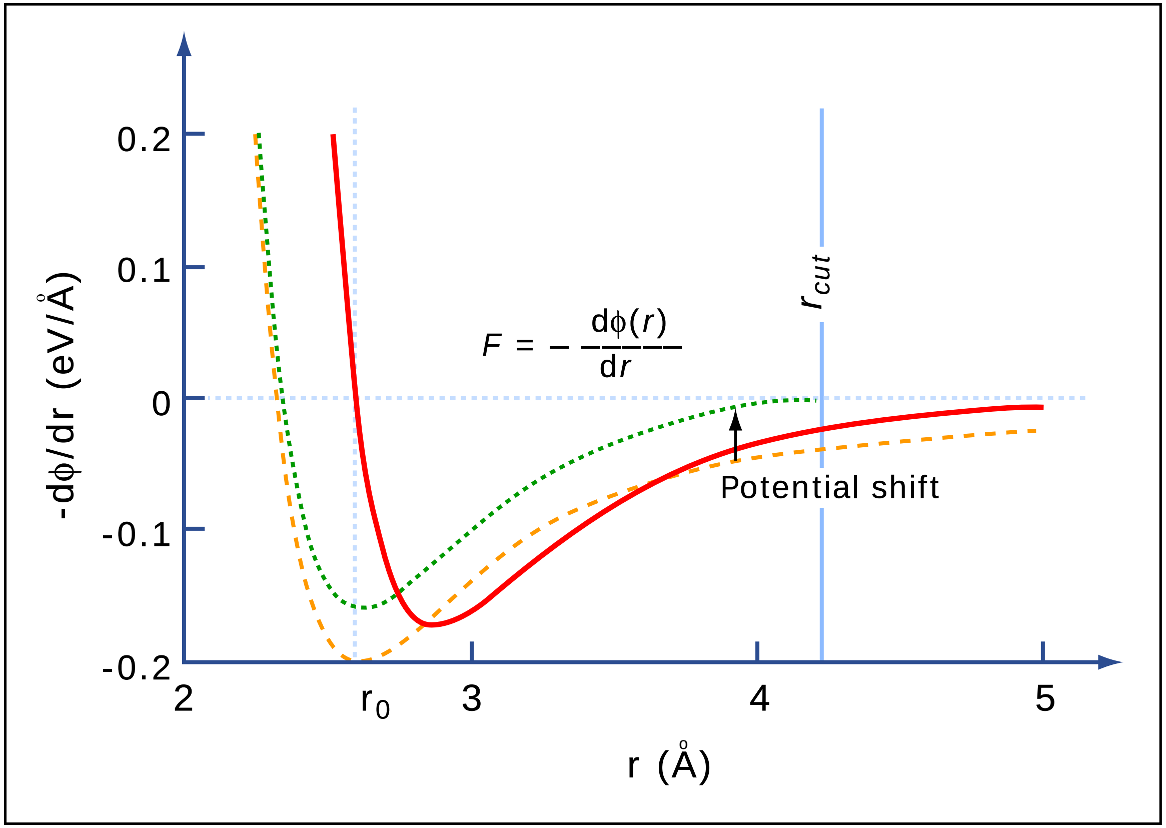


Image by MIT OpenCourseWare.

Beyond cutoff: *Changes in energy (and thus forces) small*

Putting it all together…

MD updating scheme: Complete

(1) Updating method (integration scheme)

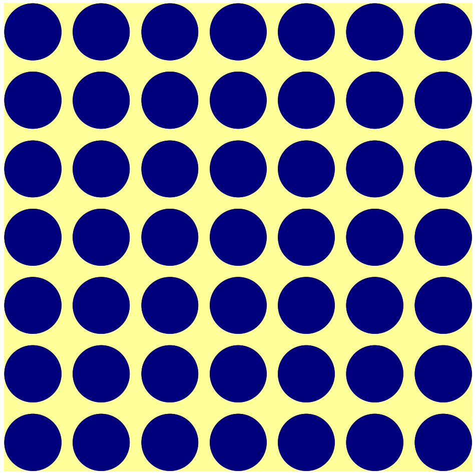
$$r_i(t_0+\Delta t) = -\underbrace{r_i(t_0-\Delta t)}_{\substack{\text{Positions}\\ \text{at } t_0\text{-}\Delta t}} + \underbrace{2r_i(t_0)\Delta t}_{\substack{\text{Positions}\\ \text{at } t_0}} + \underbrace{a_i(t_0)(\Delta t)^2}_{\substack{\text{Accelerations}\\ \text{at } t_0}} + \ldots$$

(2) Obtain accelerations from forces

$$f_i = ma_i \qquad a_i = f_i / m$$

(4) Crystal (initial conditions)

Positions at t_0



(3) Obtain forces from potential

$$F = -\frac{\mathrm{d}\,\phi(r)}{\mathrm{d}\,r} \qquad f_i = F\,\frac{x_i}{r}$$

Potential

$$\phi(r) = 4\varepsilon\left(\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^{6}\right)$$

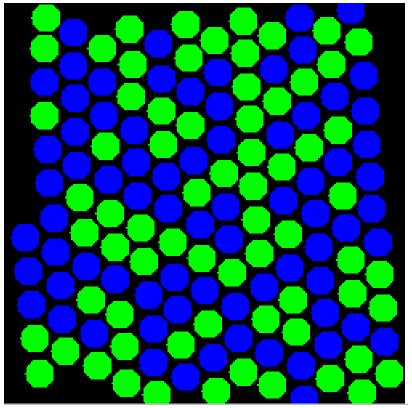
2.2 How to model metals: Multi-body potentials

Pair potential: Total energy sum of all pairs of bonds

Individual bond contribution does not depend on other atoms

"all bonds are the same"

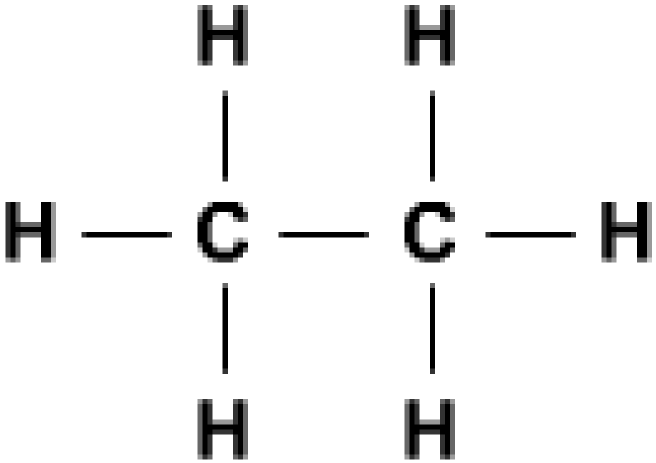
$$U_{total} = \tfrac{1}{2} \sum_{i=1, i\neq j}^{N} \sum_{j=1}^{N} \phi(r_{ij})$$



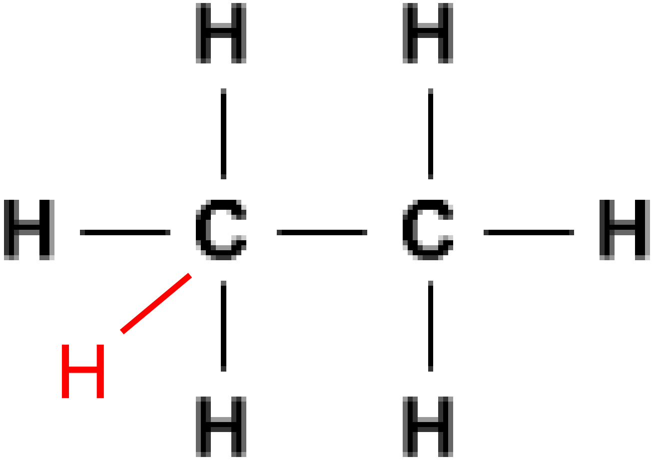
Courtesy of the Center for Polymer Studies at Boston University. Used with permission.

Is this a good assumption?

Are all bonds the same? - valency in hydrocarbons



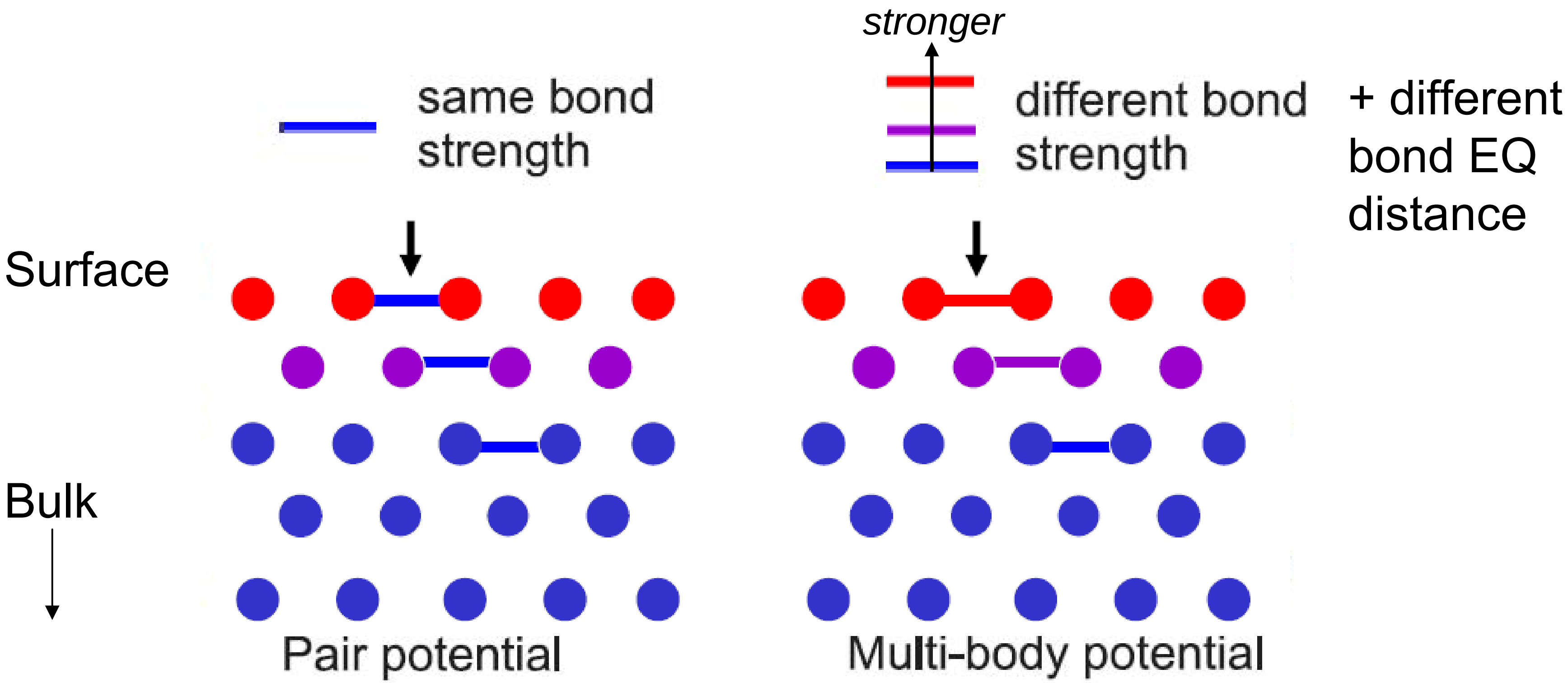
Ethane C_2H_6
(stable configuration)



All bonds are not the same!

Adding another H is not favored

Are all bonds the same? – metallic systems



stronger

same bond strength

different bond strength

+ different bond EQ distance

Surface

Bulk

Pair potential

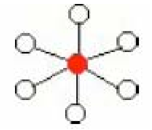
Multi-body potential

Pair potentials: All bonds are equal!

Reality: Have environment effects; it matter that there is a free surface!

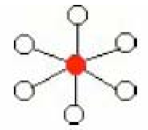
Bonds depend on the environment!

Are all bonds the same?

Bonding energy of red atom in  is six times bonding energy in 

This is in contradiction with both experiments and more accurate quantum mechanical calculations on many materials

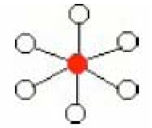
Bonding energy of atom *i* $$U_i = \sum_{j=1}^{N} \phi(r_{ij})$$



$$\boxed{U_i = \sum_{j=1}^{6} \phi(r_{ij}) \quad \longleftrightarrow \quad U_i = \phi(r_{ij})}$$

After: G. Ceder

Are all bonds the same?

Bonding energy of red atom in  is six times bonding energy in 

This is in contradiction with both experiments and more accurate quantum mechanical calculations on many materials

For pair potentials $\sim Z$

For metals $\sim \sqrt{Z}$

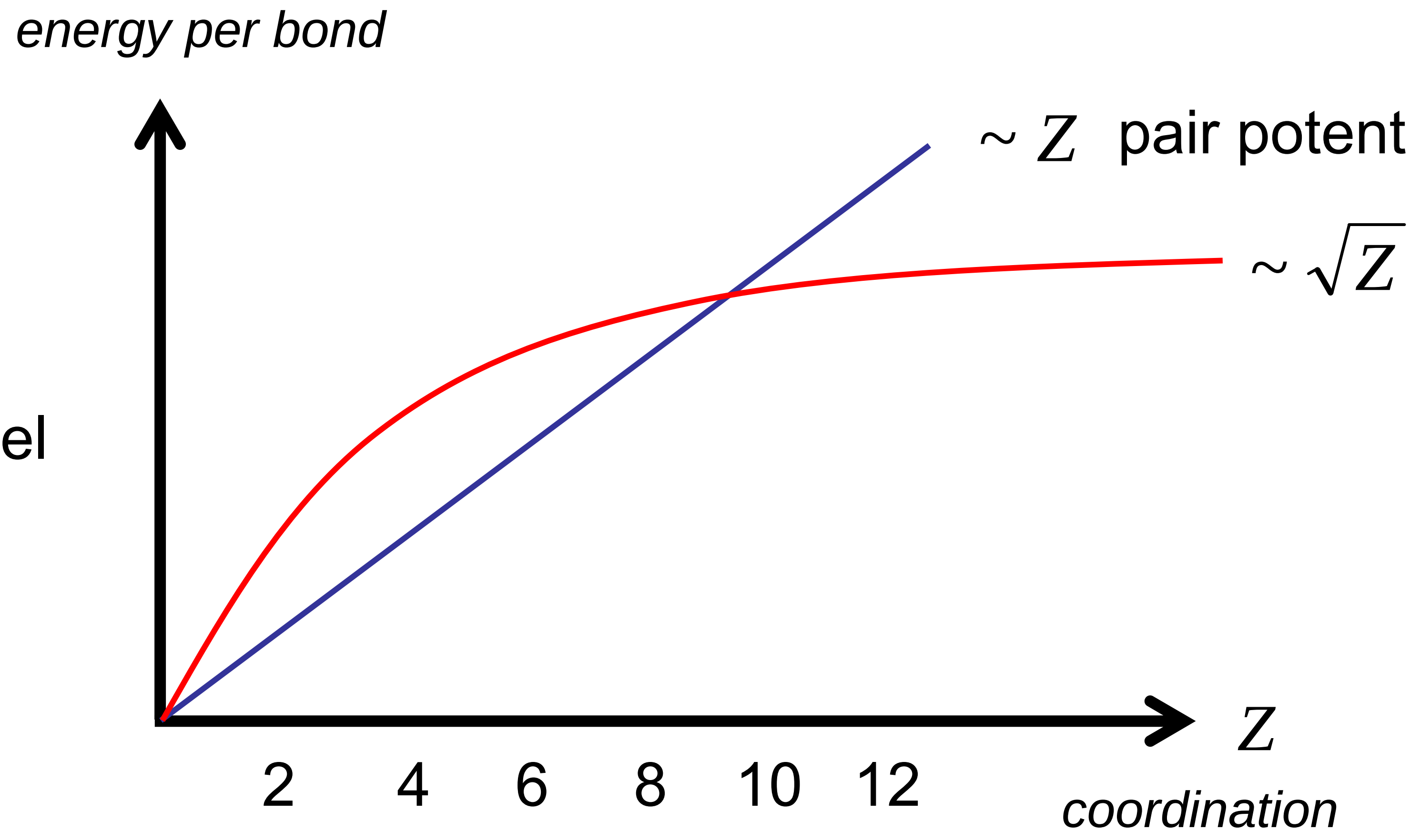
$Z:$ Coordination = how many immediate neighbors an atom has

Bonds get "weaker" as more atoms are added to central atom

After: G. Ceder

Bond strength depends on coordination

Nickel



Daw, Foiles, Baskes, *Mat. Science Reports*, 1993

Transferability of pair potentials

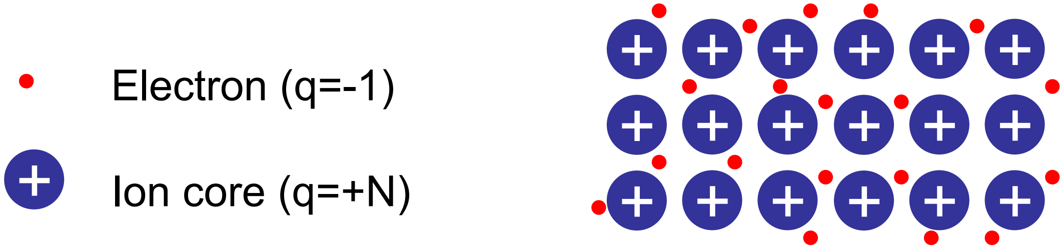
- Pair potentials have limited **transferability:**

  Parameters determined for molecules can not be used for crystals, parameters for specific types of crystals can not be used to describe range of crystal structures

- E.g. difference between FCC and BCC can not be captured using a pair potential

Metallic bonding: multi-body effects

- Need to consider more details of chemical bonding to understand environmental effects



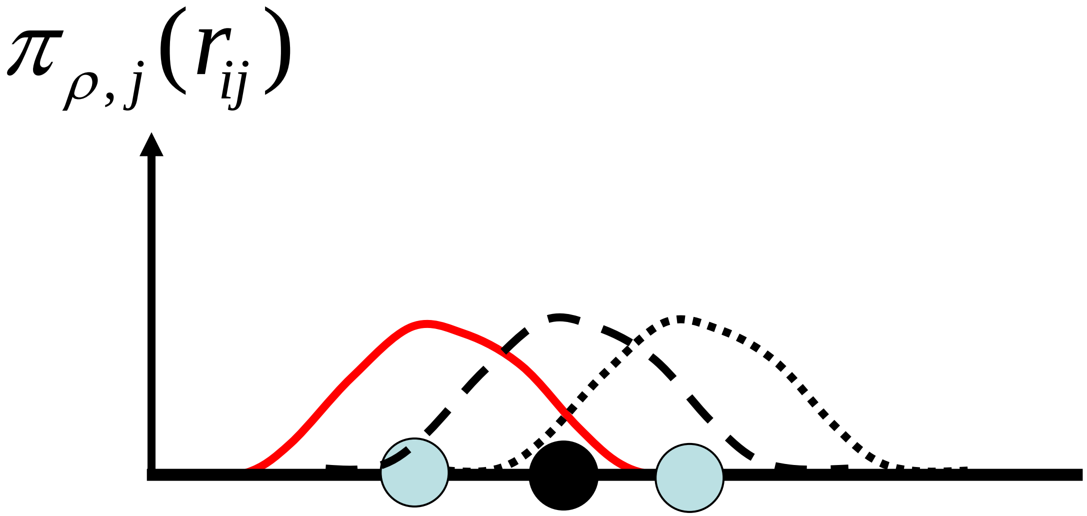
● Electron (q=-1)

⊕ Ion core (q=+N)

Delocalized valence electrons moving between nuclei generate a binding force to hold the atoms together: **Electron gas model (*positive ions in a sea of electrons*)**

Mostly non-directional bonding, but the bond strength indeed depends on the environment of an atom, precisely the electron density imposed by other atoms

Concept: include electron density effects

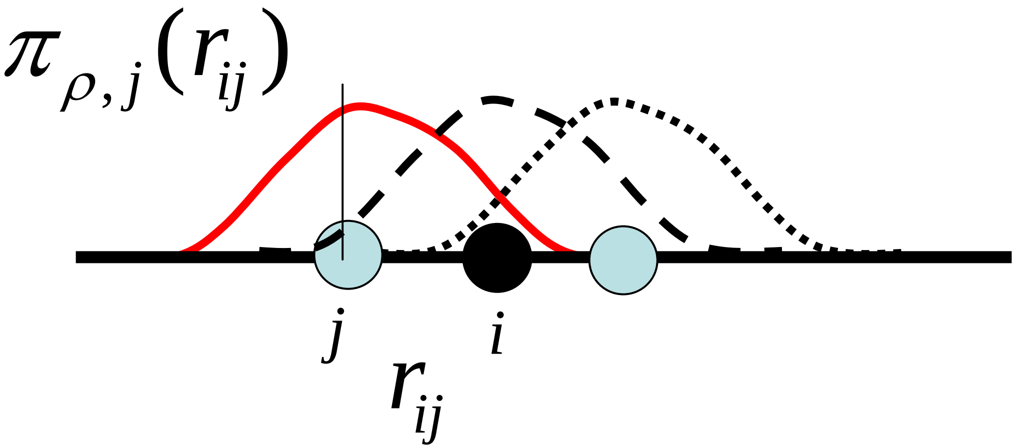


Each atom features a particular distribution of electron density

Concept: include electron density effects

Electron density at atom *i* $$\rho_i = \sum_{j=1..N_{neigh}} \pi_{\rho,j}(r_{ij})$$

Atomic electron density of atom *j*



Contribution to electron density at site i due to electron density of atom j evaluated at correct distance (r_{ij})

Concept: include electron density effects

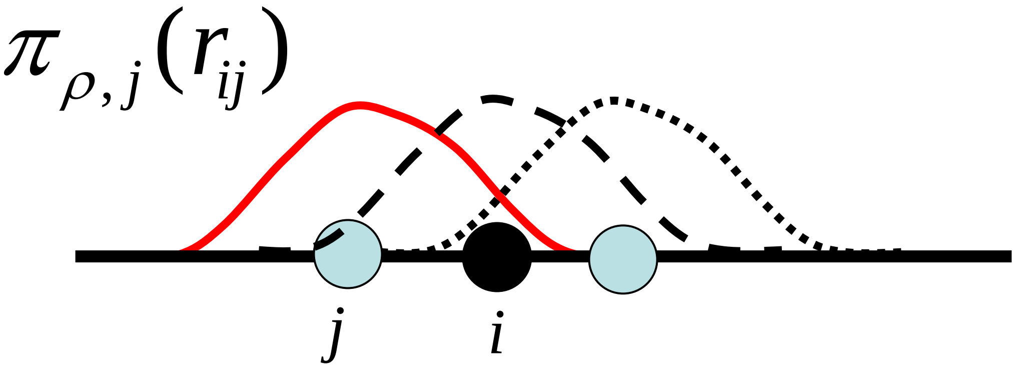
$$\phi_i = \sum_{j=1..N_{neigh}} \frac{1}{2}\phi(r_{ij}) + F(\rho_i)$$

Embedding term F (how local electron density contributes to potential energy)

Electron density at atom i

$$\rho_i = \sum_{j=1..N_{neigh}} \pi_{\rho,j}(r_{ij})$$

Atomic electron density of atom j



Embedded-atom method (EAM)

Atomic energy

$$\phi_i = \sum_{j=1..N_{neigh}} \underbrace{\frac{1}{2}\phi(r_{ij})}_{\text{Pair potential energy}} + \underbrace{\overset{\text{new}}{F(\rho_i)}}_{\text{Embedding energy as a function of electron density}}$$

Total energy

$$U_{total} = \sum_{i=1}^{N} \phi_i$$

ρ_i Electron density at atom *i* based on a "pair potential":

$$\rho_i = \sum_{j=1..N_{neigh}} \pi_{\rho,j}(r_{ij})$$

First proposed by Finnis, Sinclair, Daw, Baskes *et al.* (1980s)

Physical concept: EAM potential

- Describes bonding energy due to electron delocalization

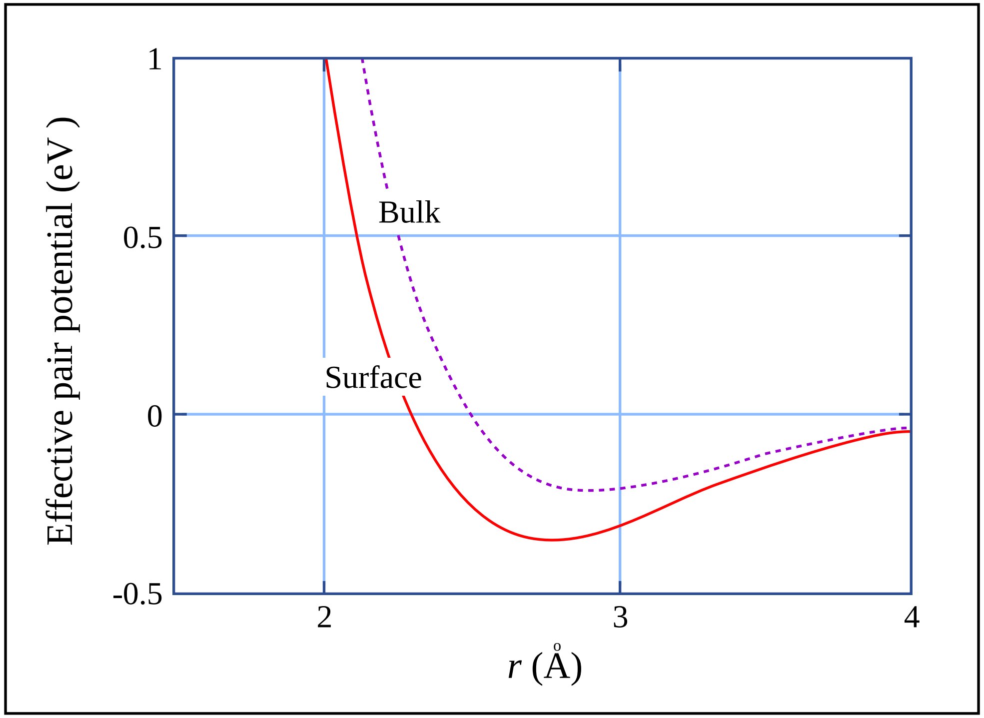
  As electrons get more states to spread out over their kinetic energy decreases

- When an impurity is put into a metal its energy is lowered because the electrons from the impurity can delocalize into the solid.

- The embedding density (electron density at the embedding site) is a measure of the number of states available to delocalize onto.

- **Inherently MANY BODY effect!**

Effective pair interactions



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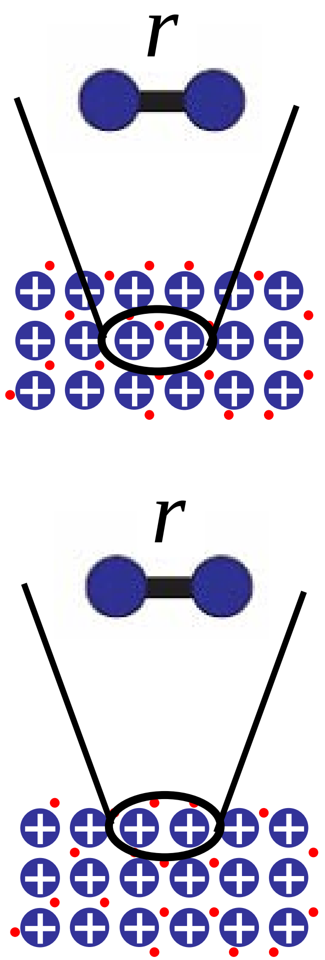

Can describe differences between bulk and surface

See also: Daw, Foiles, Baskes, *Mat. Science Reports*, 1993

Summary: EAM method

- State of the art approach to model metals
- Very good potentials available for Ni, Cu, Al since late 1990s, 2000s
- Numerically efficient, can treat billions of particles
- Not much more expensive than pair potential (approximately three times), but describes physics much better

- ***Strongly recommended for use!***

3.021J / 1.021J / 10.333J / 18.361J / 22.00J Introduction to Modeling and Simulation
Spring 2012