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

Part I – Continuum and particle methods

Review session—preparation quiz I

Lecture 12

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Content overview

I. Particle and continuum methods

Lectures 2-13

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** (Monte Carlo, advanced property calculation, introduction to chemical interactions)
- **Lecture 5: How to model chemical interactions I** (example: movie of copper deformation/dislocations, etc.)
- **Lecture 6: How to model chemical interactions II** (EAM, a bit of ReaxFF—chemical reactions)
- **Lecture 7: Application to modeling brittle materials I**
- **Lecture 8: Application to modeling brittle materials II**
- **Lecture 9: Application – Applications to materials failure**
- **Lecture 10: Applications to biophysics and bionanomechanics**
- **Lecture 11: Applications to biophysics and bionanomechanics (cont'd)**
- **Lecture 12: Review session – part I**

Check: goals of part I

You will be able to …

- Carry out atomistic simulations of various processes (diffusion, deformation/stretching, materials failure)

  Carbon nanotubes, nanowires, bulk metals, proteins, silicon crystals, …

- Analyze atomistic simulations

- Visualize atomistic/molecular data

- Understand how to link atomistic simulation results with continuum models within a multi-scale scheme

Topics covered – part I

Atomistic & molecular simulation algorithms

Property calculation

Potential/ force field models

Applications

Lecture 12: Review session – part I

1. Review of material covered in part I
    - 1.1 Atomistic and molecular simulation algorithms
    - 1.2 Property calculation
    - 1.3 Potential/force field models
    - 1.4 Applications
2. Important terminology and concepts

Goal of today's lecture:

- Review main concepts of atomistic and molecular dynamics, continuum models
- Prepare you for the quiz on Thursday

1.1 Atomistic and molecular simulation algorithms

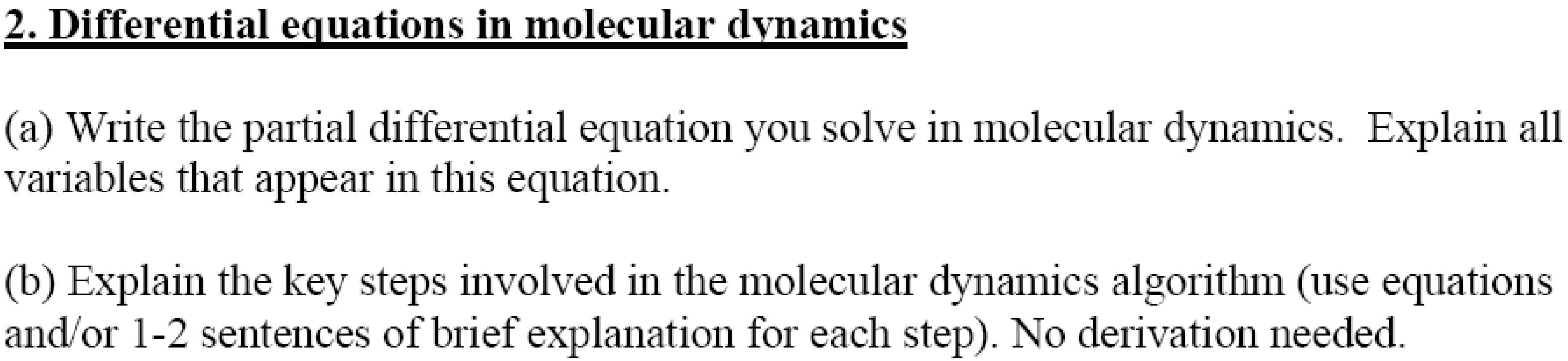
1.2 Property calculation

1.3 Potential/force field models

1.4 Applications

Goals: Basic MD algorithm (integration scheme), initial/boundary conditions, numerical issues (supercomputing)

Differential equations solved in MD



2. Differential equations in molecular dynamics

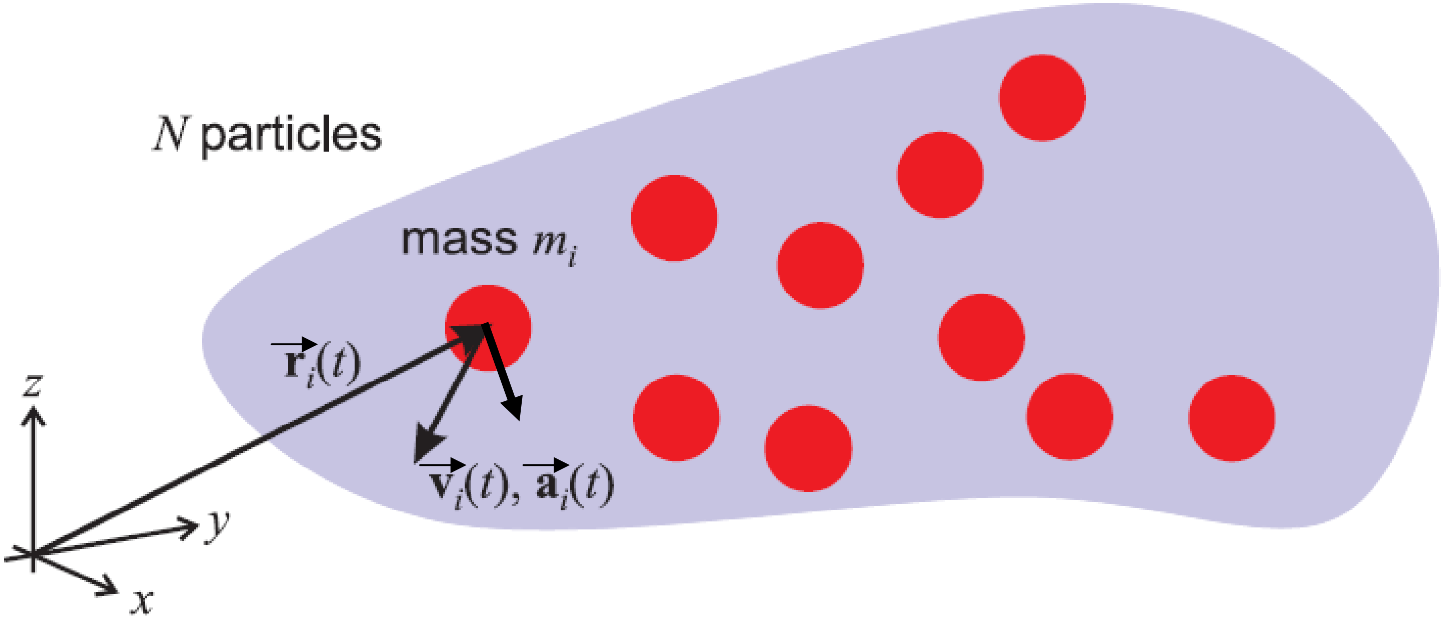
(a) Write the partial differential equation you solve in molecular dynamics. Explain all variables that appear in this equation.

(b) Explain the key steps involved in the molecular dynamics algorithm (use equations and/or 1-2 sentences of brief explanation for each step). No derivation needed.

Basic concept: atomistic methods

PDE solved in MD:
$(ma = F)$

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = -\frac{dU(r)}{d\vec{r}_i} \qquad r = \{\vec{r}_j\} \qquad i = 1..N$$



Results of MD simulation:

$$\vec{r}_i(t), \vec{v}_i(t), \vec{a}_i(t) \qquad i = 1..N$$

Complete MD updating scheme

(1) Initial conditions: Positions & velocities at t_0 (random velocities so that initial temperature is represented)

(2) Updating method (integration scheme - Verlet)

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

(3) Obtain accelerations from forces

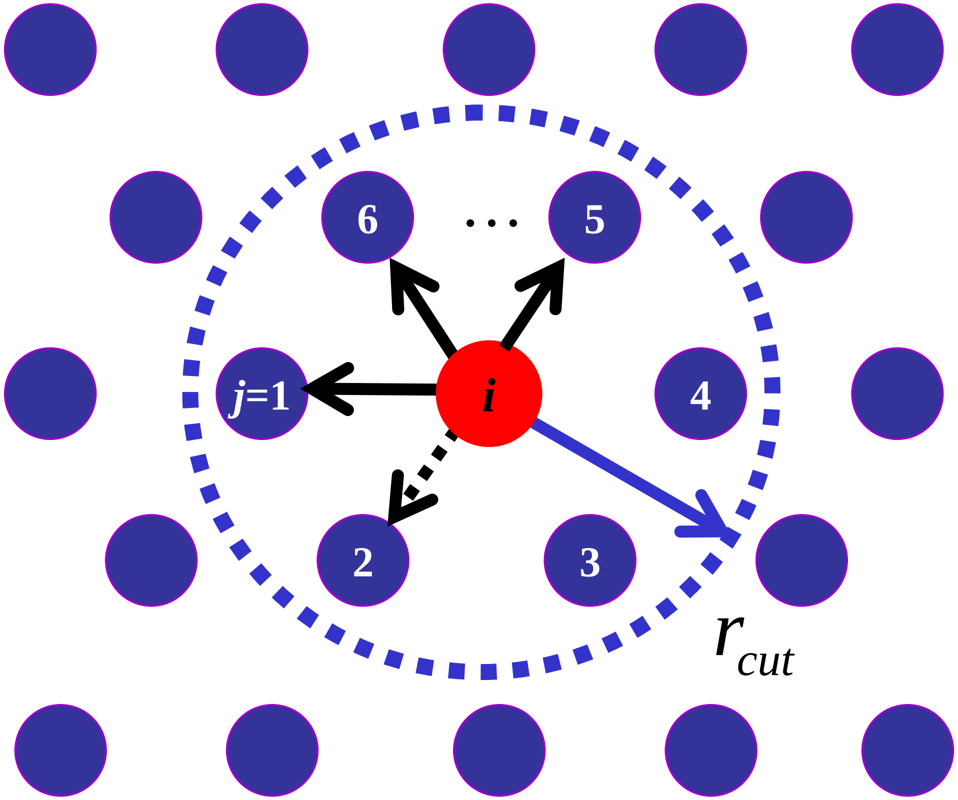
$$f_{j,i} = m_j a_{j,i} \qquad a_{j,i} = f_{j,i}/m_j \qquad \forall j = 1..N$$

(4) Obtain force vectors from potential (sum over contributions from all neighbor of atom j)

$$F = -\frac{\mathrm{d}\phi(r)}{\mathrm{d}r} \qquad f_{j,i} = F\frac{x_{j,i}}{r} \qquad \text{Potential} \quad \phi(r) = 4\varepsilon\left(\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^{6}\right)$$

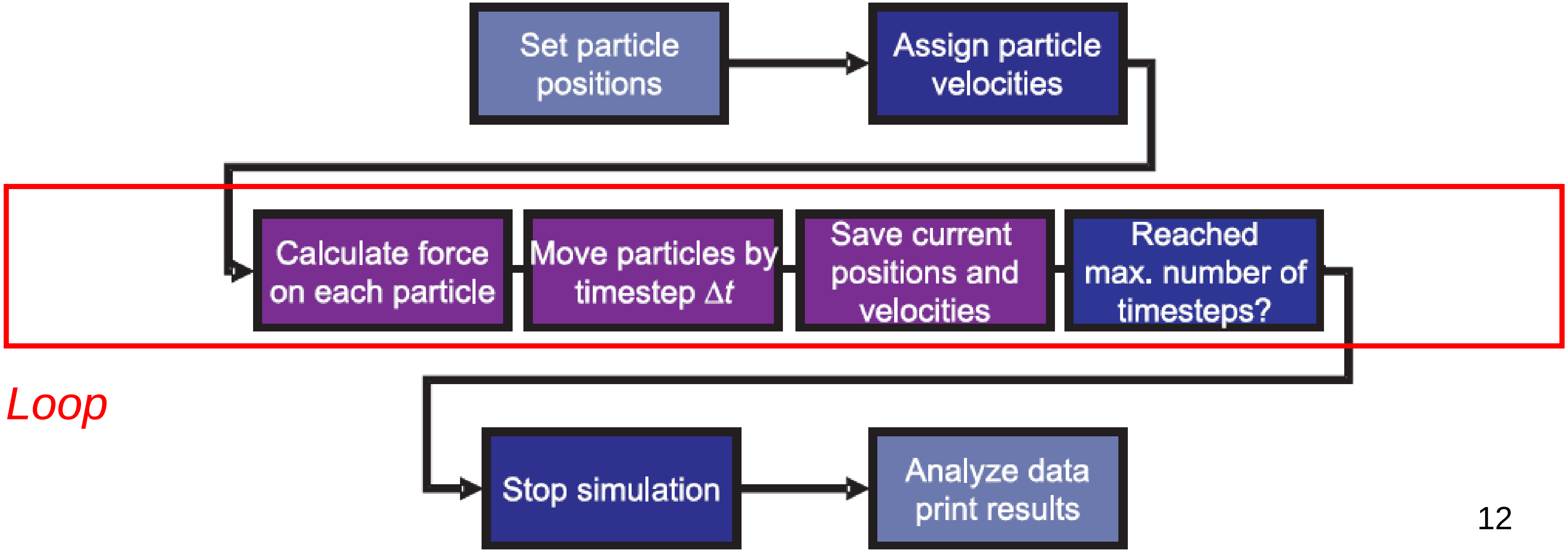
Algorithm of force calculation

```
for $i=1..N$
    for $j=1..N\ (i \neq j)$
        [add force
        contributions]
```

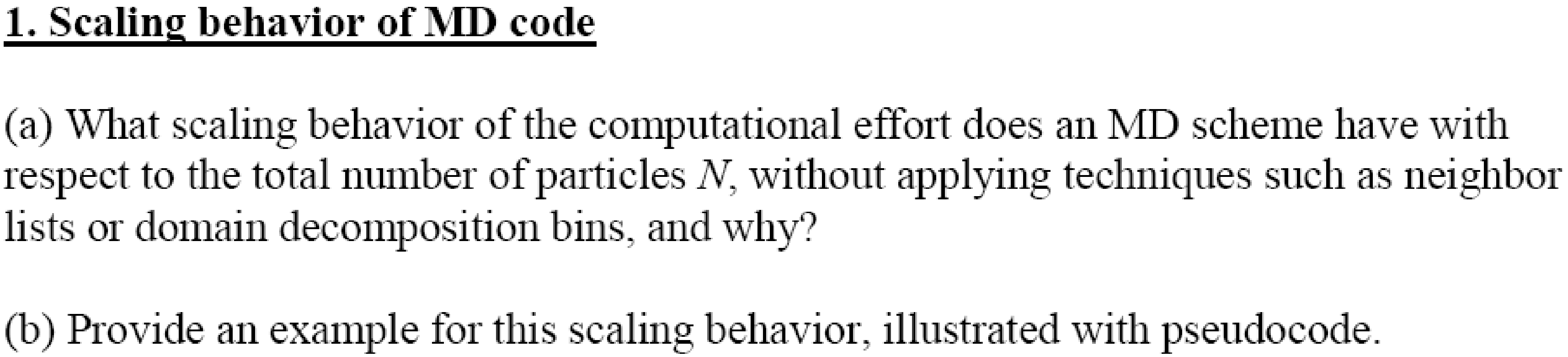


Summary: Atomistic simulation – numerical approach "molecular dynamics – MD"

- Atomistic model; requires atomistic microstructure and atomic positions at beginning (initial conditions), initial velocities from random distribution according to specified temperature
- Step through time by integration scheme (Verlet)
- Repeat force calculation of atomic forces based on their positions
- Explicit notion of chemical bonds – captured in interatomic potential



Scaling behavior of MD code



1. Scaling behavior of MD code

(a) What scaling behavior of the computational effort does an MD scheme have with respect to the total number of particles *N*, without applying techniques such as neighbor lists or domain decomposition bins, and why?

(b) Provide an example for this scaling behavior, illustrated with pseudocode.

Force calculation for N particles: pseudocode

- Requires two nested loops, first over all atoms, and then over all other atoms to determine the distance

```
for $i=1..N$:
    for $j=1..N$ ($i \neq j$):
        determine distance between $i$ and $j$
        calculate force and energy (if $r_{ij} < r_{cut}$, cutoff radius)
        add to total force vector / energy
```

$\Delta t_1 \sim N\Delta t_0$

Δt_0

$\Delta t_{\text{total}} \sim N \cdot N\Delta t_0 = N^2\Delta t_0$

time ~ N^2: ***computational disaster***

Strategies for more efficient computation

Two approaches

1. **Neighbor lists:** Store information about atoms in vicinity, calculated in an N^2 effort, and keep information for 10..20 steps

   Concept: Store information of neighbors of each atom within vicinity of cutoff radius (e.g. list in a vector); update list only every 10..20 steps

2. **Domain decomposition into bins:** Decompose system into small bins; force calculation only between atoms in local neighboring bins

   Concept: Even overall system grows, calculation is done only in a local environment (have two nested loops but # of atoms does not increase locally)

Force calculation with neighbor lists

- Requires two nested loops, first over all atoms, and then over all other atoms to determine the distance

```
for $i=1..N_{\text{neighbors},i}$:
    ~~for $j=1..N$ $(i \neq j)$:~~
        determine distance between $i$ and $j$
        calculate force and energy (if $r_{ij} < r_{cut}$, cutoff radius)
        add to total force vector / energy
```

$\Delta t_1 \sim \cancel{N} \Delta t_0$

Δt_0

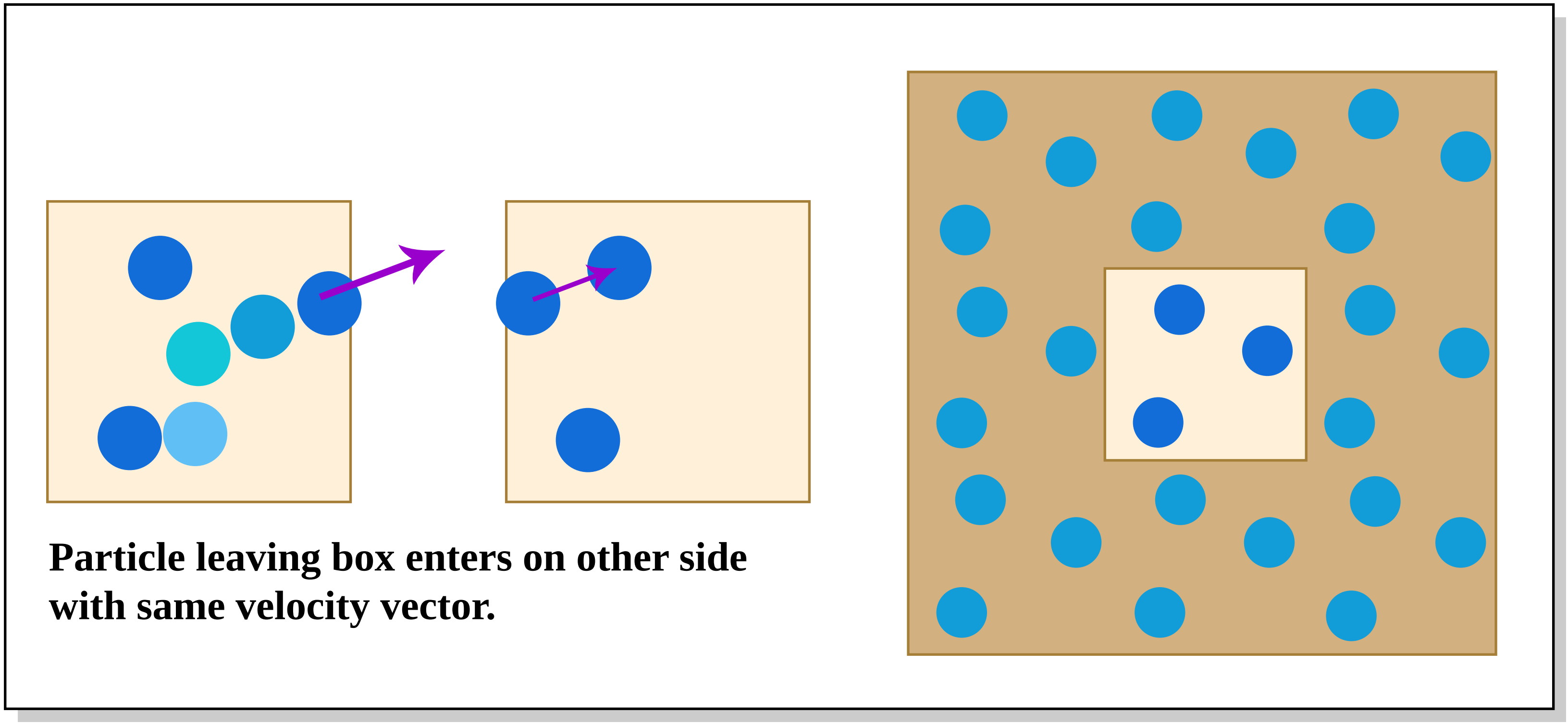
$\Delta t_{\text{total}} \sim N \Delta t_0$

time ~ N: ***computationally tractable*** ***even for large*** N

Periodic boundary conditions

- **Periodic boundary conditions** allows studying bulk properties (no free surfaces) with small number of particles *(here:* $N=3$*), all particles are "connected"*

- Original cell surrounded by 26 image cells; image particles move in exactly the same way as original particles (8 in 2D)



Particle leaving box enters on other side with same velocity vector.

Image by MIT OpenCourseWare. After Buehler.

Parallel computing – “supercomputers”

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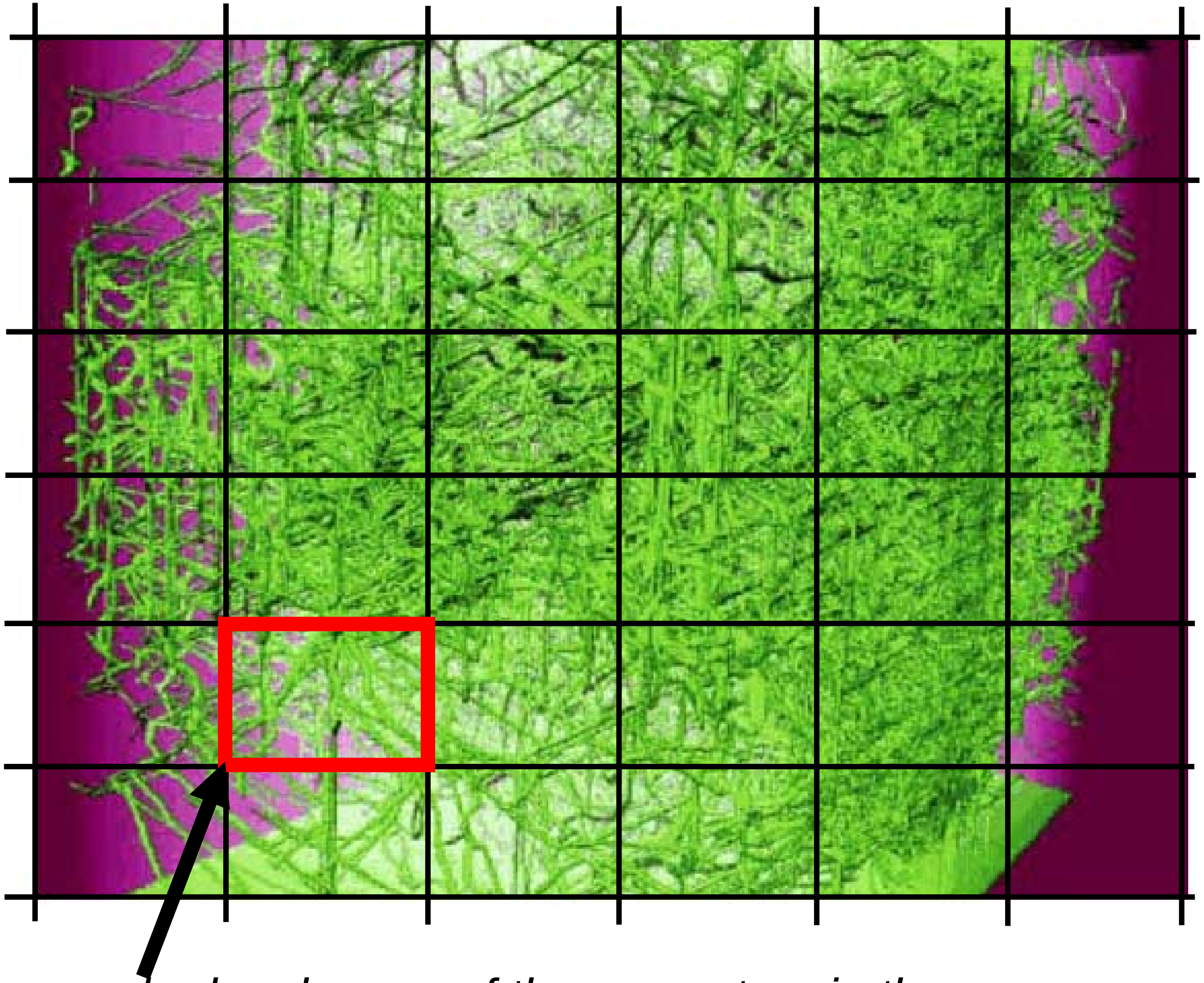
Supercomputers consist of a very large number of individual computing units (e.g. Central Processing Units, CPUs)

Domain decomposition



Each piece worked on by one of the computers in the supercomputer

Fig. 1 c from Buehler, M., et al. "The Dynamical Complexity of Work-Hardening: A Large-Scale Molecular Dynamics Simulation."
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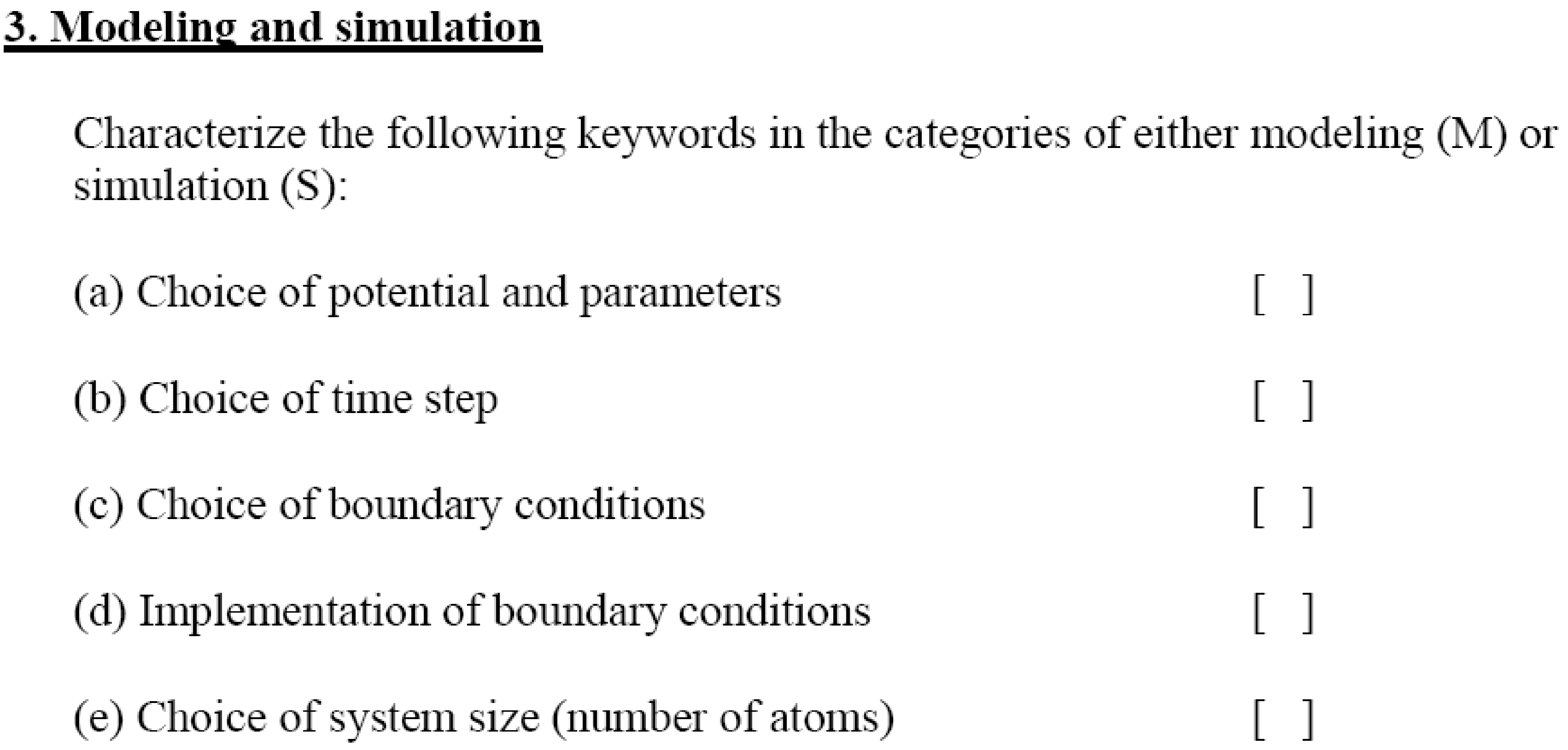
Modeling and simulation



3. Modeling and simulation

Characterize the following keywords in the categories of either modeling (M) or simulation (S):

(a) Choice of potential and parameters [ ]

(b) Choice of time step [ ]

(c) Choice of boundary conditions [ ]

(d) Implementation of boundary conditions [ ]

(e) Choice of system size (number of atoms) [ ]

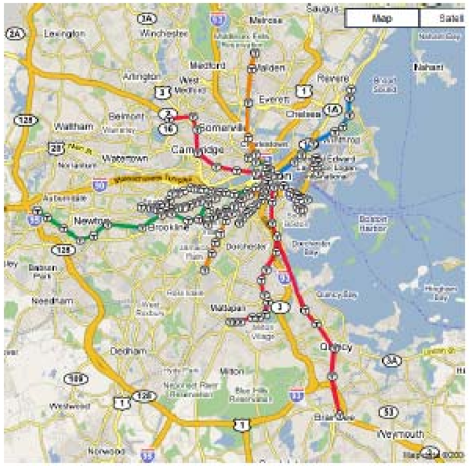
Modeling and simulation

What is a model? What is a simulation?

Modeling vs Simulation

- **Modeling**: developing a mathematical representation of a physical situation

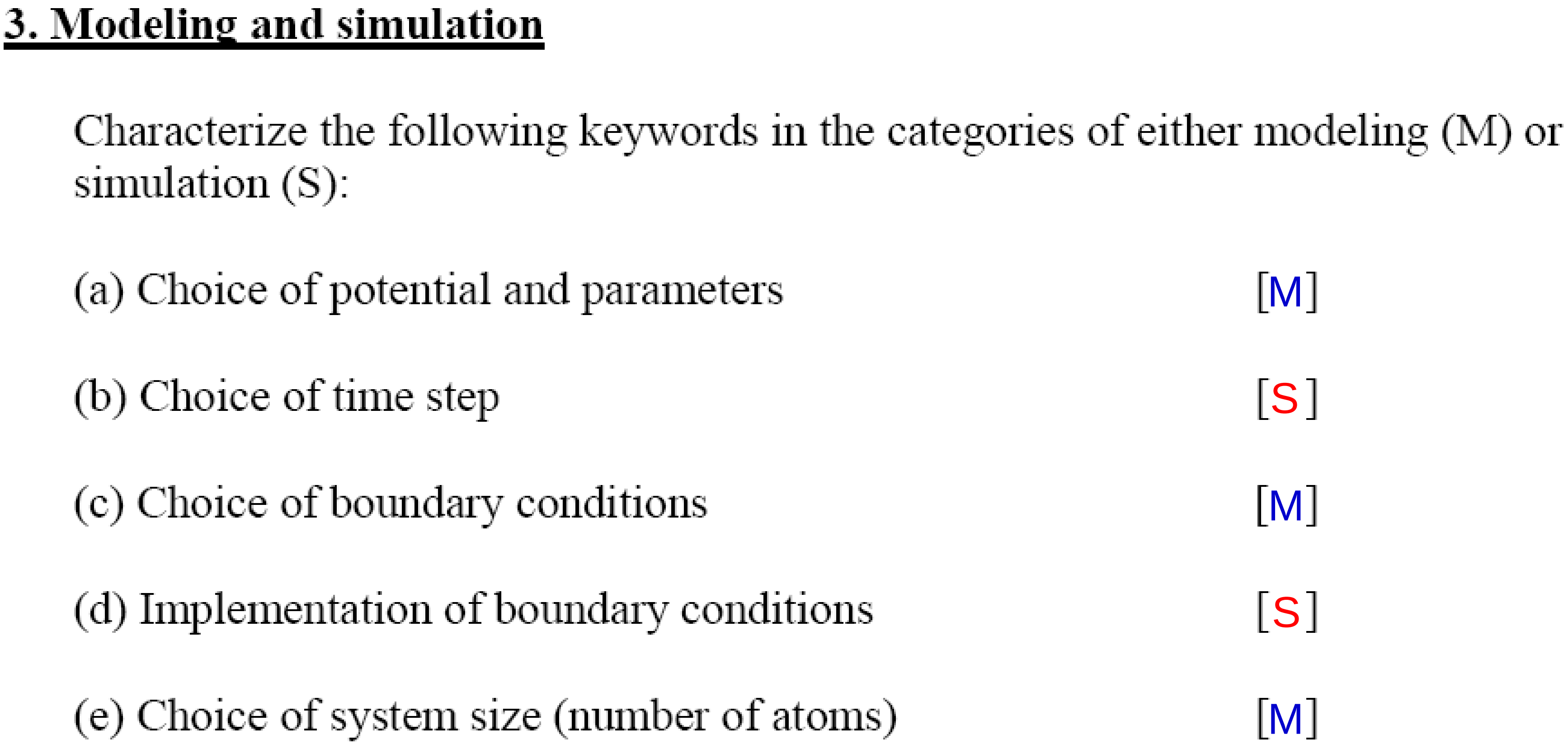
•**Simulation**: solving the equations that arose from the development of the model.



"Physical situation"

"Model"

Modeling and simulation



3. Modeling and simulation

Characterize the following keywords in the categories of either modeling (M) or simulation (S):

(a) Choice of potential and parameters [M]

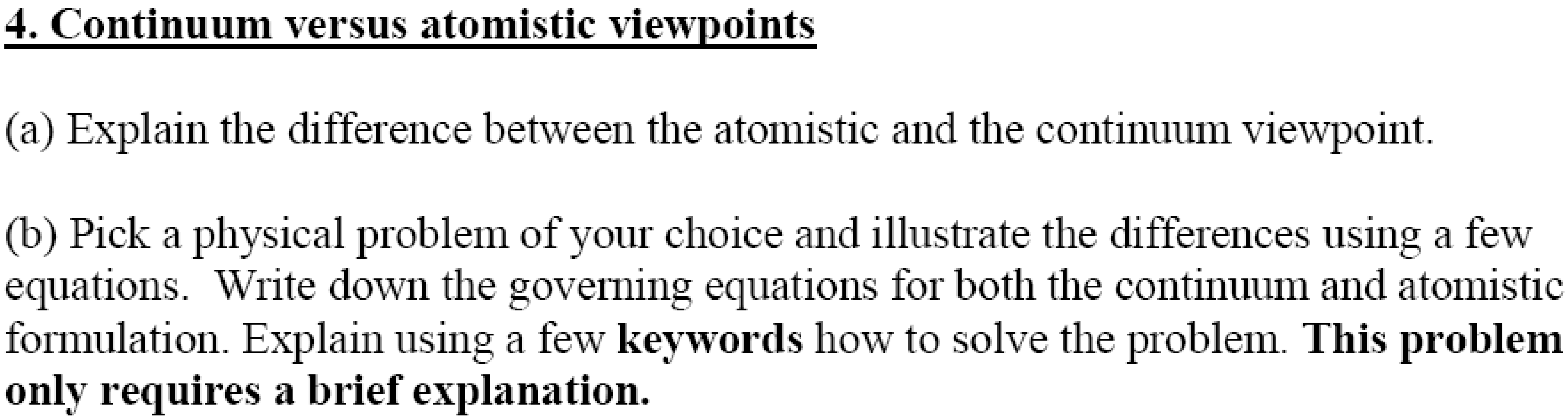
(b) Choice of time step [S]

(c) Choice of boundary conditions [M]

(d) Implementation of boundary conditions [S]

(e) Choice of system size (number of atoms) [M]

Atomistic versus continuum viewpoint



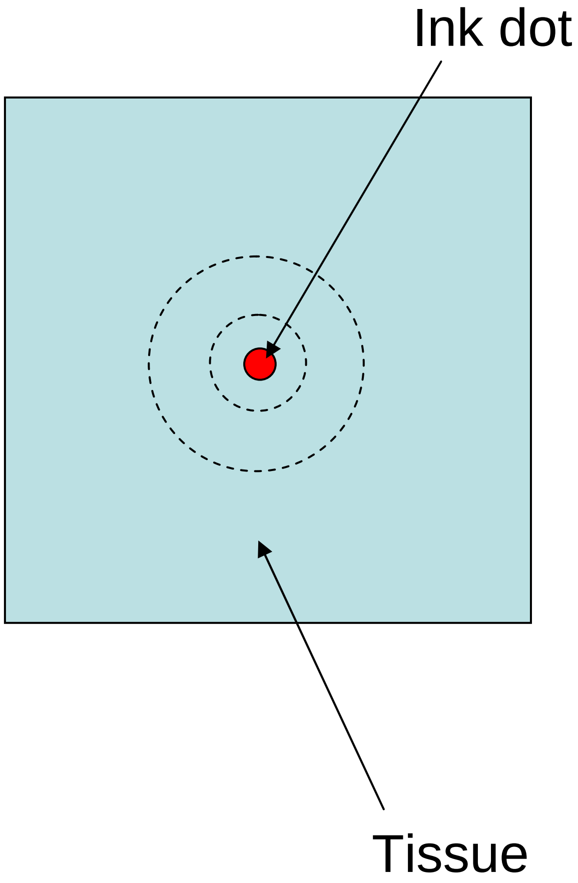
4. Continuum versus atomistic viewpoints

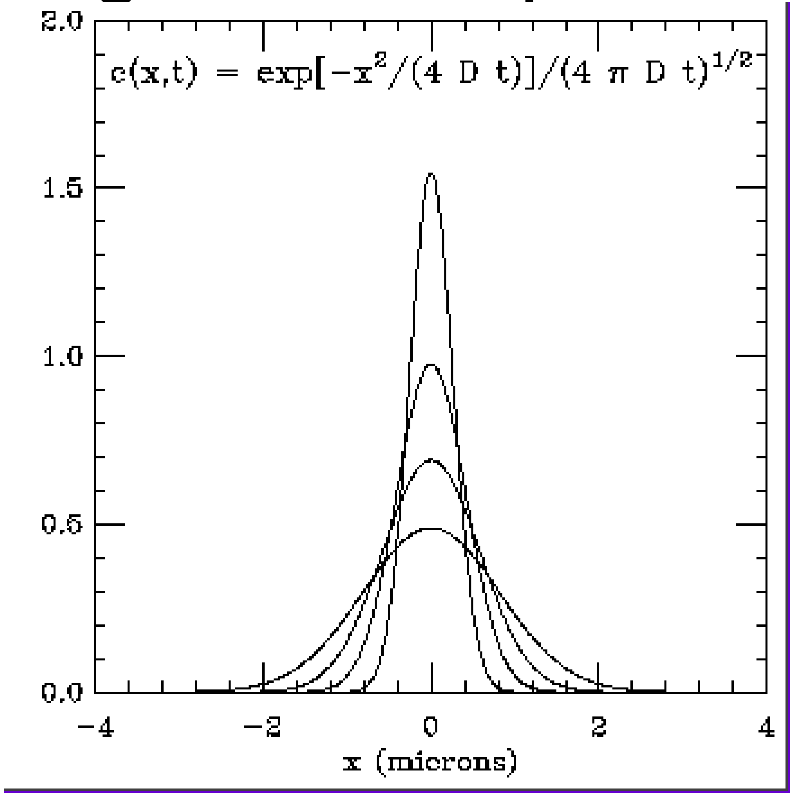
(a) Explain the difference between the atomistic and the continuum viewpoint.

(b) Pick a physical problem of your choice and illustrate the differences using a few equations. Write down the governing equations for both the continuum and atomistic formulation. Explain using a few **keywords** how to solve the problem. **This problem only requires a brief explanation.**

Diffusion: Phenomenological description

Physical problem





$$\frac{\partial c}{\partial t} = D\frac{d^2 c}{dx^2}$$

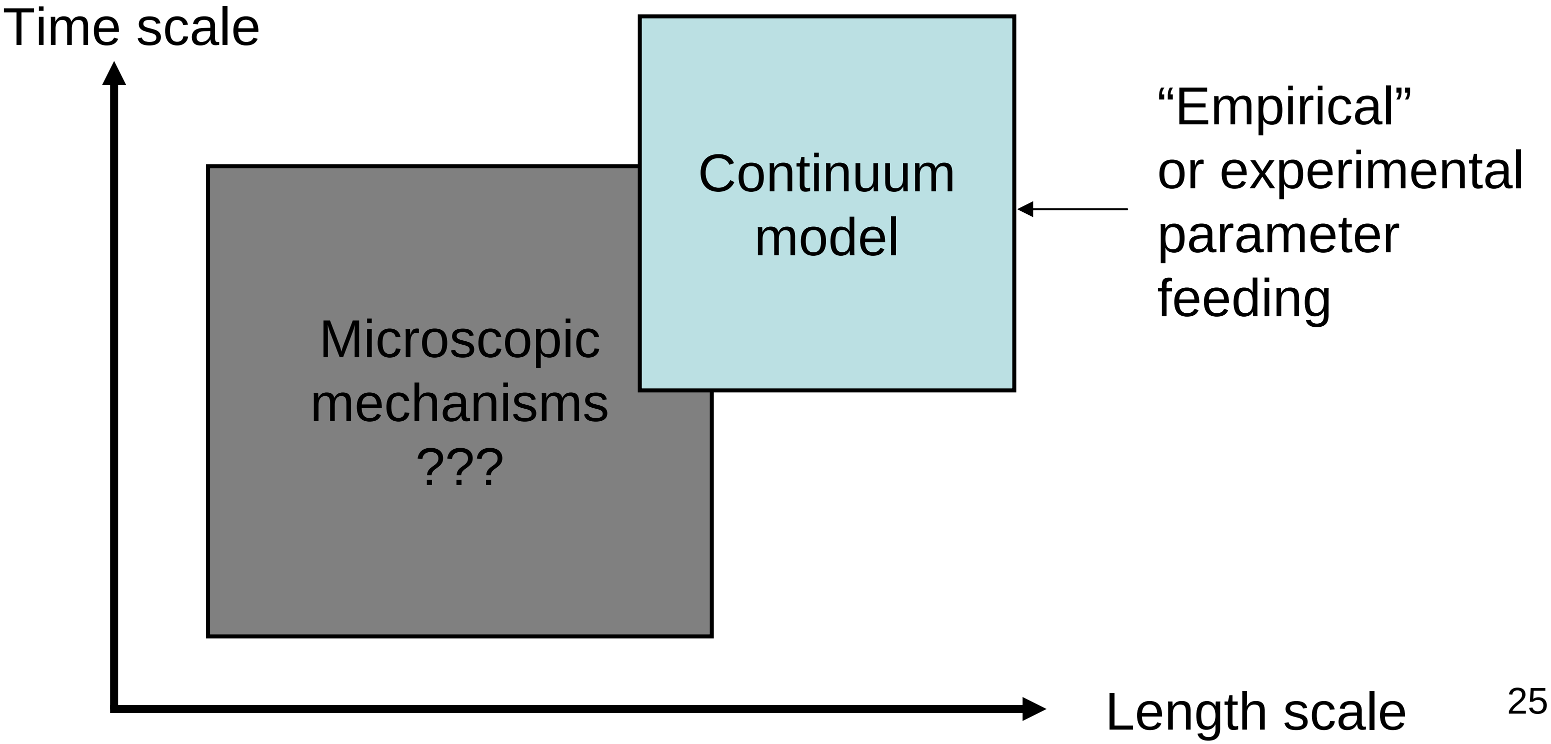
2nd Fick law (governing equation)

BC: $c\ (r = \infty) = 0$

IC: $c\ (r=0,\ t = 0) = c_0$

Continuum model: Empirical parameters

- Continuum model requires parameter that describes microscopic processes inside the material
- Need experimental measurements to calibrate



How to solve continuum problem: Finite difference scheme

$$\frac{\partial c}{\partial t} = D\frac{d^2 c}{dx^2}$$

$i =$ space

$j =$ time

Concentration at i
at old time

$$c_{i,j+1} = c_{i,j} + \frac{\delta t}{\delta x^2} D\left(c_{i+1,j} - 2c_{i,j} - c_{i-1,j}\right)$$

"explicit" numerical scheme (new concentration directly from concentration at earlier time)

Concentration at i
at old time

Concentration at i-1
at old time

Concentration at i
at new time

Concentration at $i+1$
at old time

***Other methods**: Finite element method*

Atomistic model of diffusion

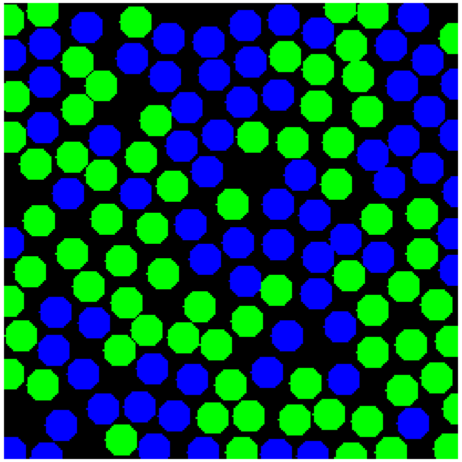
- Diffusion at macroscale (change of concentrations) is result of microscopic processes, random motion of particle
- Atomistic model provides an alternative way to describe diffusion
- Enables us to directly calculate the diffusion constant from the trajectory of atoms
- Follow trajectory of atoms and calculate how fast atoms leave their initial position

Concept:
follow this quantity over time

$$\boxed{D = -p \frac{\Delta x^2}{\Delta t}}$$

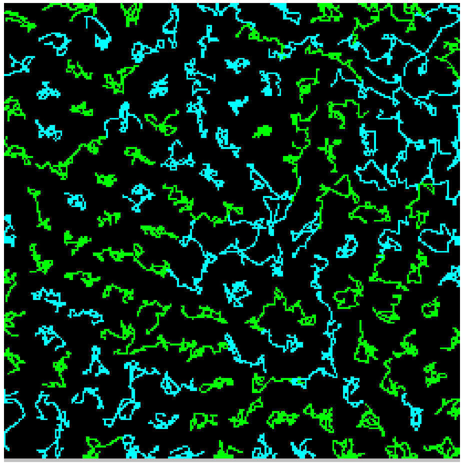
Atomistic model of diffusion

$$m_i \frac{d^2\vec{r}_i}{dt^2} = -\frac{dU(r)}{d\vec{r}_i} \qquad r = \{\vec{r}_j\} \qquad i = 1..N$$



Particles

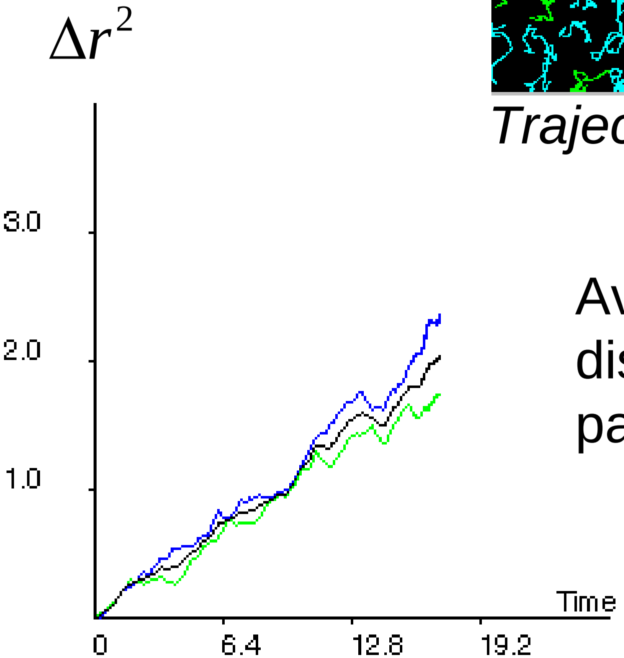
Images courtesy of the Center for Polymer Studies at Boston University. Used with permission.



Trajectories

Mean Squared Displacement function

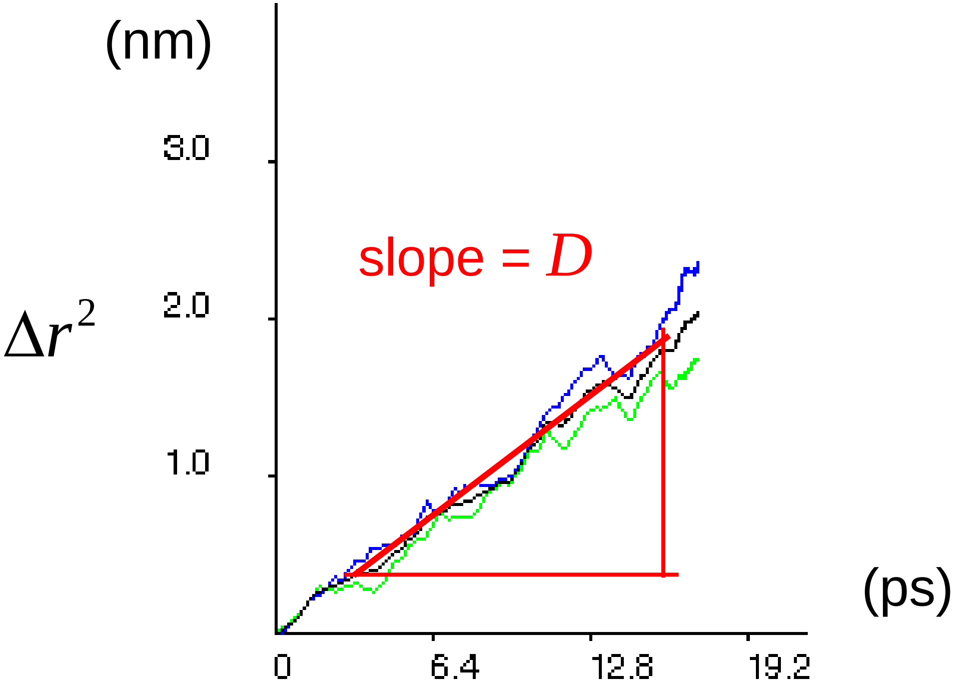
$$\Delta r^2(t) = \frac{1}{N}\sum_i \left(\vec{r}_i(t) - \vec{r}_i(t=0)\right)^2$$



Average squares of displacements of all particles

Calculation of diffusion coefficient

$$\Delta r^2(t) = \frac{1}{N}\sum_i \left(\underbrace{r_i(t)}_{\text{Position of atom } i \text{ at time } t} - \underbrace{r_i(t=0)}_{\text{Position of atom } i \text{ at time } t=0}\right)^2$$



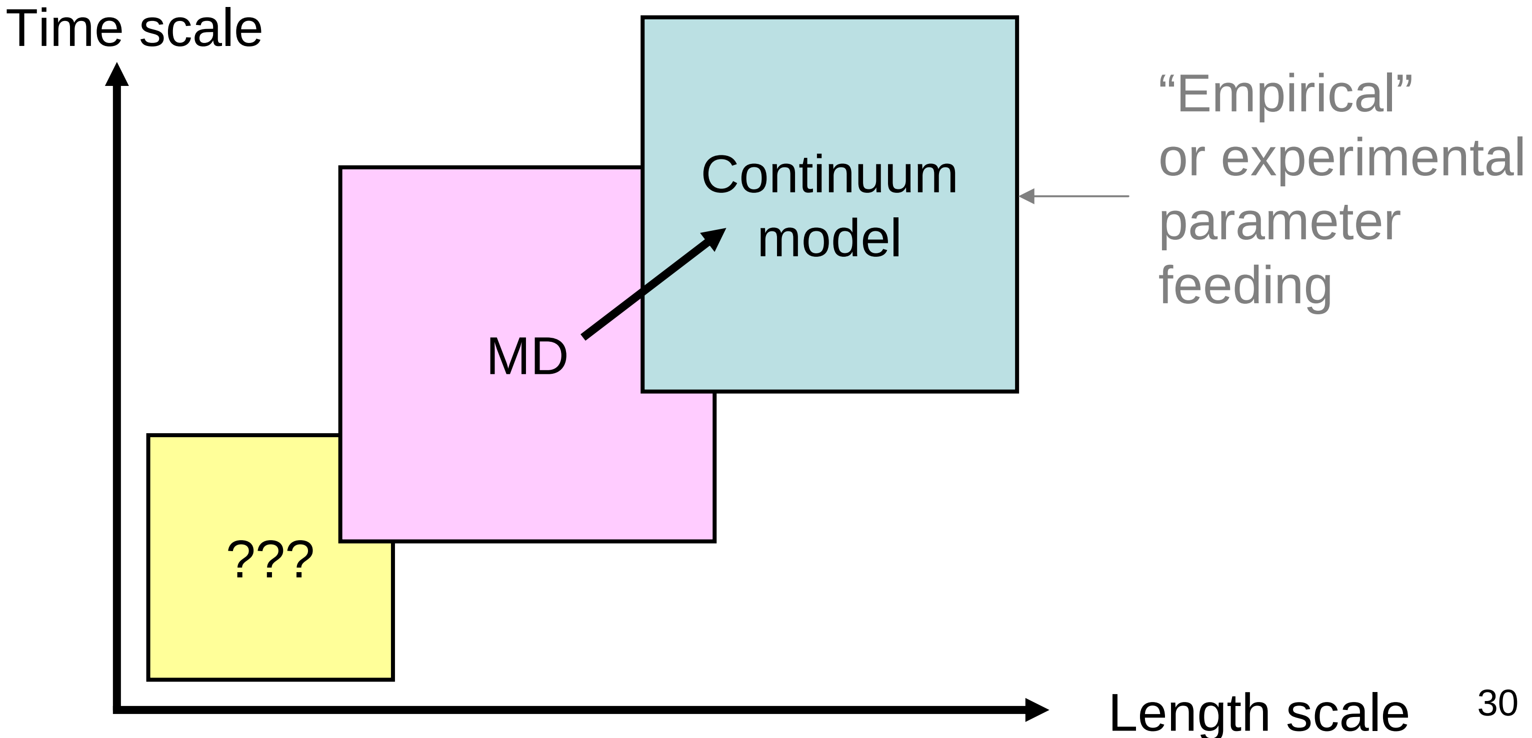
Einstein equation

$$\boxed{D = \frac{1}{2d}\lim_{t\to\infty}\frac{d}{dt}\left(\Delta r^2(t)\right)}$$

1D=1, 2D=2, 3D=3

Summary

- Molecular dynamics provides a powerful approach to relate the diffusion constant that appears in continuum models to atomistic trajectories
- Outlines multi-scale approach: Feed parameters from atomistic simulations to continuum models



1.1 Atomistic and molecular simulation algorithms

1.2 Property calculation

1.3 Potential/force field models

1.4 Applications

Goals: How to calculate “useful” properties from MD runs (temperature, pressure, RDF, VAF,..); significance of averaging; Monte Carlo schemes

Property calculation: Introduction

Have:

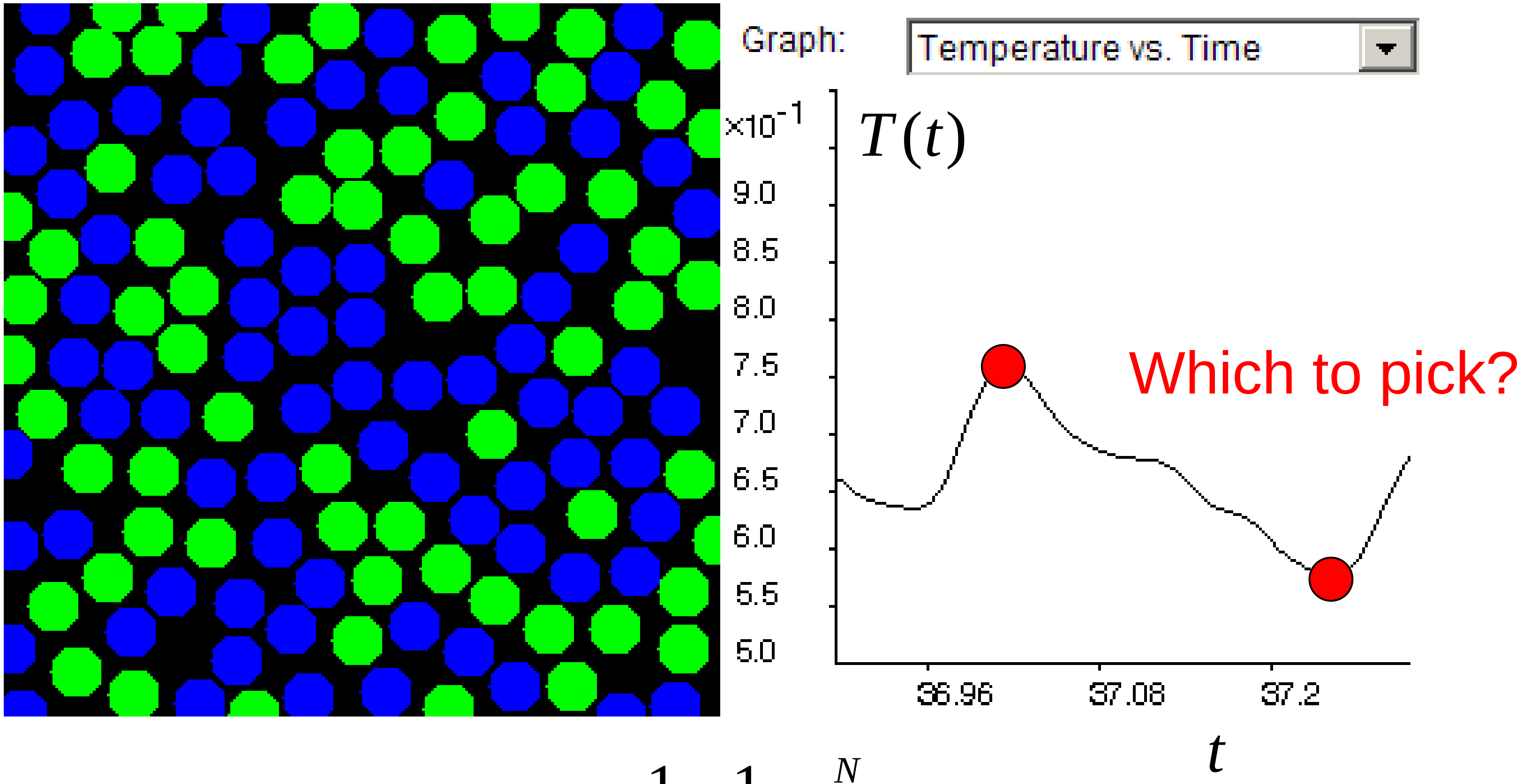
$$\vec{r}_i(t), \vec{v}_i(t), \vec{a}_i(t) \qquad i = 1..N$$

“microscopic information”

Want:

- Thermodynamical properties (temperature, pressure, ..)
- Transport properties (diffusivities, shear viscosity, ..)
- Material’s state (gas, liquid, solid)

Micro-macro relation



Which to pick?

$$T(t) = \frac{1}{3}\frac{1}{Nk_B}\sum_{i=1}^{N} m_i \vec{v}_i^{\,2}(t)$$

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

Specific (individual) microscopic states are insufficient to relate to macroscopic properties

Ergodic hypothesis: significance of averaging

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

property must be properly averaged

- Ergodic hypothesis:

Ensemble (statistical) average = time average

- All microstates are sampled with appropriate probability density over long time scales

$$\underbrace{\frac{1}{N_A}\sum_{i=1..N_A} A(i)} =< A >_{Ens} =< A >_{Time} = \underbrace{\frac{1}{N_t}\sum_{i=1..N_t} A(i)}$$

Monte Carlo
Average over Monte Carlo steps
NO DYNAMICAL INFORMATION

MD
Average over time steps
DYNAMICAL INFORMATION

Monte Carlo scheme

- Concept: Find convenient way to solve the integral

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

- Use idea of “random walk” to step through relevant microscopic states and thereby create proper weighting (visit states with higher probability density more often)

- Monte Carlo schemes: Many applications (beyond what is discussed here; general method to solve complex integrations)

Monte Carlo scheme: area calculation

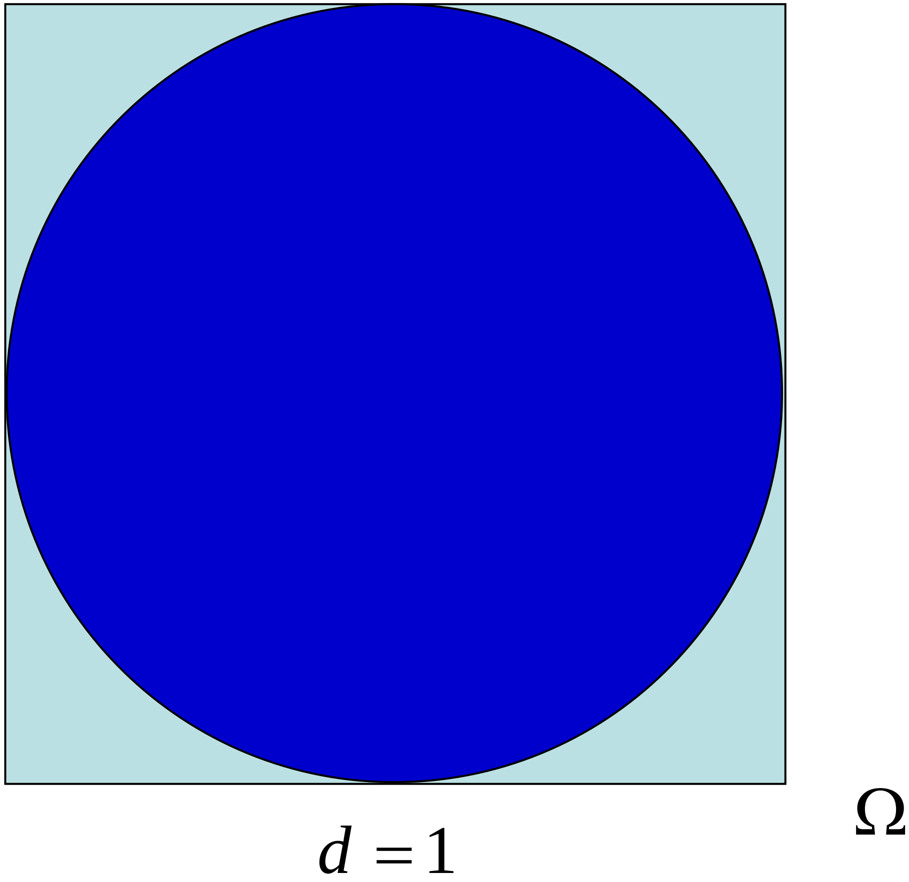
Method to carry out integration (illustrate general concept)

Want:

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

E.g.: Area of circle (value of π)

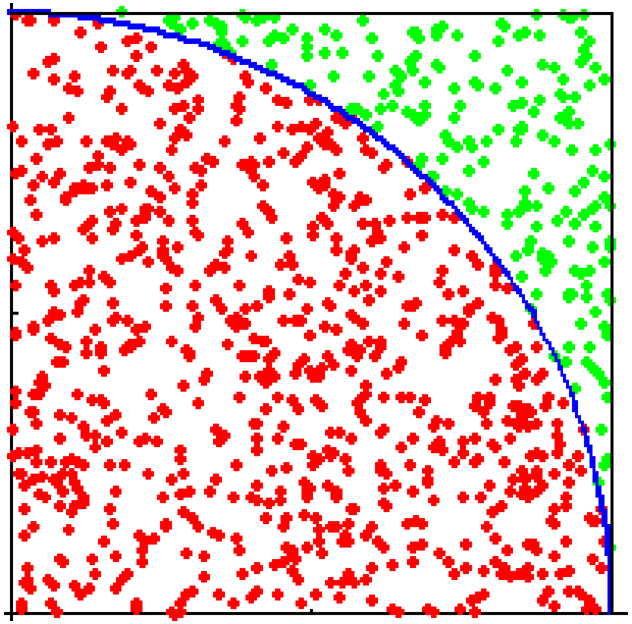
$$A_C = \frac{\pi d^2}{4} \qquad A_C = \frac{\pi}{4}$$



Monte Carlo scheme

- 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 otherwise $f(\vec{x}_i) = 0$

$d = 1/2$



Courtesy of John H. Mathews. Used with permission.

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

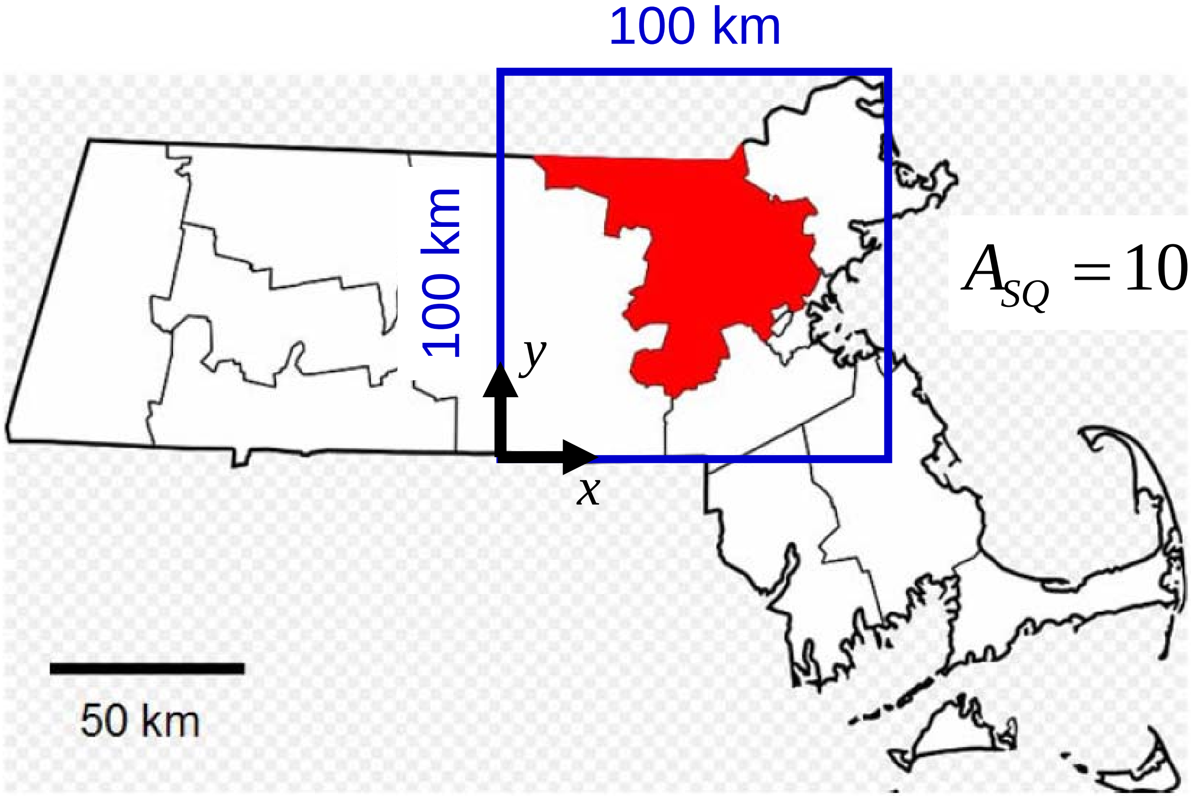
$$\Updownarrow$$

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

N_A: Attempts made

See also: http://math.fullerton.edu/mathews/n2003/MonteCarloPiMod.html

Area of Middlesex County (MSC)



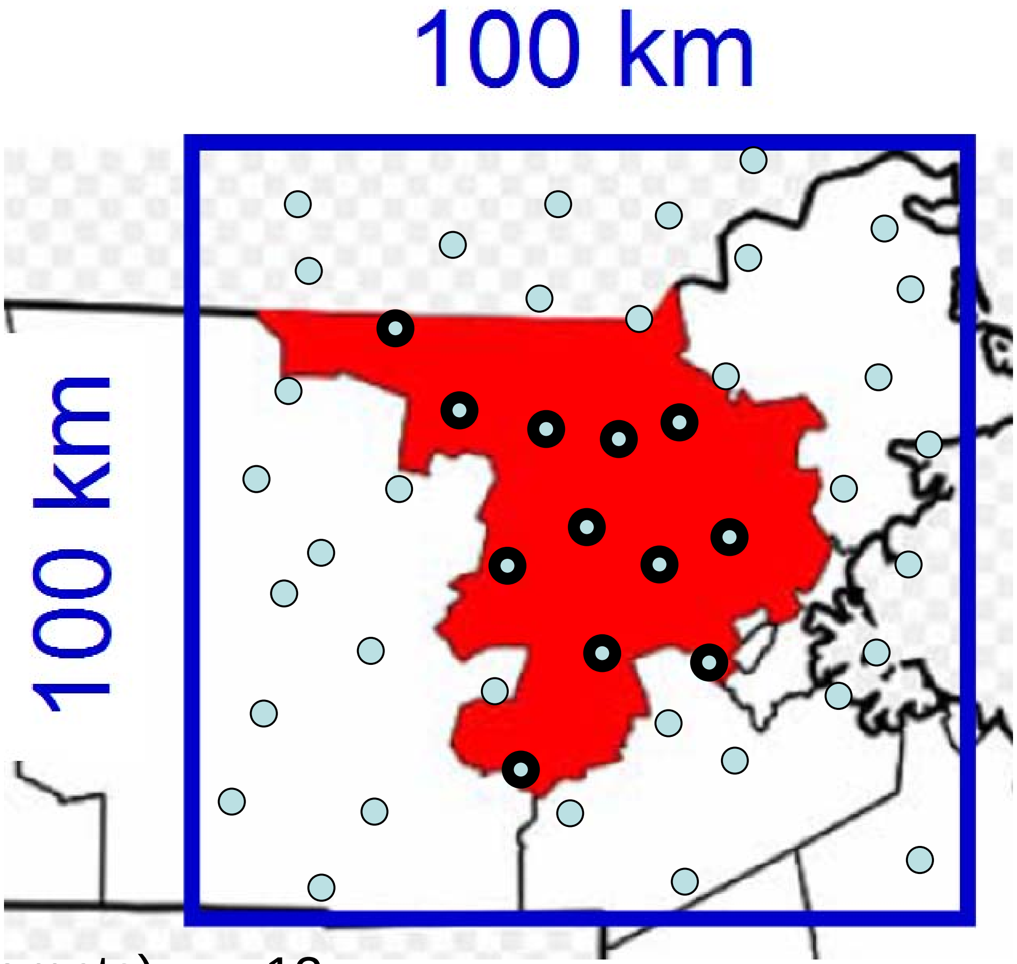
$$A_{SQ} = 10{,}000\,\text{km}^2$$

Image courtesy of Wikimedia Commons.

$$A_{MSC} = A_{SQ}\overbrace{\frac{1}{N_A}\sum_i f(\vec{x}_i)}^{\textit{Fraction of points that lie within MS County}}$$

Expression provides area of MS County

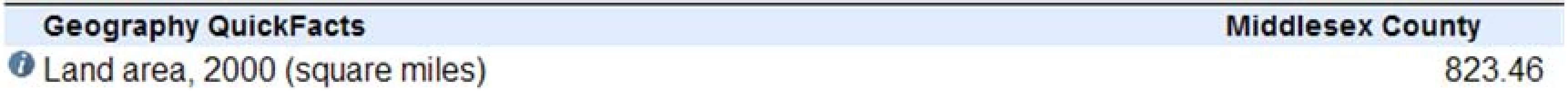
Detailed view - schematic



N_A=55 points (attempts)
12 points within

$$A_{MSC} = A_{SQ}\frac{1}{N_A}\overbrace{\sum_i f(\vec{x}_i)}^{12} = 10000 \cdot 0.22\,\mathrm{km}^2 = 2181.8\,\mathrm{km}^2$$

Results U.S. Census Bureau



Geography QuickFacts	Middlesex County
Land area, 2000 (square miles)	823.46

823.46 square miles = 2137 km^2 (1 square mile=2.58998811 km^2)

Taken from: http://quickfacts.census.gov/qfd/states/25/25017.html

Monte Carlo result: $A_{MSC} = 2181.8\,\mathrm{km}^2$

Analysis of satellite images

Image removed due to copyright restrictions.

Google Satellite image of Spy Pond, in Cambridge, MA.

200 m

Metropolis Hastings algorithm

Images removed due to copyright restrictions.

Please see: Fig. 2.7 in Buehler, Markus J. *Atomistic Modeling of Materials Failure*. Springer, 2008.

Images removed due to copyright restrictions.

Please see: Fig. 2.8 in Buehler, Markus J. *Atomistic Modeling of Materials Failure*. Springer, 2008.

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

Molecular Dynamics vs. Monte Carlo

- MD provides actual **dynamical data for nonequilibrium processes** (fracture, deformation, instabilities)

  Can study onset of failure, instabilities

- MC provides **information about equilibrium properties** (diffusivities, temperature, pressure)

  Not suitable for processes like fracture

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

Property calculation: Temperature and pressure

- Temperature

$$T = \frac{1}{3}\frac{1}{Nk_B} < \sum_{i=1}^{N} m_i \vec{v}_i^{\,2} > \qquad \vec{v}_i^{\,2} = \vec{v}_i \cdot \vec{v}_i$$

$$\boxed{\begin{gathered} T \sim v^2 \\ v \sim \sqrt{T} \end{gathered}}$$

Temperature control in MD (*NVT* ensemble)

Berendsen thermostat

$$r_i(t_0+\Delta t) = 2r_i(t_0) - r_i(t_0-\Delta t) + a_i(t_0)\Delta t^2 + \dots$$

Calculate temperature $$T = \frac{1}{3}\frac{1}{Nk_B} < \sum_{i=1}^{N} m_i \vec{v}_i^{\,2} >$$

$$v \sim \sqrt{T}$$

Rescaling parameter

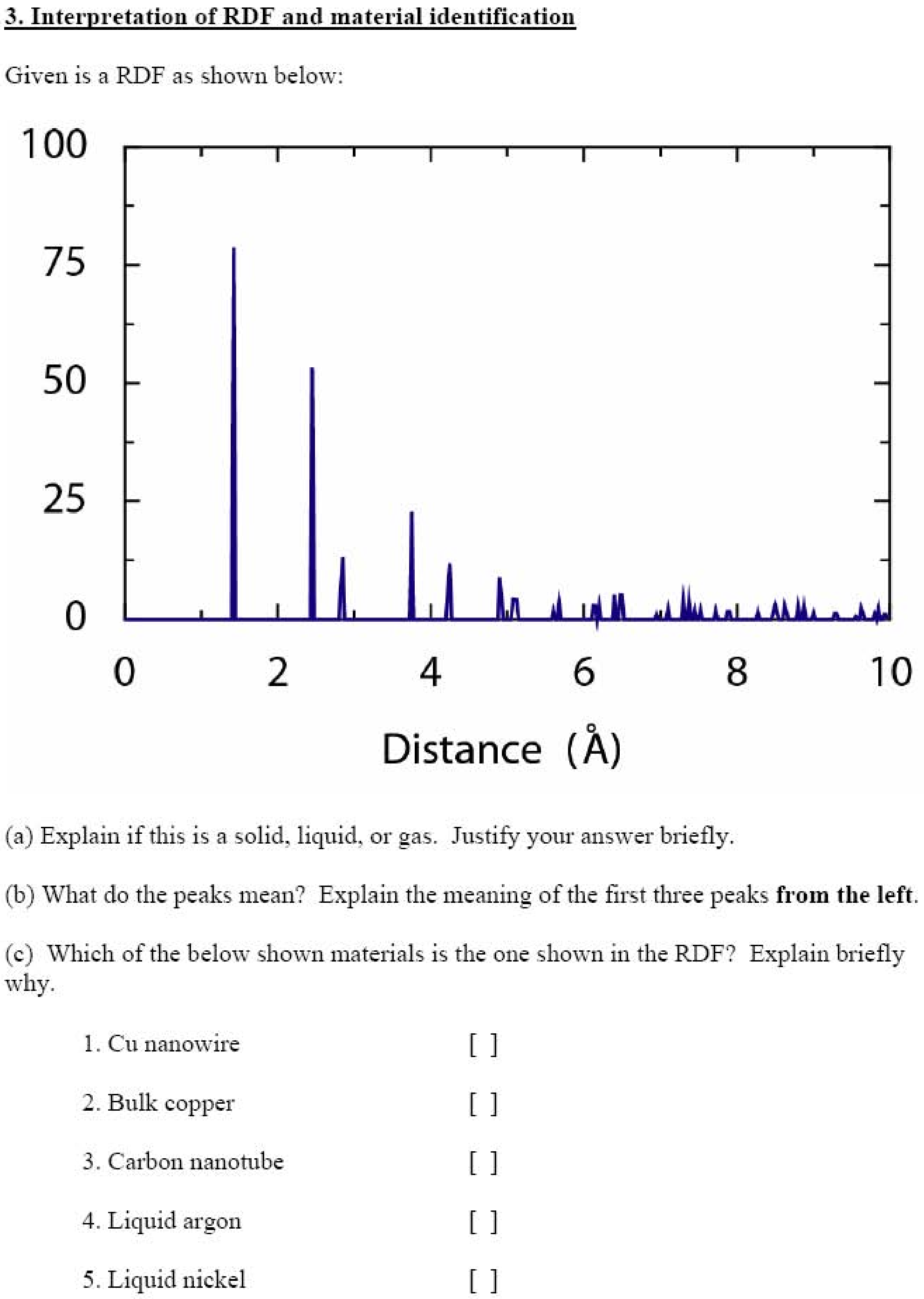
Calculate ratio of current vs. desired temperature $$\eta = \sqrt{\frac{T}{T_{\mathrm{set}}}}$$

desired “set” temperature

Modification of velocities

Rescale velocities $$v_{\mathrm{new}} = v\eta \qquad \bar{v}_{i,\mathrm{new}} = \bar{v}_i\eta$$

Interpretation of RDF



3. Interpretation of RDF and material identification

Given is a RDF as shown below:

(a) Explain if this is a solid, liquid, or gas. Justify your answer briefly.

(b) What do the peaks mean? Explain the meaning of the first three peaks **from the left**.

(c) Which of the below shown materials is the one shown in the RDF? Explain briefly why.

1. Cu nanowire [ ]
2. Bulk copper [ ]
3. Carbon nanotube [ ]
4. Liquid argon [ ]
5. Liquid nickel [ ]

Formal approach: Radial distribution function (RDF)

The radial distribution function is defined as

$$g(r) = \underbrace{\rho(r)}_{\text{Local density}} / \overbrace{\rho}^{\text{Density of atoms (volume)}}$$

Provides information about the density of atoms at a given radius r; $\rho(r)$ is the local density of atoms

$$g(r) = \frac{\overbrace{< N(r \pm \tfrac{\Delta r}{2}) >}^{\text{Number of atoms in the interval } r \pm \frac{\Delta r}{2}}}{\underbrace{\Omega(r \pm \tfrac{\Delta r}{2})}_{\text{Volume of this shell } (dr)}} \frac{1}{\rho}$$

$g(r) 2\pi r^2 dr =$ Number of particles that lie in a spherical shell of radius *r* and thickness *dr*

Radial distribution function: Solid versus liquid versus gas

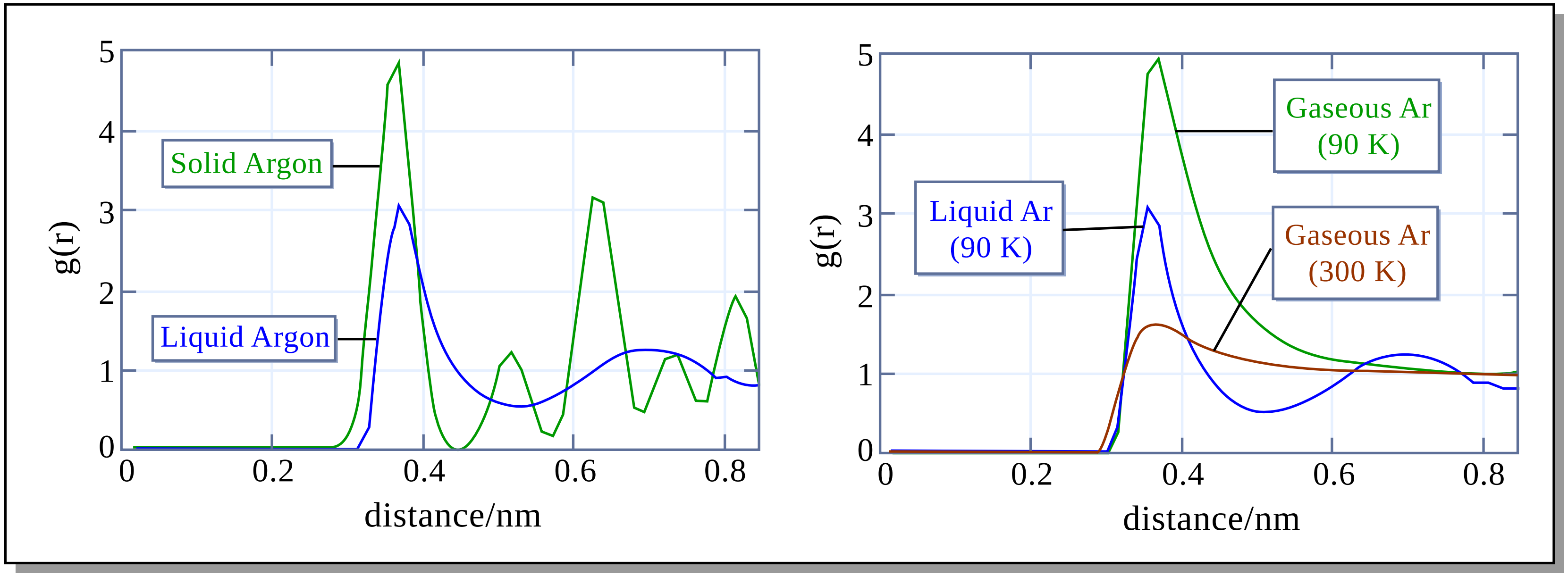


Image by MIT OpenCourseWare.

Note: The first peak corresponds to the nearest neighbor shell, the second peak to the second nearest neighbor shell, etc.

In FCC: 12, 6, 24, and 12 in first four shells

RDF and crystal structure

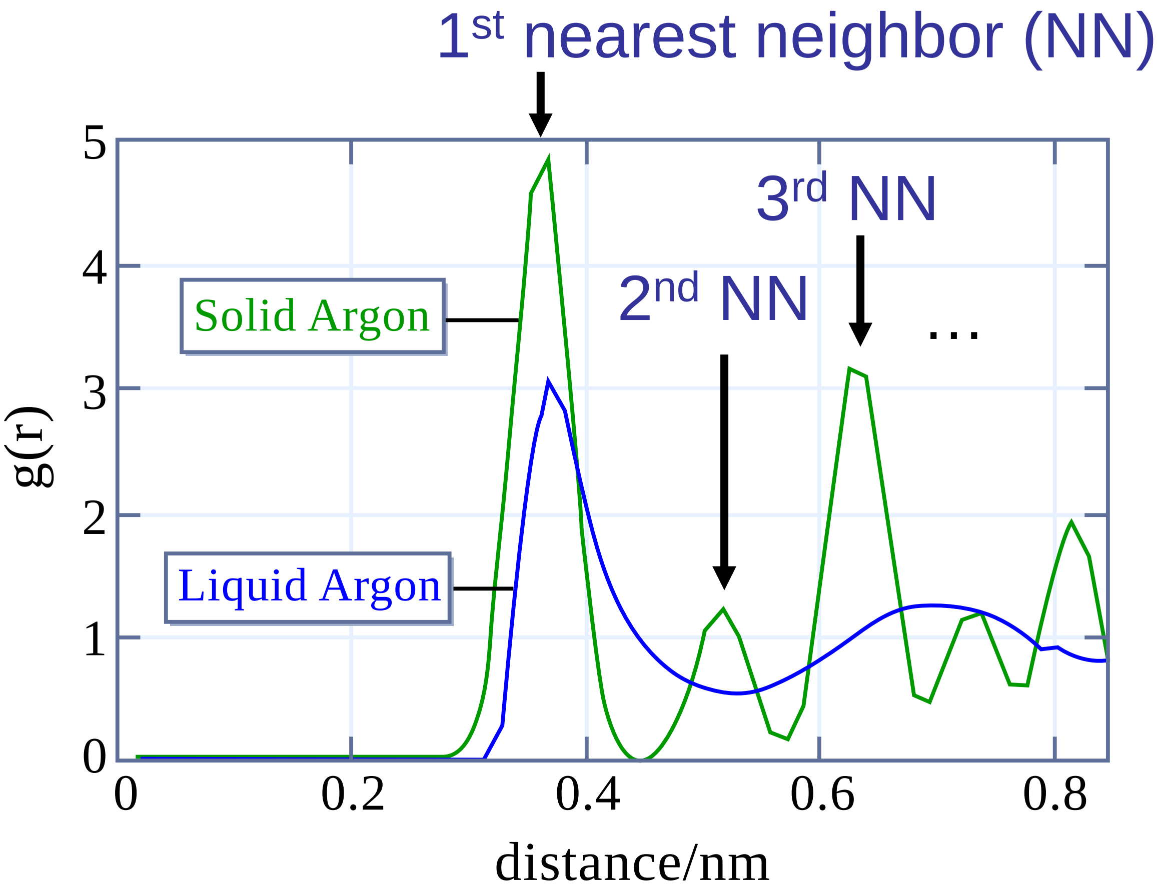
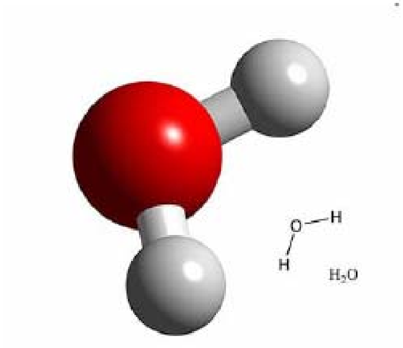


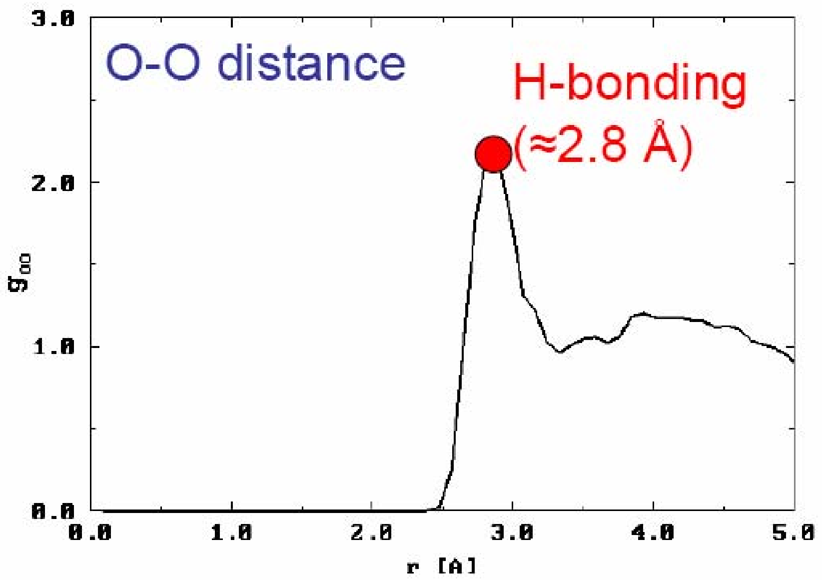
Image by MIT OpenCourseWare.

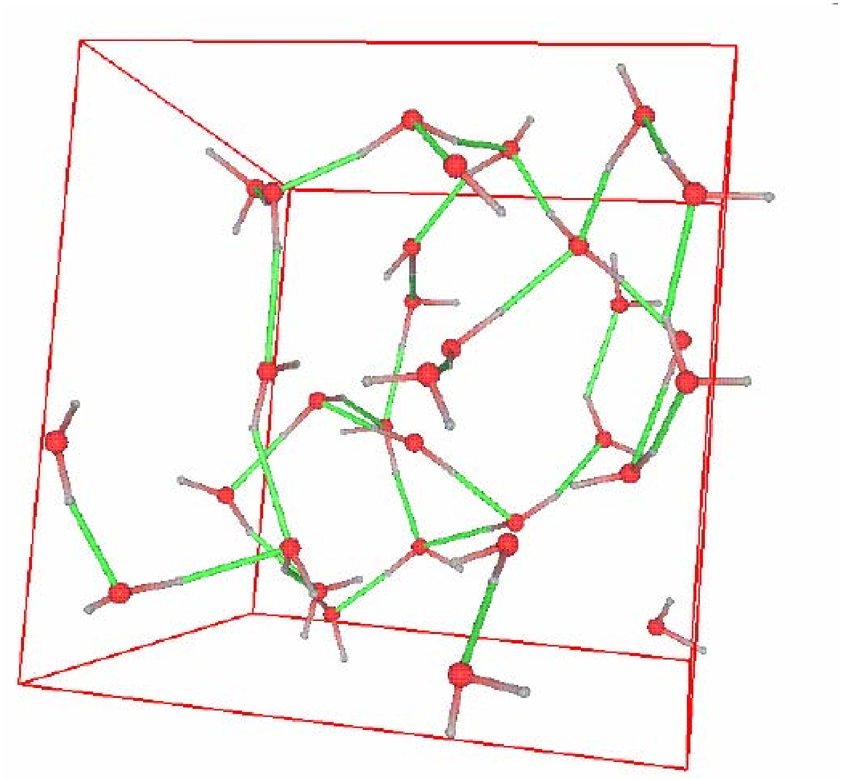
Peaks in RDF characterize NN distance, can infer from RDF about crystal structure

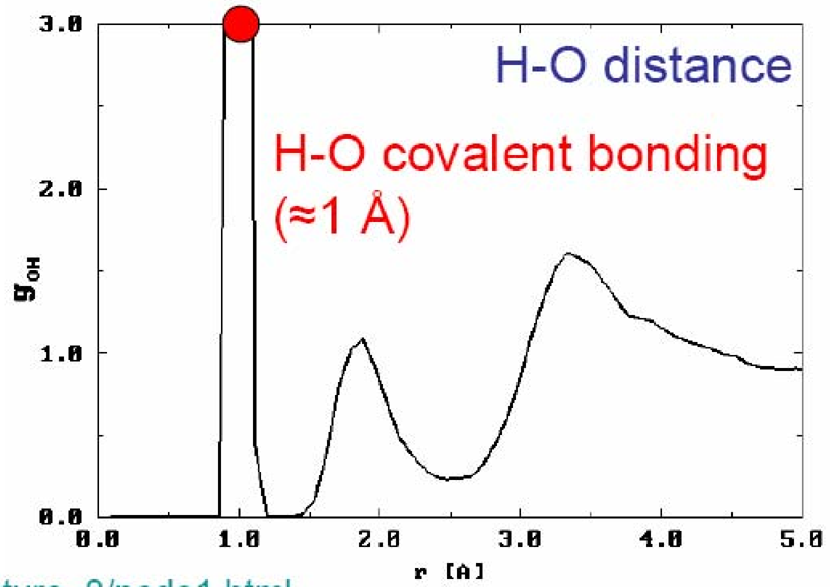
http://physchem.ox.ac.uk/~rkt/lectures/liqsolns/liquids.html

RDF of water (H_2O)









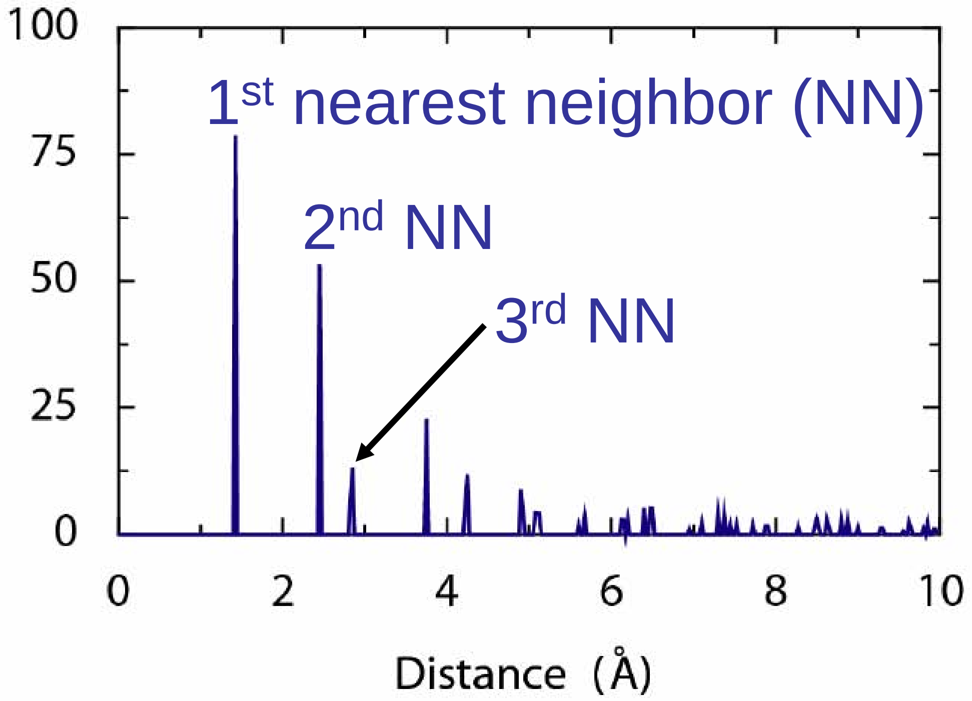
Images courtesy of Mark Tuckerman. Used with permission.

http://www.nyu.edu/classes/tuckerman/stat.mech/lectures/lecture_8/node1.html

Interpretation of RDF

3. Interpretation of RDF and material identification

Given is a RDF as shown below:



(a) Explain if this is a solid, liquid, or gas. Justify your answer briefly.

(b) What do the peaks mean? Explain the meaning of the first three peaks **from the left**.

(c) Which of the below shown materials is the one shown in the RDF? Explain briefly why.

1. Cu nanowire [ ]
2. Bulk copper [ ]
3. Carbon nanotube [X]
4. Liquid argon [ ]
5. Liquid nickel [ ]

copper: NN distance > 2 Å

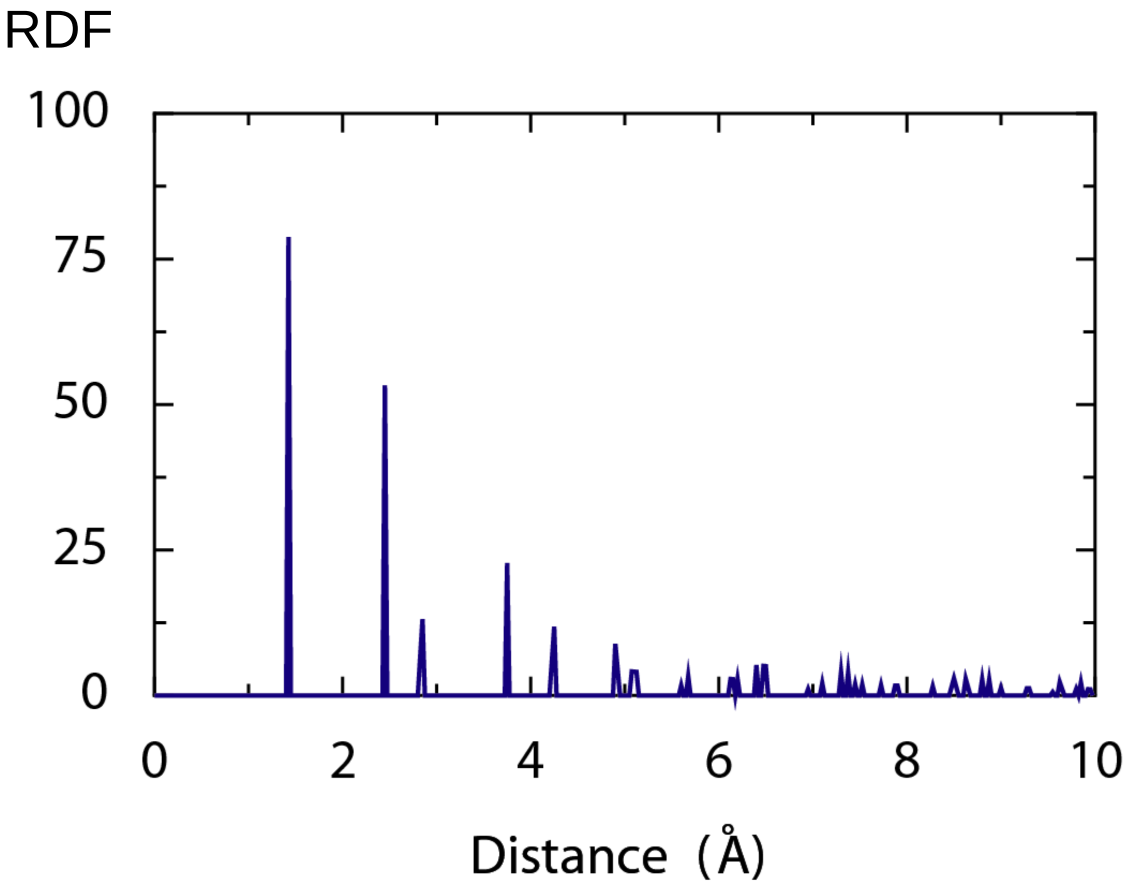
not a liquid (sharp peaks)

Graphene/carbon nanotubes

Images of graphene/carbon nanutubes:

http://weblogs3.nrc.nl/techno/wp-content/uploads/080424_Grafeen/Graphene_xyz.jpg

http://depts.washington.edu/polylab/images/cn1.jpg



Graphene/carbon nanotubes (rolled up graphene)
NN: 1.42 Å, second NN 2.46 Å …

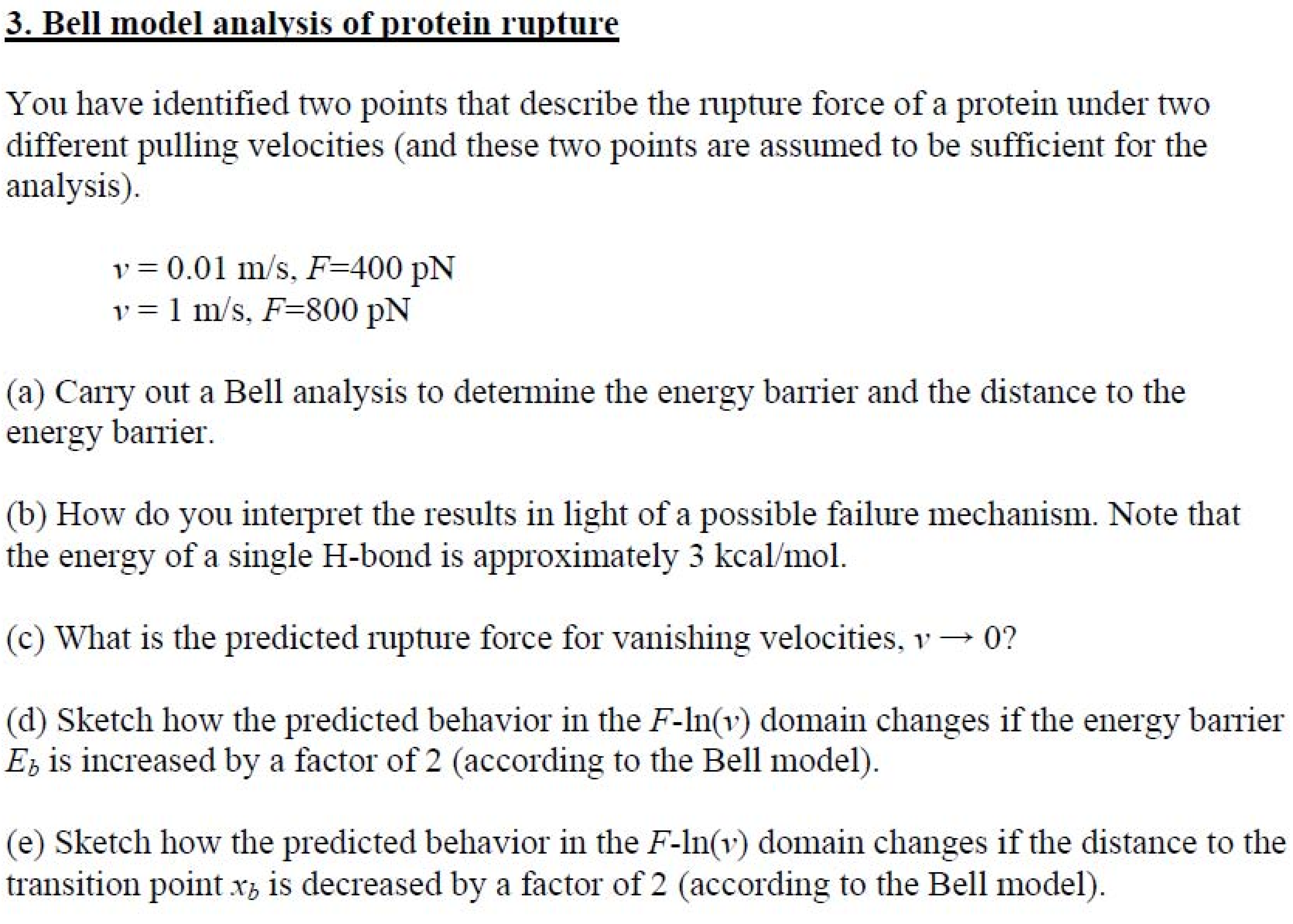
Summary – property calculation

Property	*Definition*	*Application*
Temperature	$T = \frac{1}{3}\frac{1}{Nk_B} < \sum_{i=1}^{N} m_i \vec{v}_i^{\,2} > \qquad \vec{v}_i^{\,2} = \vec{v}_i \cdot \vec{v}_i$	Direct
MSD	$< \Delta r^2(t) >= \frac{1}{N} \sum_i \left(r_i(t) - r_i(t=0) \right)^2$	Diffusivity
RDF	$g(r) =< \frac{N(r \pm \frac{\Delta r}{2})}{\Omega(r \pm \frac{\Delta r}{2})\rho} >$	Atomic structure (signature)

Material properties: Classification

- Structural – crystal structure, **RDF**
- Thermodynamic -- equation of state, heat capacities, thermal expansion, free energies, use **RDF, temperature, pressure/stress**
- Mechanical -- elastic constants, cohesive and shear strength, elastic and plastic deformation, fracture toughness, use **stress**
- Transport -- diffusion, viscous flow, thermal conduction, use **MSD, temperature**

Bell model analysis (protein rupture)



3. Bell model analysis of protein rupture

You have identified two points that describe the rupture force of a protein under two different pulling velocities (and these two points are assumed to be sufficient for the analysis).

$v = 0.01$ m/s, F=400 pN
$v = 1$ m/s, F=800 pN

(a) Carry out a Bell analysis to determine the energy barrier and the distance to the energy barrier.

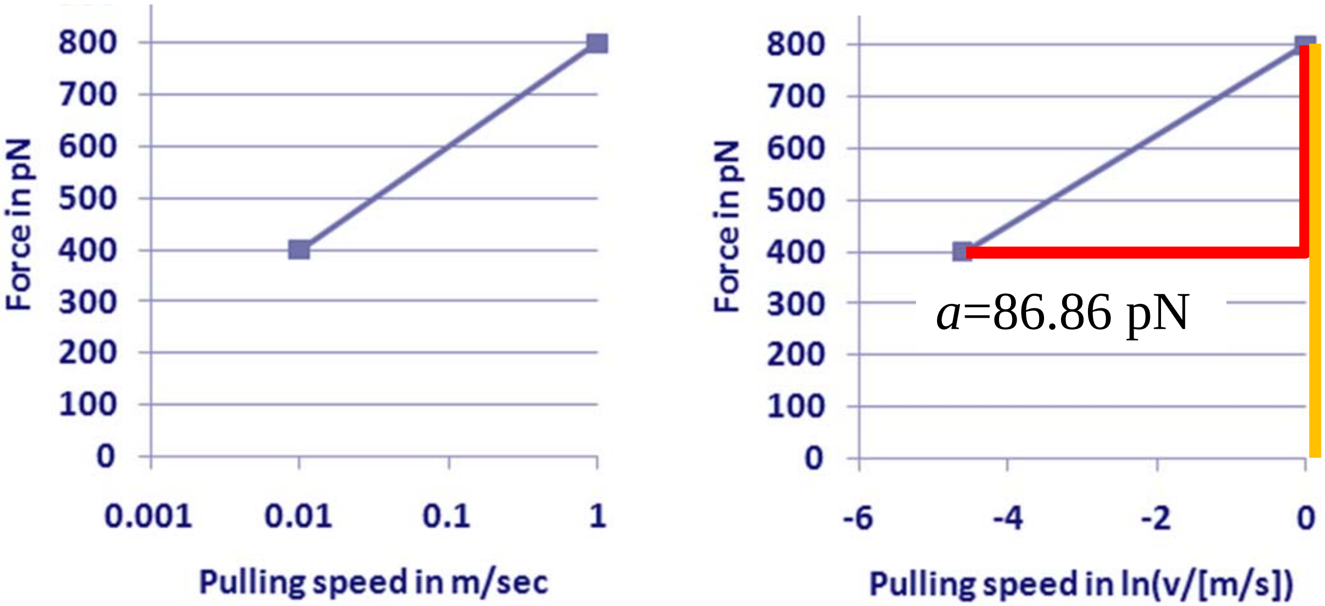
(b) How do you interpret the results in light of a possible failure mechanism. Note that the energy of a single H-bond is approximately 3 kcal/mol.

(c) What is the predicted rupture force for vanishing velocities, $v \rightarrow 0$?

(d) Sketch how the predicted behavior in the F-ln(v) domain changes if the energy barrier E_b is increased by a factor of 2 (according to the Bell model).

(e) Sketch how the predicted behavior in the F-ln(v) domain changes if the distance to the transition point x_b is decreased by a factor of 2 (according to the Bell model).

Bell model analysis (protein rupture)



a=86.86 pN

b=800 pN

$$f(v;x_b,E_b)=a\cdot\ln v+b$$

$$a=\frac{k_BT}{x_b} \quad (1)$$

k_B=1.3806505E-23 J/K

$$b=-\frac{k_bT}{x_b}\ln\left(\omega_0 x_b \exp\left(-\frac{E_b}{k_bT}\right)\right) \quad (1)$$

$$\omega_0=1\times10^{13}\,1/\sec$$

Get a and b from fitting to the graphs

Solve (1) for a, use (2) to solve for E_b

a=(800-400)/(0-(-4.6))) pN
=86.86 pN → x_b=0.47 Å

Determining the energy barrier

$$b = -\frac{k_b T}{x_b}\ln\left(\omega_0 x_b \exp\left(-\frac{E_b}{k_b T}\right)\right) = -\frac{k_b T}{x_b}\left[\ln(\omega_0 x_b) - \frac{E_b}{k_b T}\right]$$

$$-\frac{b x_b}{k_b T} = \ln(\omega_0 x_b) - \frac{E_b}{k_b T}$$

$$\frac{E_b}{k_b T} = \ln(\omega_0 x_b) + \frac{b x_b}{k_b T}$$

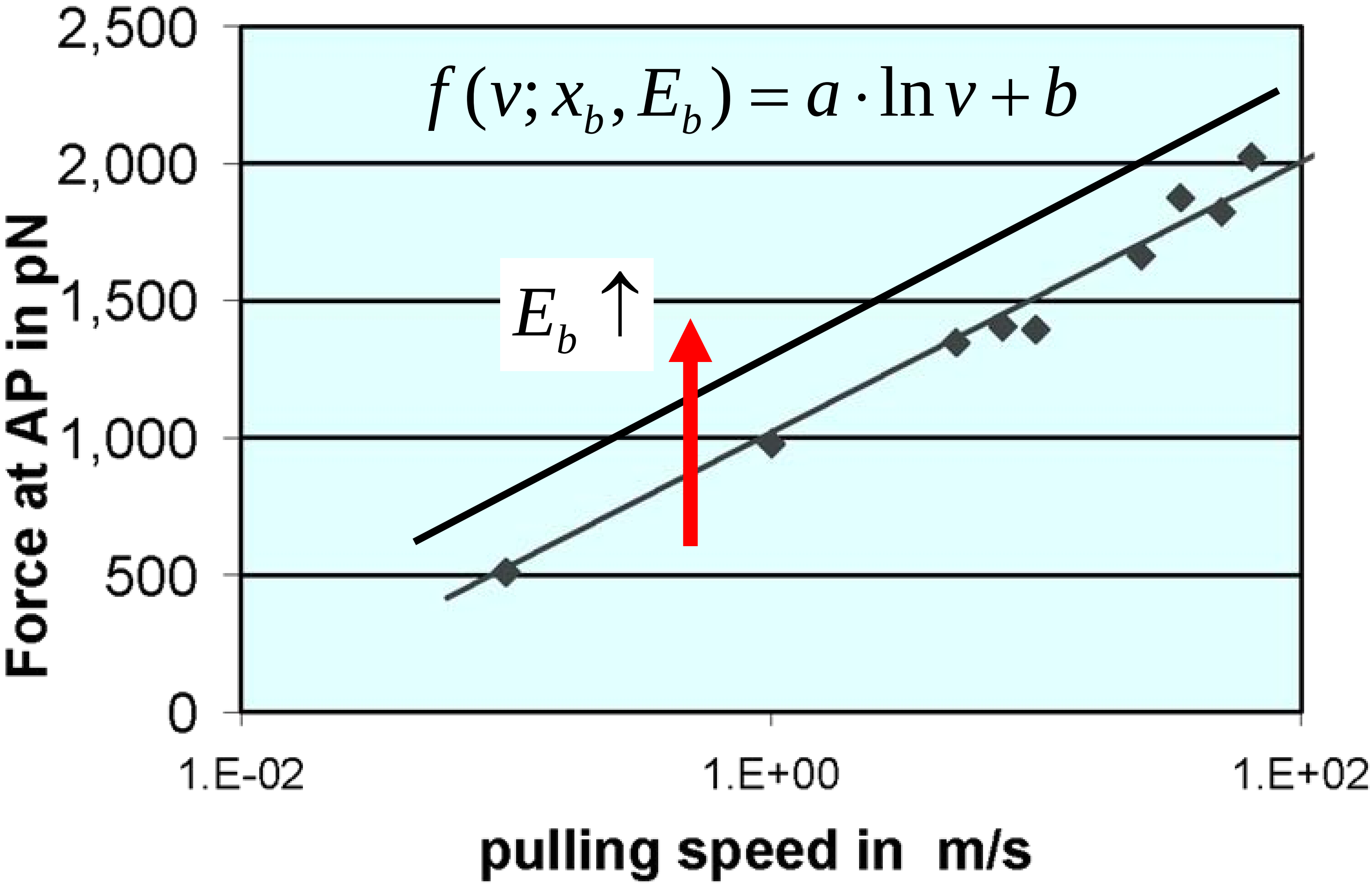
$$E_b = \left[\ln(\omega_0 x_b) + \frac{b x_b}{k_b T}\right] k_b T$$

b=800 pN → $E_b \approx$9 kcal/mol

1 kcal/mol=6.9477E-21 J

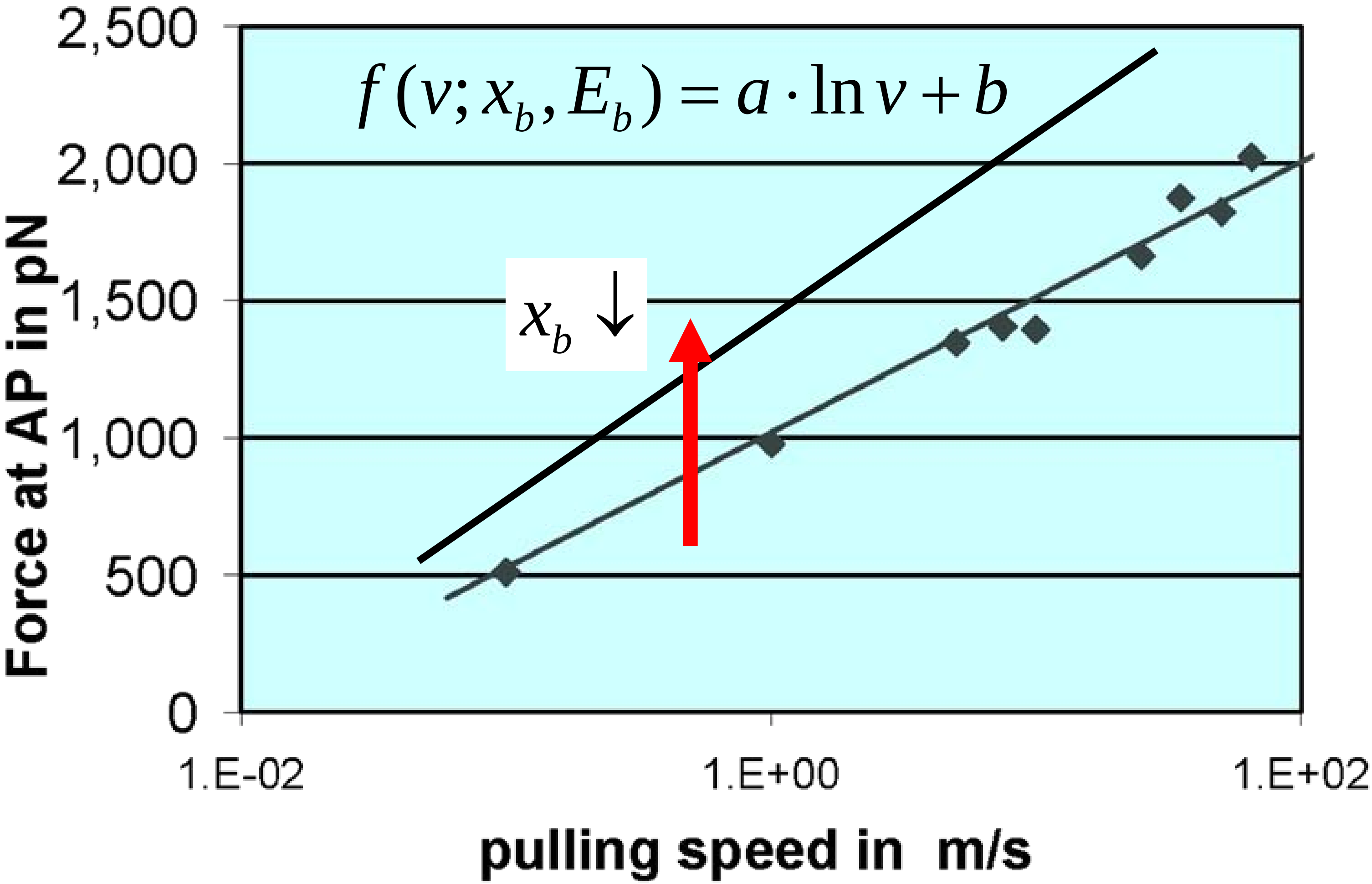
Possible mechanism: Rupture of **3 H-bonds** (H-bond energy 3 kcal/mol)

Scaling with E_b: shifts curve



$$a = \frac{k_B \cdot T}{x_b} \qquad b = -\frac{k_B \cdot T}{x_b} \cdot \ln v_0 \qquad v_0 = \omega_0 \cdot x_b \cdot \exp\left(-\frac{E_b}{k_b \cdot T}\right)$$

Scaling with x_b: changes slope



$$a = \frac{k_B \cdot T}{x_b} \qquad b = -\frac{k_B \cdot T}{x_b} \cdot \ln v_0 \qquad v_0 = \omega_0 \cdot x_b \cdot \exp\left(-\frac{E_b}{k_b \cdot T}\right)$$

1.1 Atomistic and molecular simulation algorithms

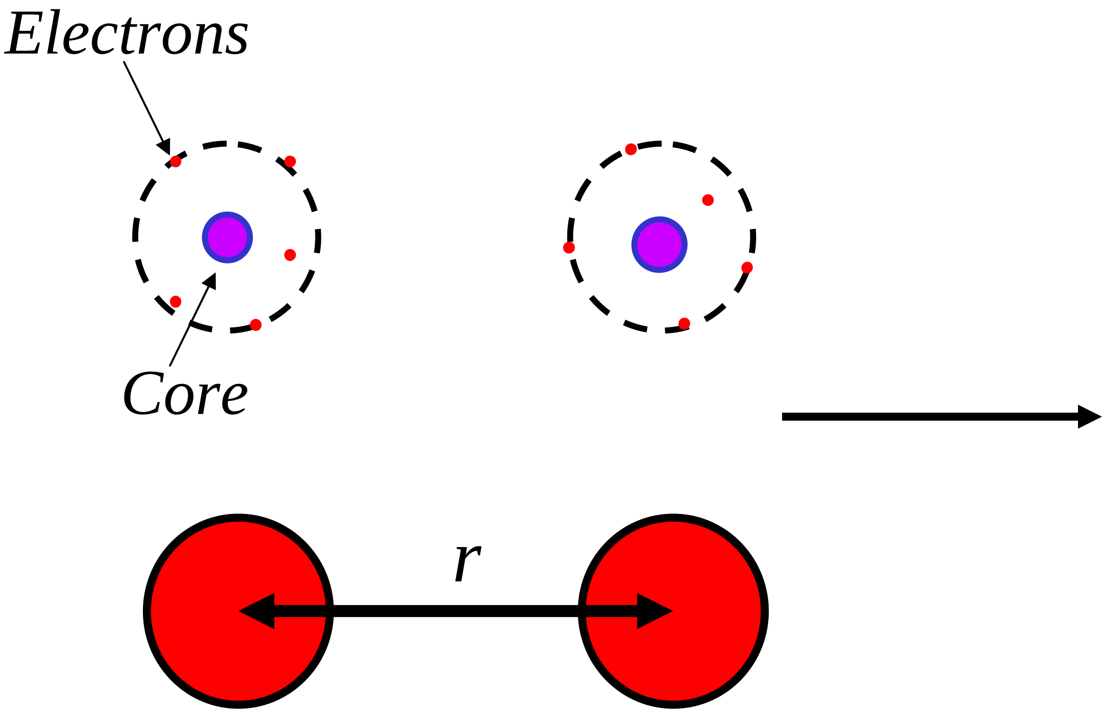
1.2 Property calculation

1.3 Potential/force field models

1.4 Applications

Goals: How to model chemical interactions between particles (interatomic potential, force fields); applications to metals, proteins

Concept: Repulsion and attraction



"point particle representation"

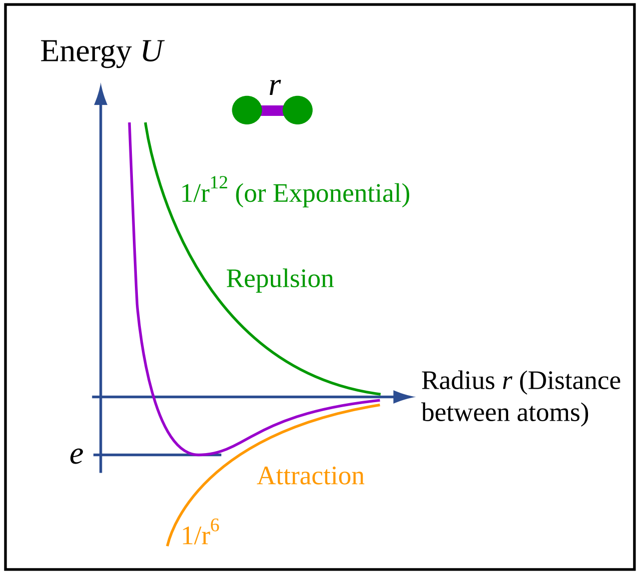


Image by MIT OpenCourseWare.

Attraction: Formation of chemical bond by sharing of electrons
Repulsion: Pauli exclusion (too many electrons in small volume)

Generic shape of interatomic potential

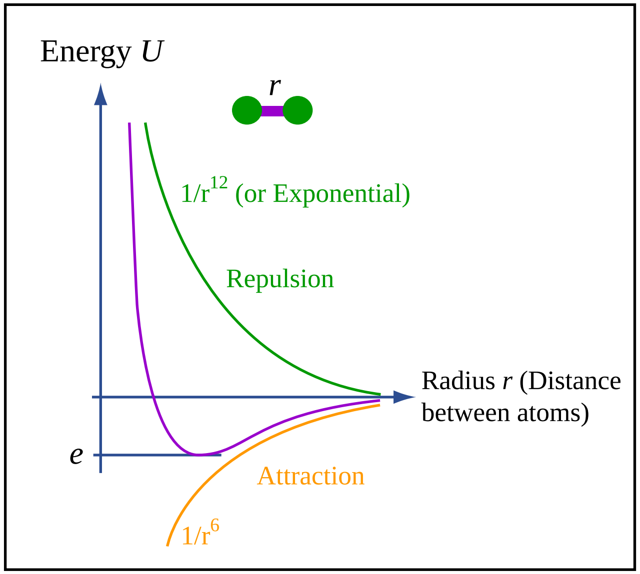


Image by MIT OpenCourseWare.

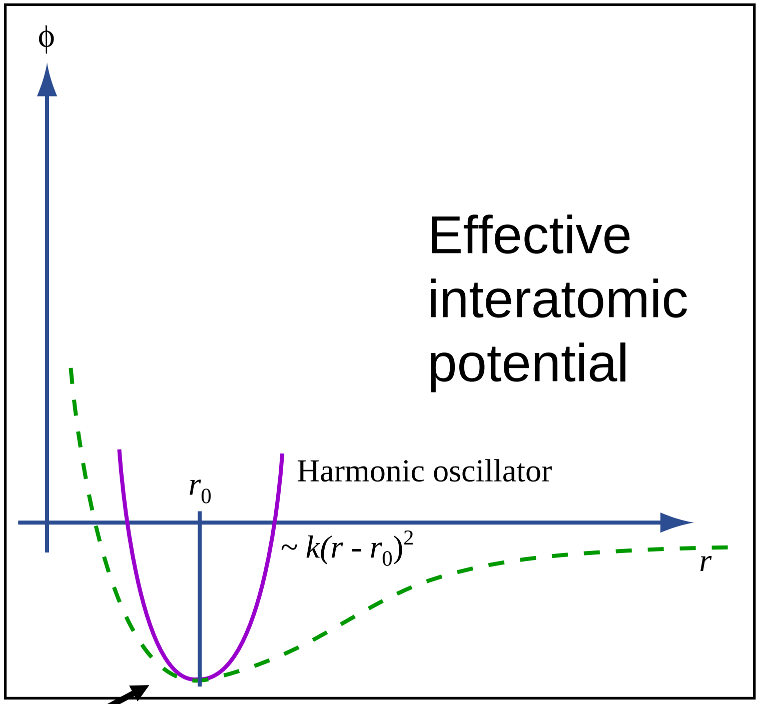


Image by MIT OpenCourseWare.

Many chemical bonds show this generic behavior

Attraction: Formation of chemical bond by sharing of electrons

Repulsion: Pauli exclusion (too many electrons in small volume)

Atomic interactions – different types of chemical bonds

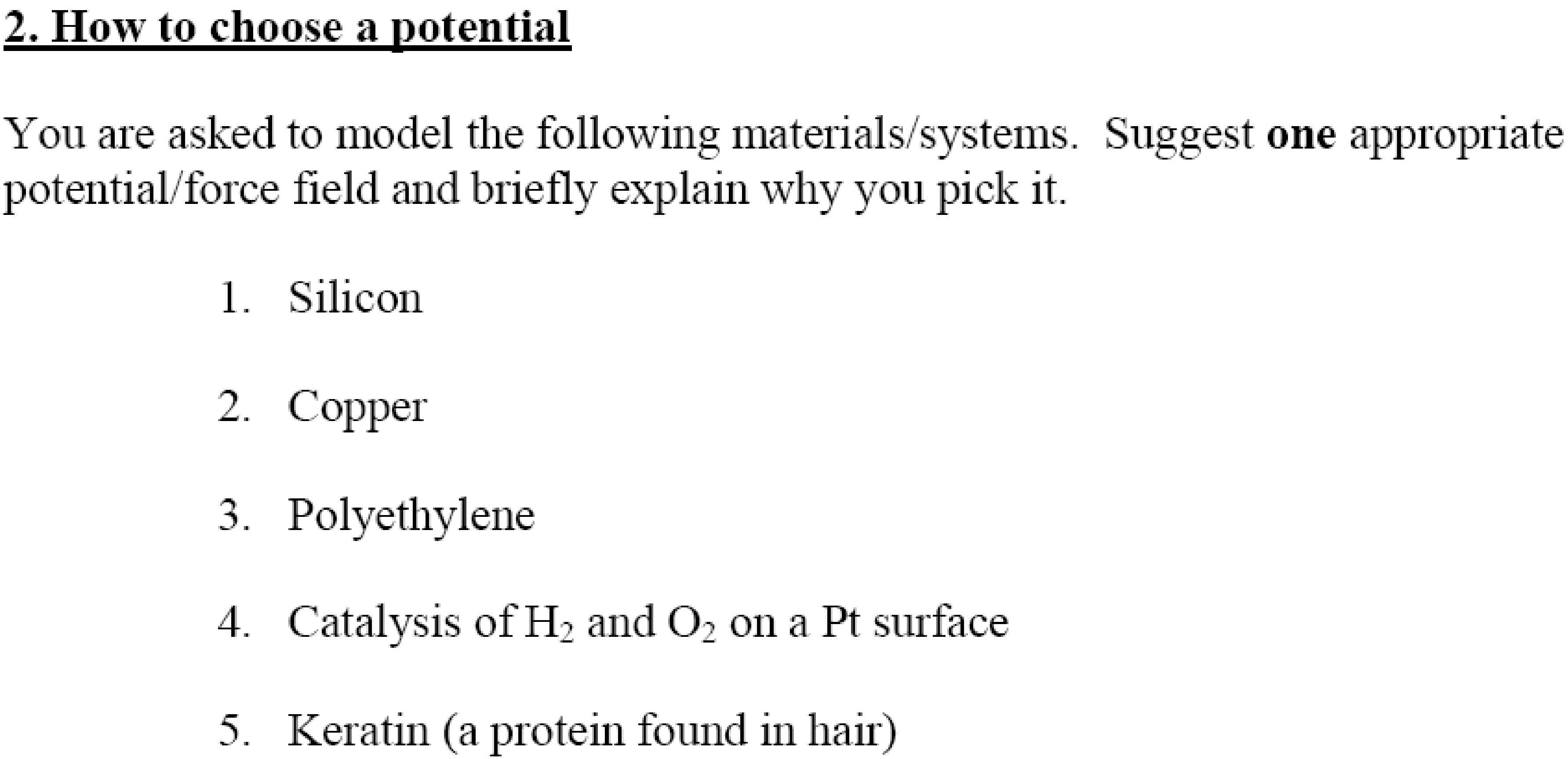
Weaker bonding

- **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)

- Ionic: Non-directional (point charges interacting)
- Covalent: Directional (bond angles, torsions matter)
- Metallic: Non-directional (electron gas concept)

Know models for all types of chemical bonds!

How to choose a potential



2. How to choose a potential

You are asked to model the following materials/systems. Suggest **one** appropriate potential/force field and briefly explain why you pick it.

1. Silicon

2. Copper

3. Polyethylene

4. Catalysis of H_2 and O_2 on a Pt surface

5. Keratin (a protein found in hair)

How to calculate forces from the “potential” or “force field”

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

- **“Potential” = “force field”**

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

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

Depends on position of all other atoms

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

Position vector of atom *i*

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

Change of potential energy due to change of position of particle *i* (“gradient”)

Force calculation

4. Force calculation

You are given an interatomic pair potential of the form:

$$\phi(r_{ij}) = \frac{k}{4}\left(r_{ij} - r_0\right)^4 \qquad \text{(C2)}$$

Pair potential
Note cutoff!

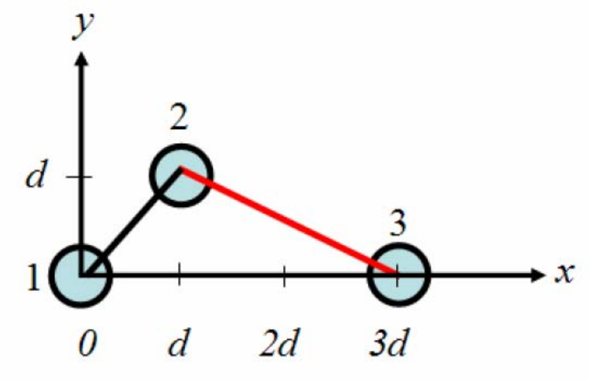
with a cutoff radius $r_{\text{cut}} = 2.5d$. For the atomic system given below:

(a) Calculate the interatomic distances r_{ij} for all pairs of atoms. Indicate the distances r_{ij} in the plot below.

(b) Calculate the total energy U_{tot}, as a function of d, r_0 and k.

(c) Calculate the force vector of particle 3, as a function of d, r_0 and k.

Coordinates of atoms in this 2D problem are given as follows:



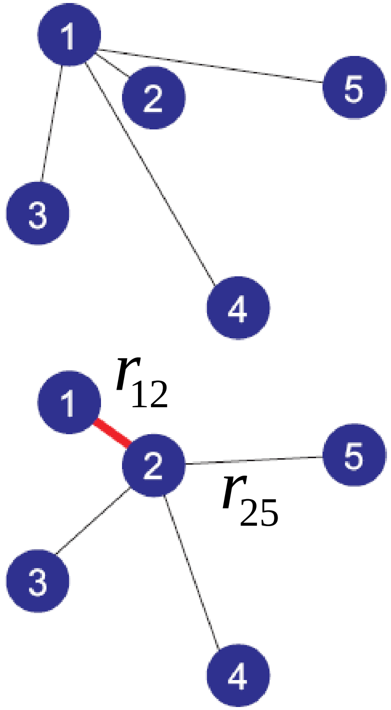
Atom 1: $(0,0)$
Atom 2: (d,d)
Atom 3: $(3d,0)$

Pair potentials: 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

avoid double counting

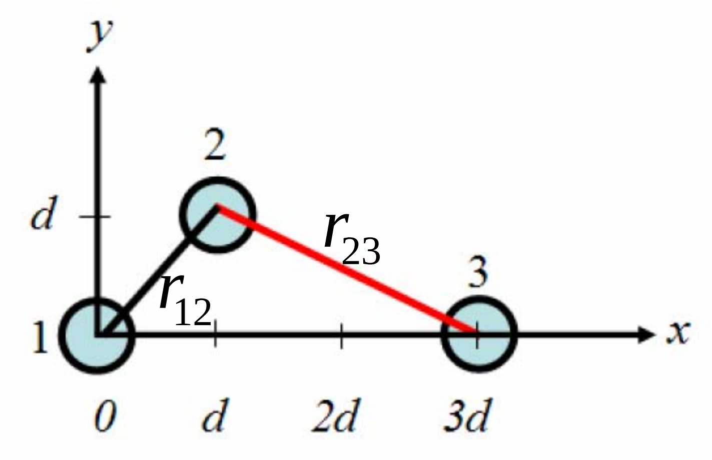
$$U_{\text{tot}} = \frac{1}{2} \sum_{i=1, i\neq j}^{N} \underbrace{\sum_{j=1}^{N} \phi(r_{ij})}$$

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

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

Total energy of pair potential

- **Assumption:** Total energy of system is expressed as sum of the energy due to pairs of atoms



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

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

with

$$U_{total} = \frac{1}{2}\left(\phi_{12} + \underset{=0}{\cancel{\phi_{13}}} + \phi_{21} + \phi_{23} + \overset{=0}{\cancel{\phi_{31}}} + \phi_{32}\right)$$

beyond cutoff

Force calculation – pair potential

Forces can be calculated by taking derivatives from the potential function

Force magnitude: Negative derivative of potential energy with respect to atomic distance

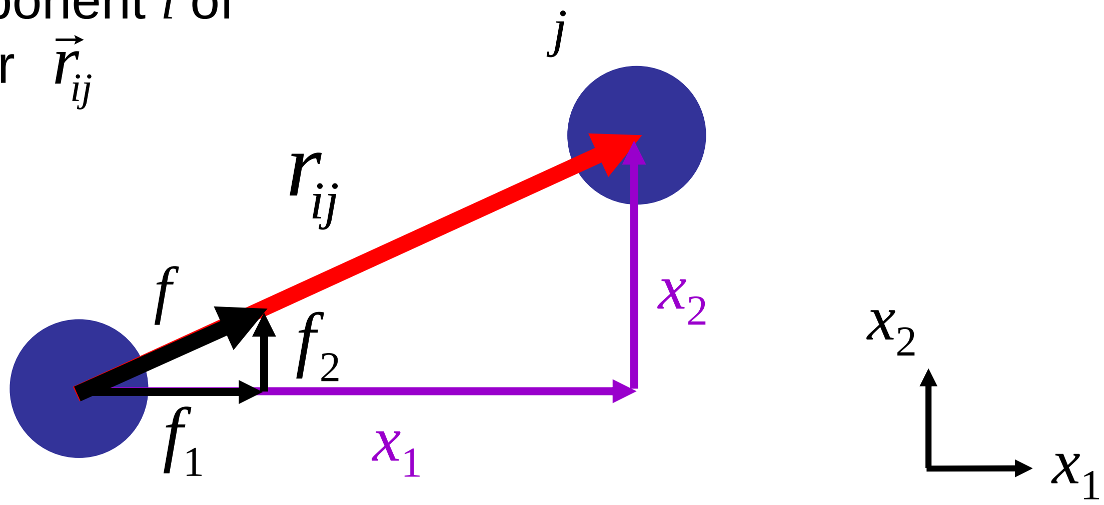
$$F = -\frac{\mathrm{d}\,\phi(r_{ij})}{\mathrm{d}\,r_{ij}}$$

To obtain force vector F_i, take projections into the three axial directions

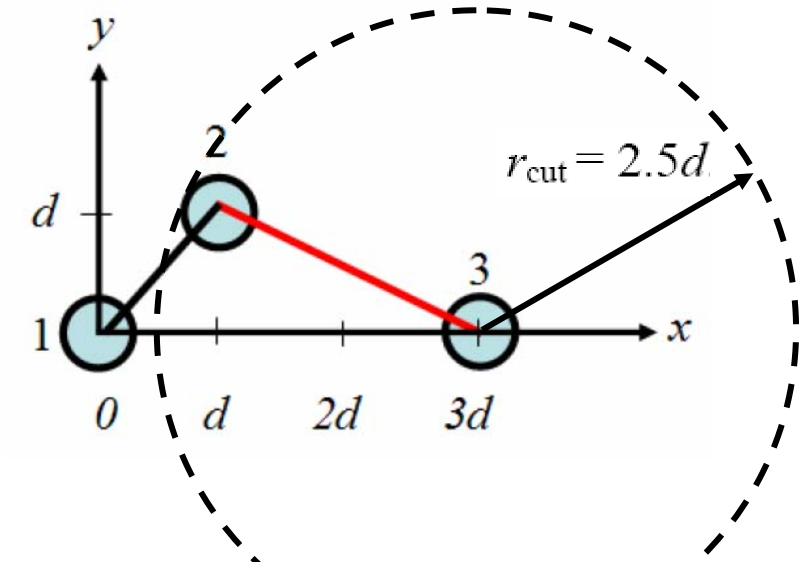
Component i of vector $\vec{r}_{ij}$

$$f_i = F\,\frac{x_i}{r_{ij}}$$

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



Force calculation – pair potential



Forces on atom 3: only interaction with atom 2 (cutoff)

1. Determine distance between atoms 3 and 2, r_{23}
2. Obtain magnitude of force vector based on derivative of potential
3. To obtain force vector F_i, take projections into the three axial directions

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

$$F = -\frac{\mathrm{d}\,\phi(r_{23})}{\mathrm{d}\,r_{23}} \qquad f_i = F\,\frac{x_i}{r_{23}} \qquad r_{23} = \left|\vec{r}_{23}\right|$$

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

Lennard-Jones potential – example for copper

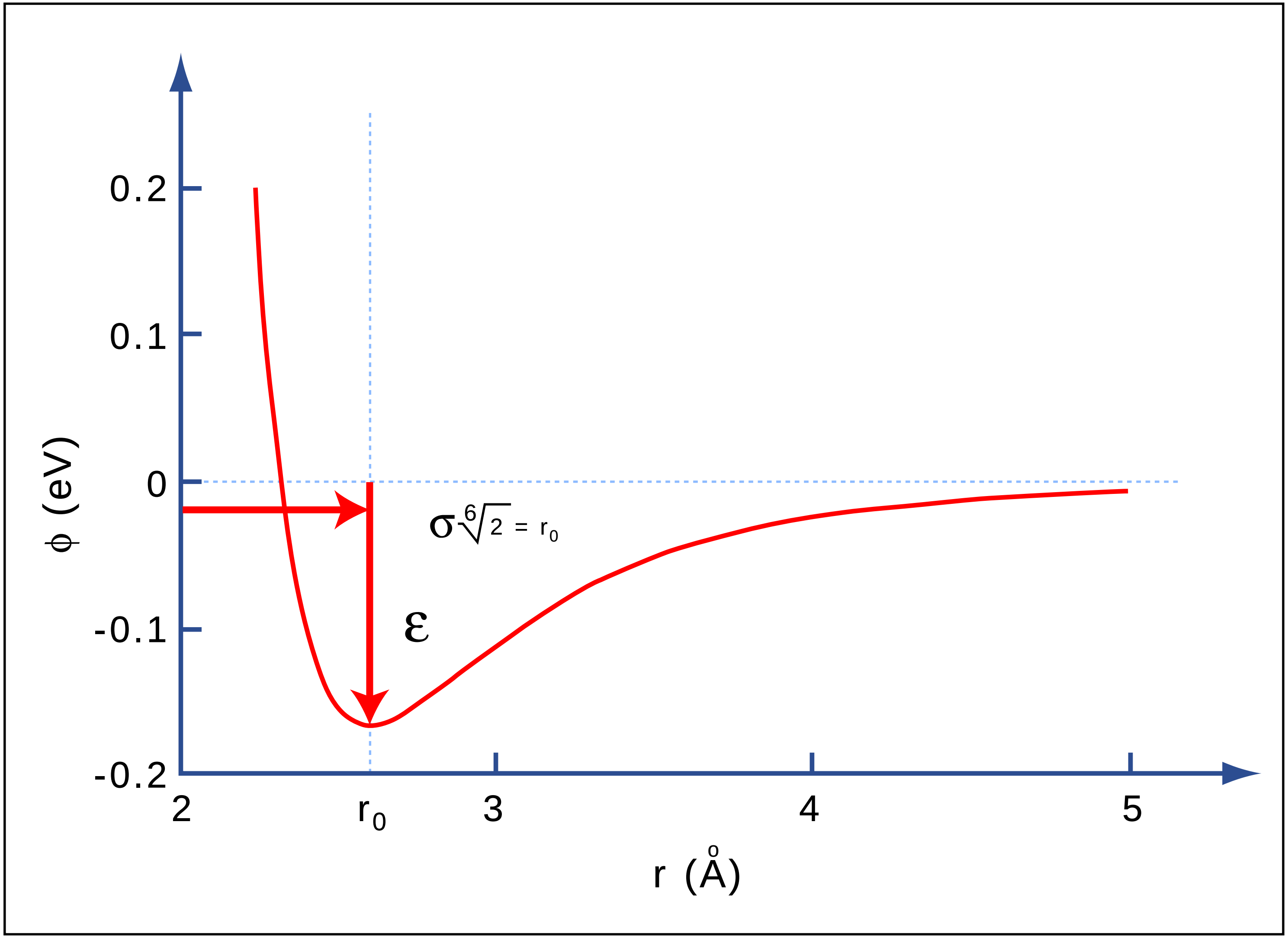


Image by MIT OpenCourseWare.

LJ potential – parameters for copper (e.g.: Cleri *et al*., 1997)

Derivative of LJ potential ~ force

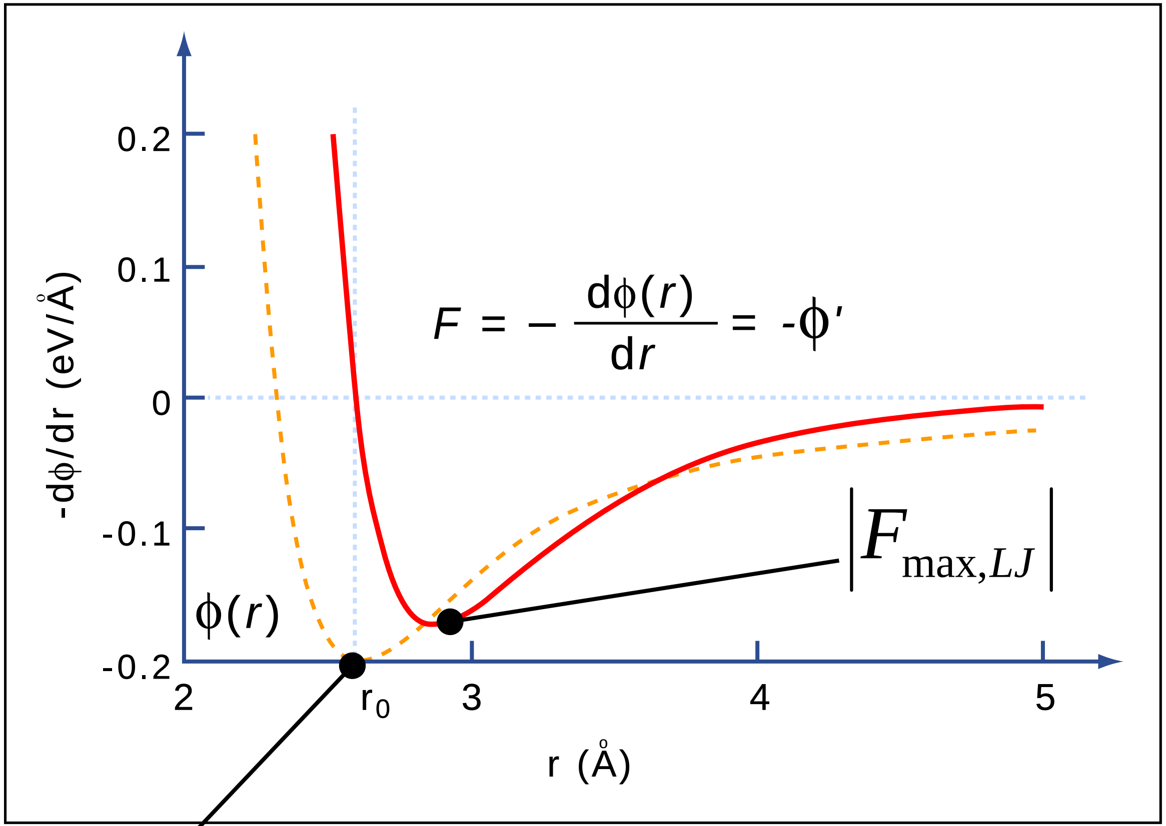


Image by MIT OpenCourseWare.

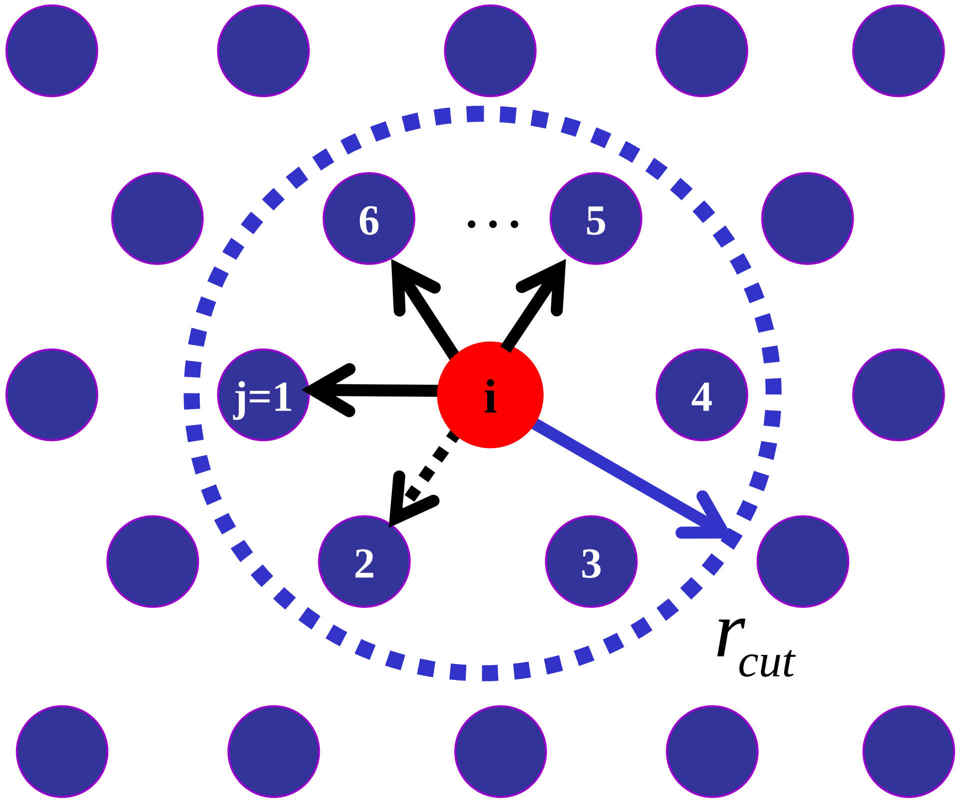
EQ r_0

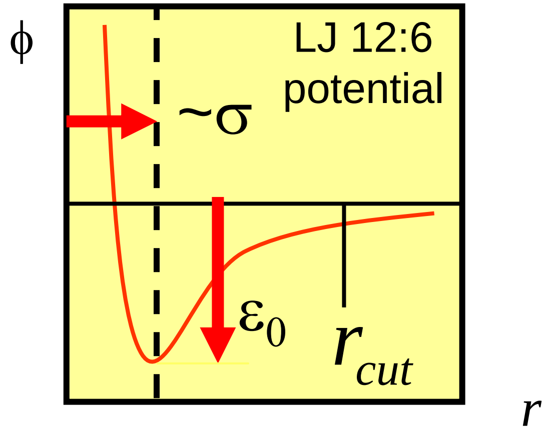
Cutoff radius

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

↓

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

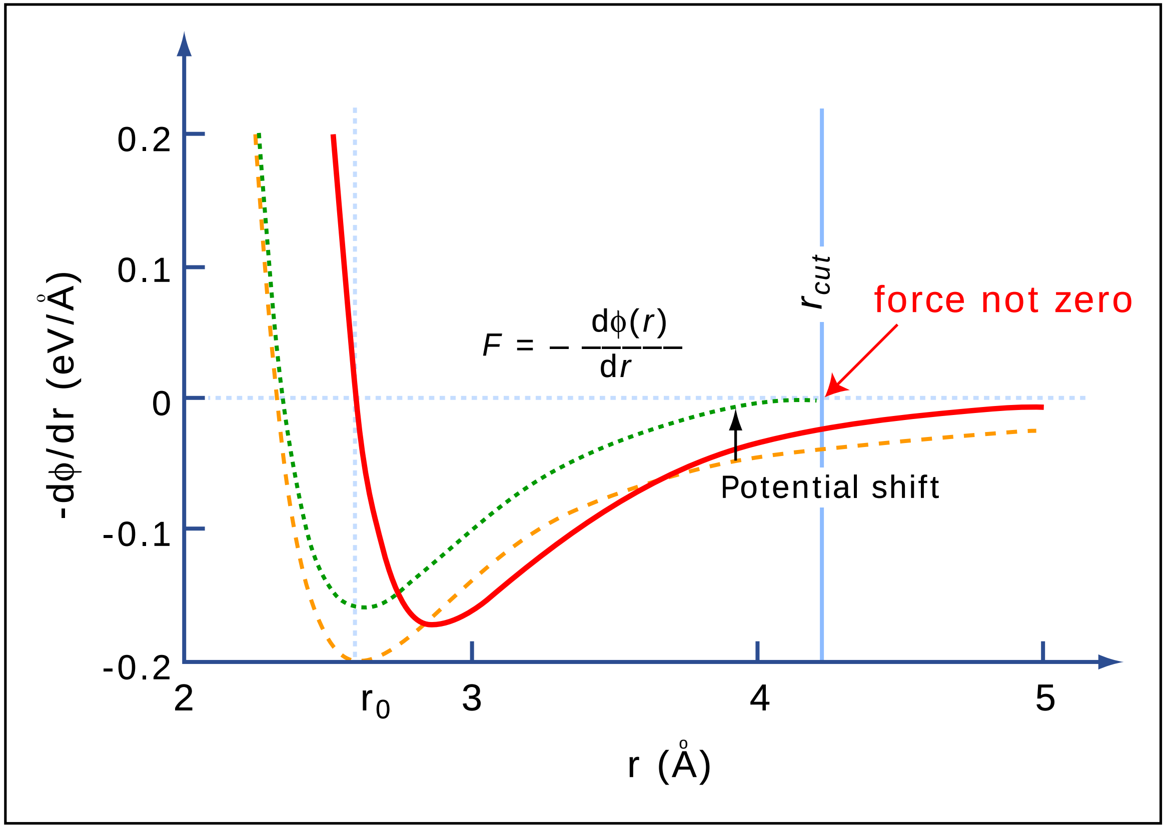




Cutoff radius = considering interactions only to a certain distance

Basis: Force contribution negligible (slope)

Derivative of LJ potential ~ force



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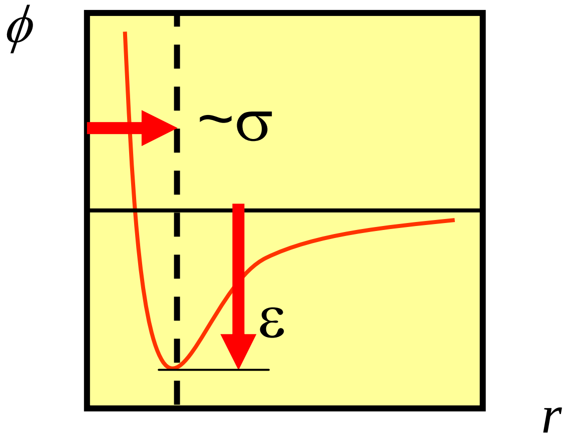
Beyond cutoff: *Changes in energy (and thus forces) small*

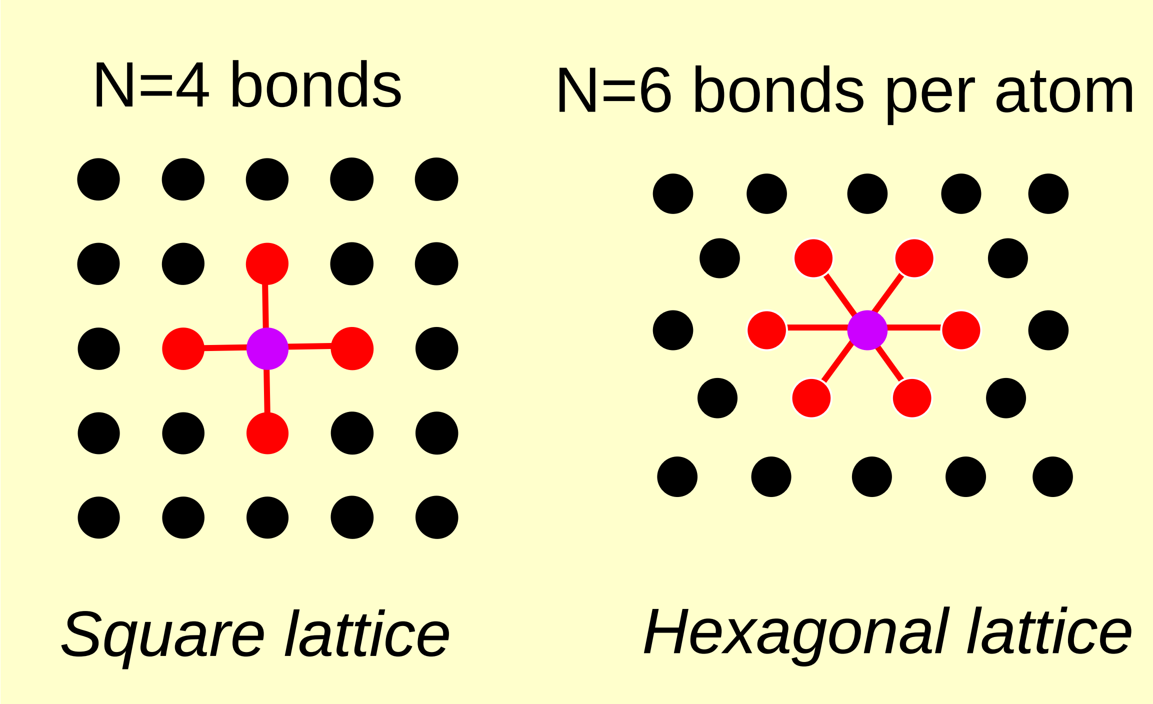
Crystal structure and potential

- The regular packing (ordering) of atoms into crystals is closely related to the potential details
- Many **local minima** for crystal structures exist, but materials tend to go to the structure that minimizes the energy; often this can be understood in terms of the energy per atomic bond and the equilibrium distance (at which a bond features the most potential energy)

LJ 12:6 potential



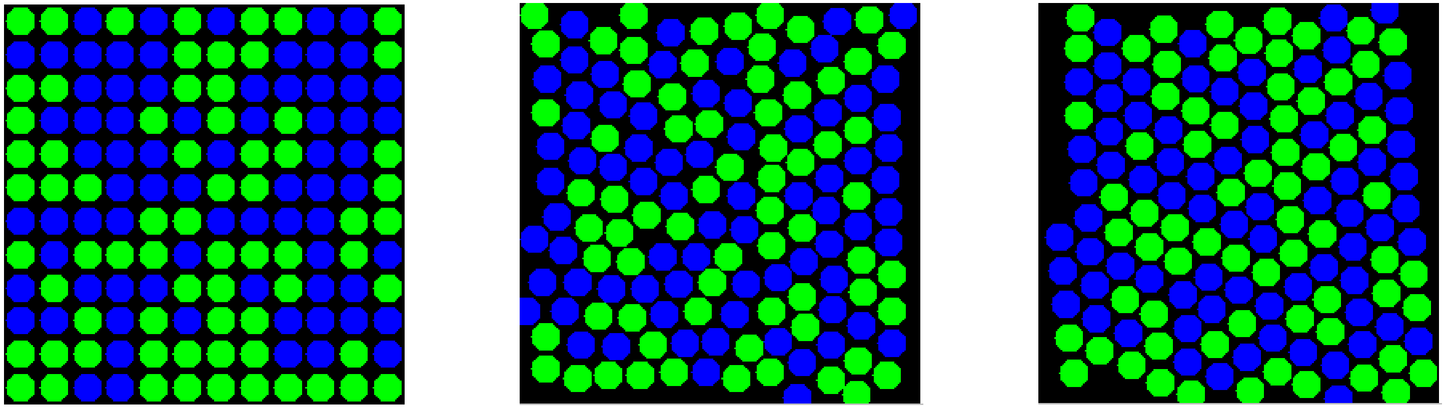
2D example



Example

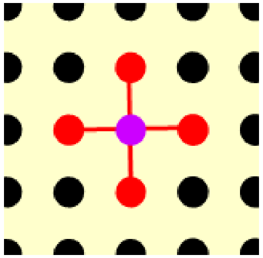
Initial: cubic lattice

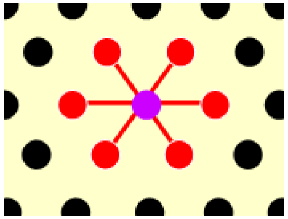
Transforms into triangular lattice



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

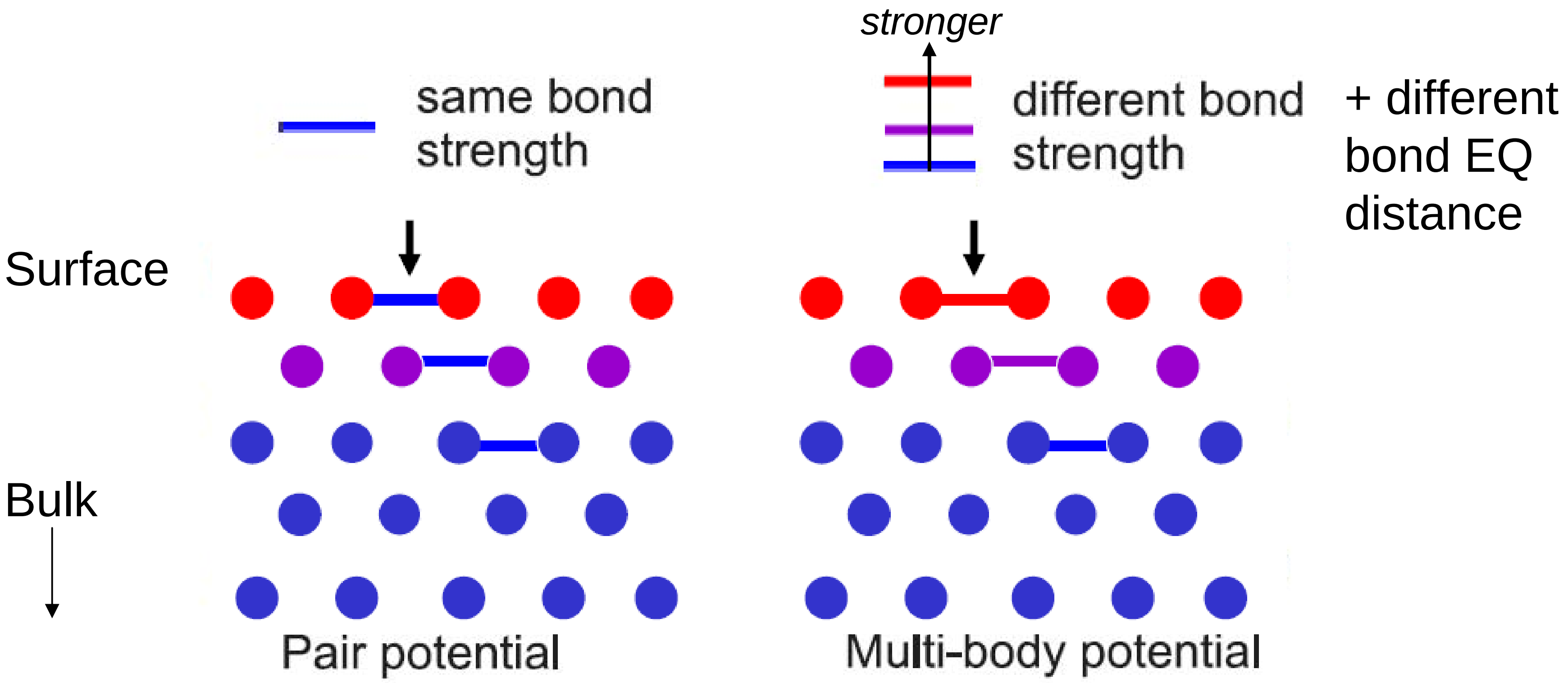
time





http://polymer.bu.edu/java/java/LJ/index.html

All bonds are not the same – metals



Pair potentials: All bonds are equal!

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

Embedded-atom method (EAM): multi-body potential

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

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

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

Models other than EAM (alternatives):
Glue model (Ercolessi, Tosatti, Parrinello)
Finnis Sinclair
Equivalent crystal models (Smith and Banerjee)

Effective pair interactions: EAM potential

EAM=Embedded atom method

Can describe differences between bulk and surface

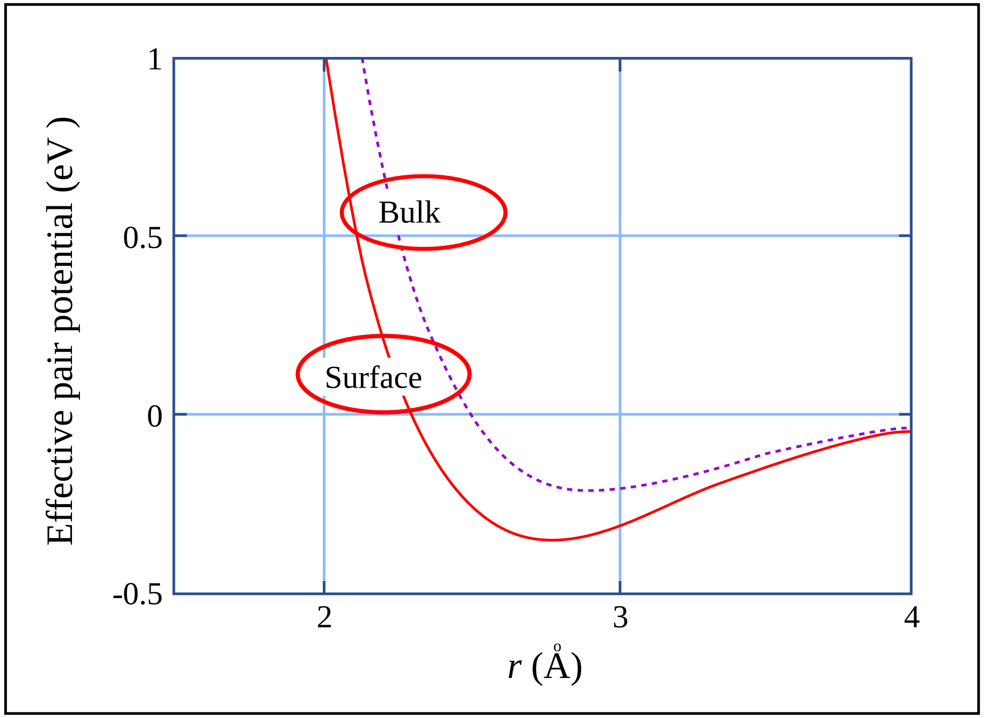
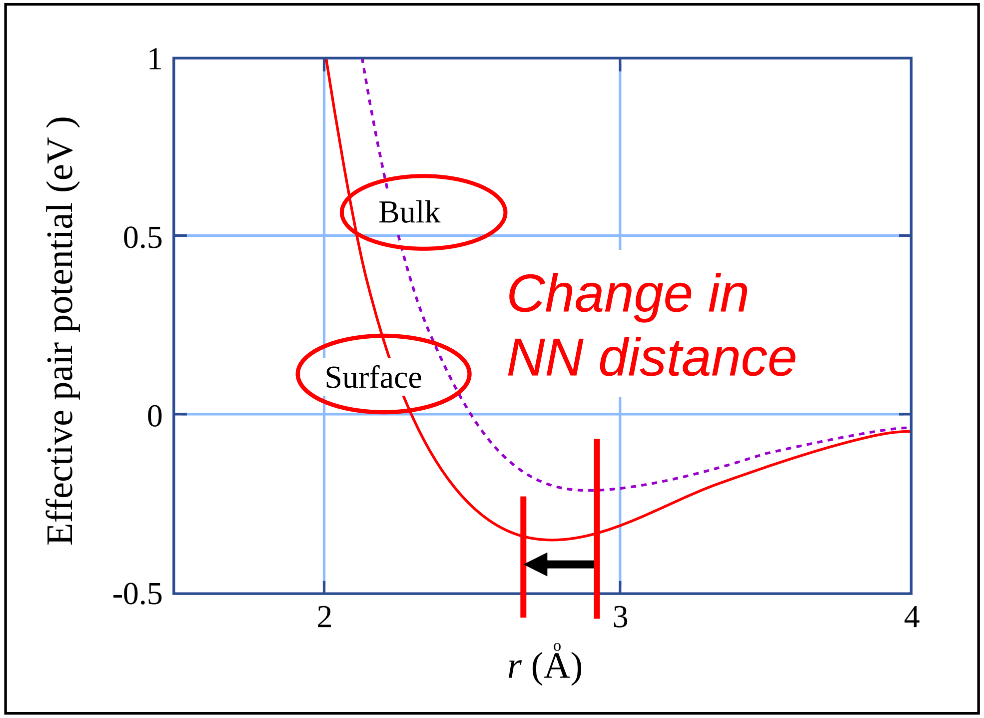


Image by MIT OpenCourseWare.

$$U = \overbrace{\frac{1}{2}\sum_{i,i\neq j}\sum_{j}\phi(r_{ij})}^{\text{Pair potential energy}} + \overbrace{\sum_{i} F(\rho_i)}^{\text{Embedding energy as a function of electron density}}$$

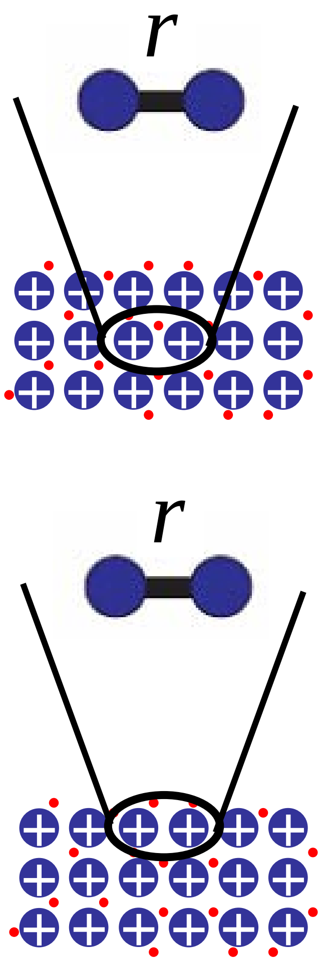
Embedding term: depends on environment, "multi-body"

Effective pair interactions: EAM



Change in NN distance

Image by MIT OpenCourseWare.

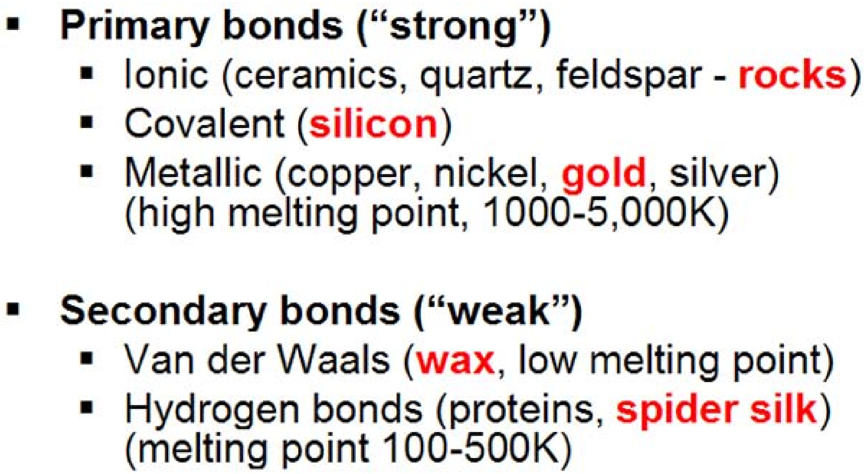


Can describe differences between bulk and surface

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

Model for chemical interactions

- **Similarly:** Potentials for chemically complex materials – assume that total energy is the sum of the energy of 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)

$$U_{total} = U_{\mathrm{Elec}} + U_{\mathrm{Covalent}} + U_{\mathrm{Metallic}} + U_{\mathrm{vdW}} + U_{\mathrm{H-bond}}$$

Concept: energy landscape for chemically complex materials

$$U_{total} = U_{\mathrm{Elec}} + U_{\mathrm{Covalent}} + U_{\mathrm{Metallic}} + U_{\mathrm{vdW}} + U_{\mathrm{H-bond}}$$

- Different energy contributions from different kinds of chemical bonds are summed up individually, independently
- Implies that bond properties of covalent bonds are not affected by other bonds, e.g. vdW interactions, H-bonds

Force fields for organic substances are constructed based on this concept:

water, polymers, biopolymers, proteins …

Summary: CHARMM-type potential

$$U_{total} = \overset{\checkmark}{U_{\mathrm{Elec}}} + \overset{\checkmark}{U_{\mathrm{Covalent}}} + \overset{=0 \text{ for proteins}}{\cancel{U_{\mathrm{Metallic}}}} + \overset{\checkmark}{U_{\mathrm{vdW}}} + \overset{\checkmark}{U_{\mathrm{H-bond}}}$$

U_{Elec} : Coulomb potential $\phi(r_{ij}) = \dfrac{q_i q_j}{\varepsilon_1 r_{ij}}$

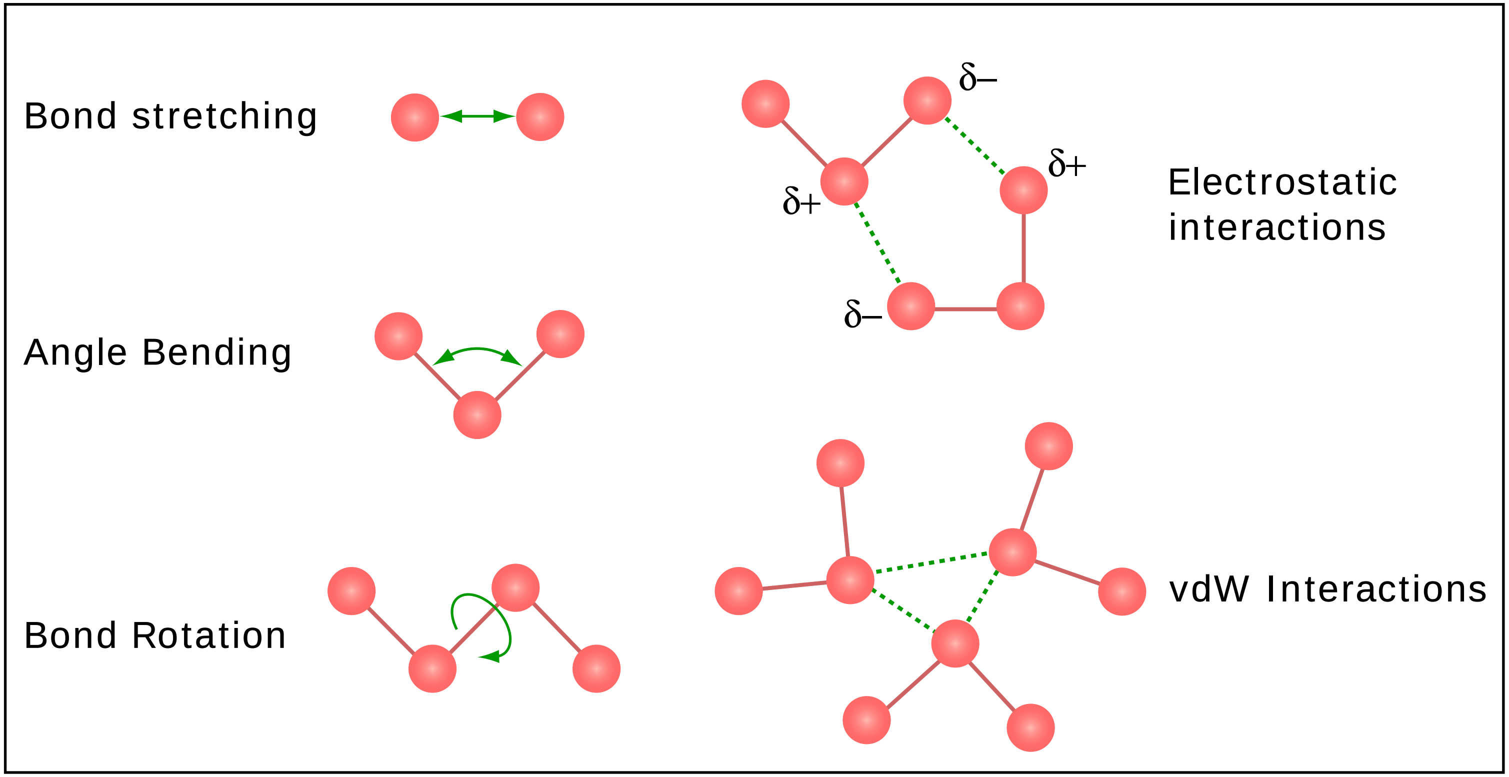
$$U_{\mathrm{Covalent}} = U_{\mathrm{stretch}} + U_{\mathrm{bend}} + U_{\mathrm{rot}} \quad \begin{cases} \phi_{\mathrm{stretch}} = \dfrac{1}{2} k_{\mathrm{stretch}} (r - r_0)^2 \\ \phi_{\mathrm{bend}} = \dfrac{1}{2} k_{\mathrm{bend}} (\theta - \theta_0)^2 \\ \phi_{\mathrm{rot}} = \dfrac{1}{2} k_{\mathrm{rot}} (1 - \cos(\vartheta)) \end{cases}$$

U_{vdW} : LJ potential $\phi(r_{ij}) = 4\varepsilon \left[\left(\dfrac{\sigma}{r_{ij}} \right)^{12} - \left(\dfrac{\sigma}{r_{ij}} \right)^{6} \right]$

$U_{\mathrm{H-bond}}$: $\phi(r_{ij}) = D_{\mathrm{H-bond}} \left[5 \left(\dfrac{R_{\mathrm{H-bond}}}{r_{ij}} \right)^{12} - 6 \left(\dfrac{R_{\mathrm{H-bond}}}{r_{ij}} \right)^{10} \right] \cos^4(\theta_{\mathrm{DHA}})$

Summary of energy expressions: CHARMM, DREIDING, etc.

$$U_{\text{system}} = \quad U_{\text{bond}} + U_{\text{angle}} + U_{\text{torsion}} + U_{\text{Coulomb}} + U_{\text{vdW}} + \ldots$$



vdW ONLY between atoms of different molecules

Image by MIT OpenCourseWare.

$$\phi_{\text{bend}} = b_0 + \frac{1}{2}k_{\text{bend}}(\theta_{ijk} - \theta_0)^2 \qquad \phi(r_{ij}) = a_0 + \frac{1}{2}k(r_{ij} - r_0)^2$$

....

Identify a strategy to model the change of an interatomic bond under a chemical reaction (based on harmonic potential) – from single to double bond

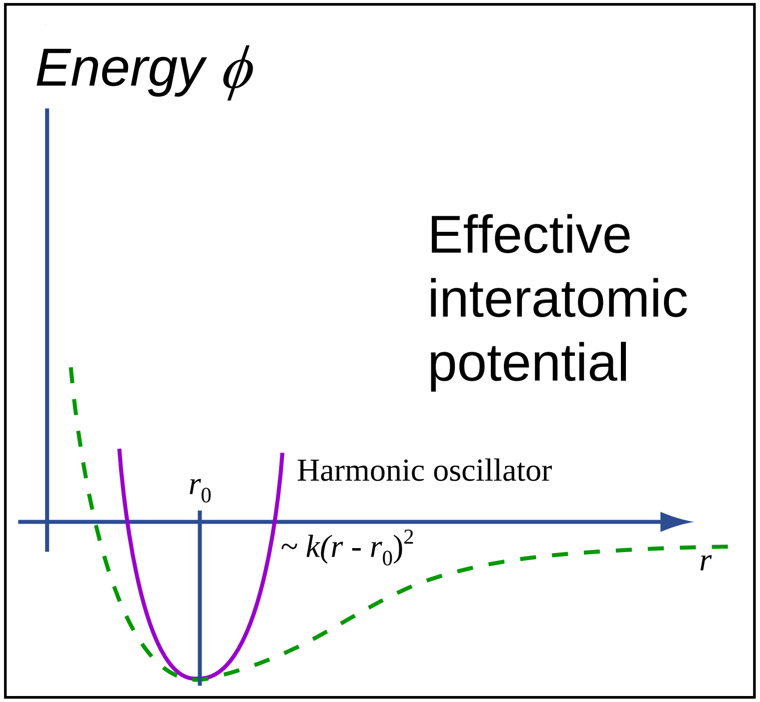


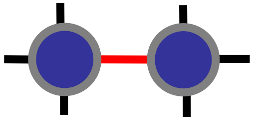
Image by MIT OpenCourseWare.

$$\phi_{\text{stretch}} = \frac{1}{2} k_{\text{stretch}} (r - r_0)^2$$

r

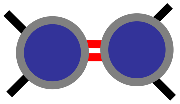
focus on C-C bond

sp^3

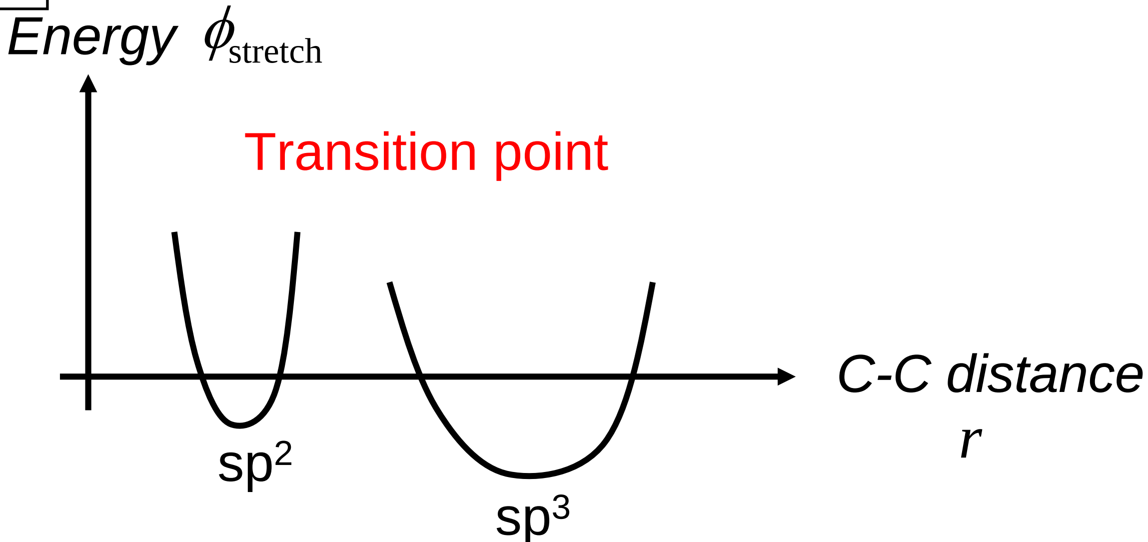


BO=1

sp^2



BO=2



Solution sketch/concept

$$\phi_{\text{stretch}} = \frac{1}{2} k_{\text{stretch}} (r - r_0)^2$$

$$k_{\text{stretch}} = k_{\text{stretch}}(\text{BO})$$

$$r_0 = r_0(\text{BO})$$

Make potential parameters k_{stretch} and r_0 a function of the chemical state of the molecule (“modulate parameters”)

E.g. use bond order as parameter, which allows to smoothly interpolate between one type of bonding and another one dependent on geometry of molecule

See lecture notes (lecture 7): Bond order potential for silicon

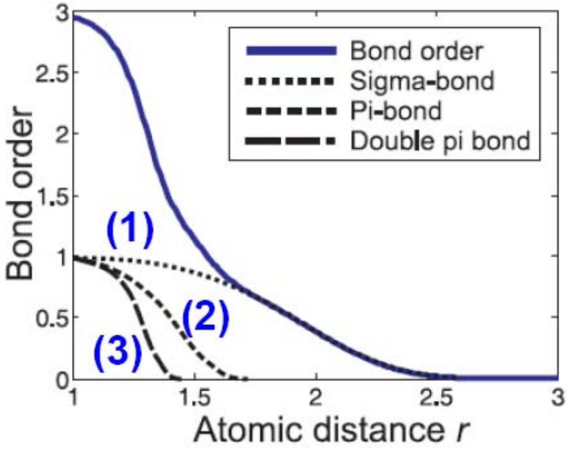
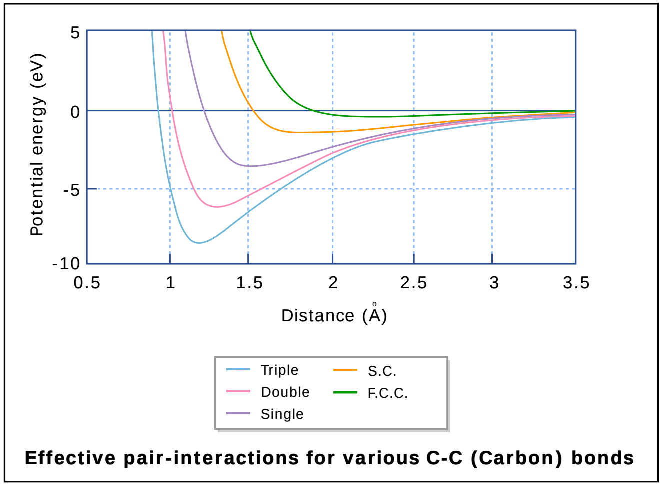


Fig. 2.21c in Buehler, Markus J. *Atomistic Modeling of Materials Failure*. Springer, 2008.



Effective pair-interactions for various C-C (Carbon) bonds

Image by MIT OpenCourseWare.

Summary: CHARMM force field

- Widely used and accepted model for protein structures

- Programs such as NAMD have implemented the CHARMM force field

  E.g., problem set 3, nanoHUB stretchmol/NAMD module, study of a protein domain part of human vimentin intermediate filaments

Overview: force fields discussed in IM/S

- Pair potentials (LJ, Morse, harmonic potentials, biharmonic potentials), used for single crystal elasticity (pset #1) and fracture model (pset #2)
  Pair potential

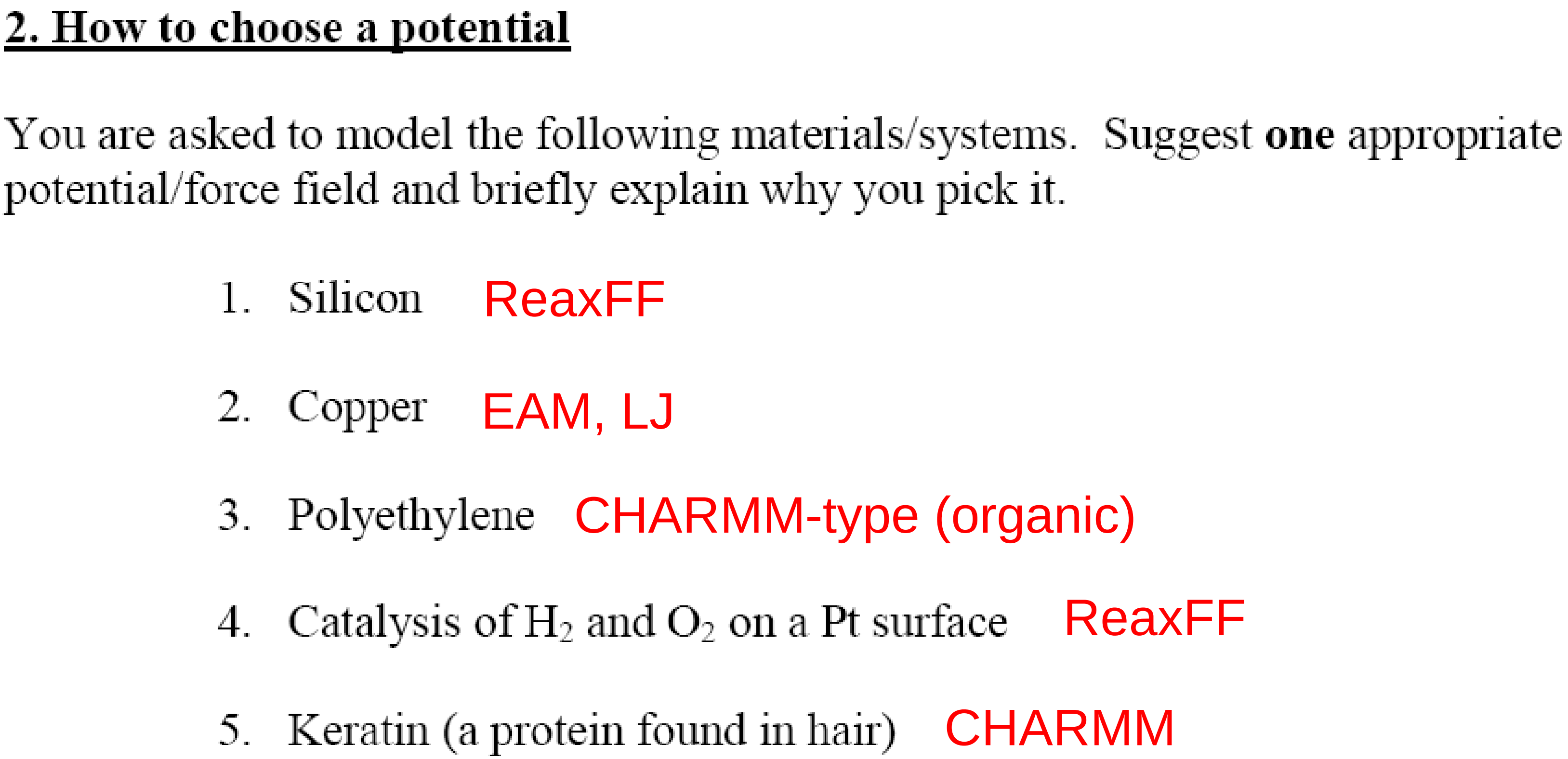
- EAM (=Embedded Atom Method), used for nanowire (pset #1), suitable for metals
  Multi-body potential

- ReaxFF (reactive force field), used for CMDF/fracture model of silicon (pset #2) – very good to model breaking of bonds (chemistry)
  Multi-body potential (bond order potential)

- Tersoff (nonreactive force field), used for CMDF/fracture model of silicon (note: Tersoff only suitable for elasticity of silicon, pset #2)
  Multi-body potential (bond order potential)

- CHARMM force field (organic force field), used for protein simulations (pset #3)
  Multi-body potential (angles, for instance)

How to choose a potential



2. How to choose a potential

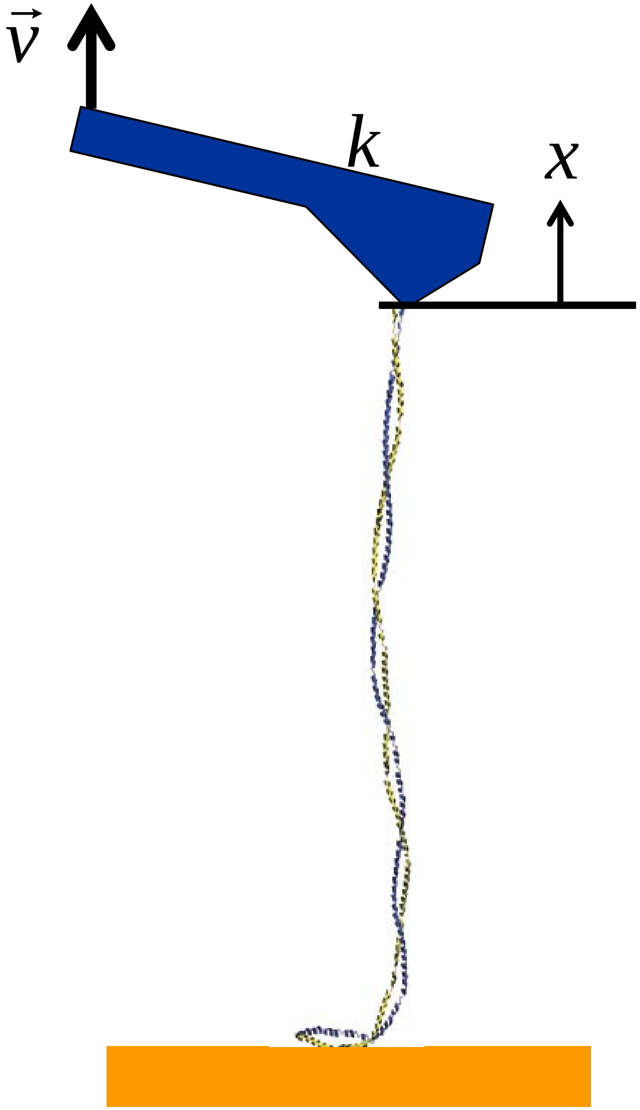
You are asked to model the following materials/systems. Suggest **one** appropriate potential/force field and briefly explain why you pick it.

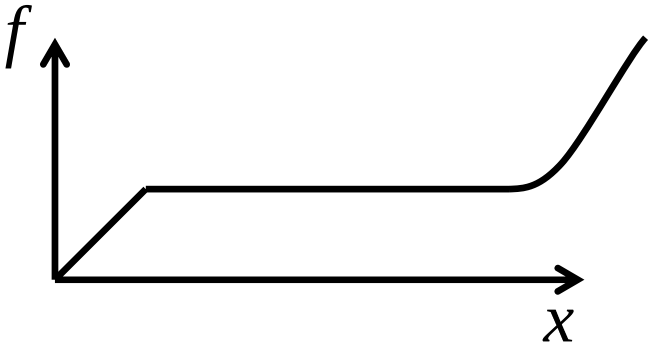
1. Silicon ReaxFF
2. Copper EAM, LJ
3. Polyethylene CHARMM-type (organic)
4. Catalysis of H_2 and O_2 on a Pt surface ReaxFF
5. Keratin (a protein found in hair) CHARMM

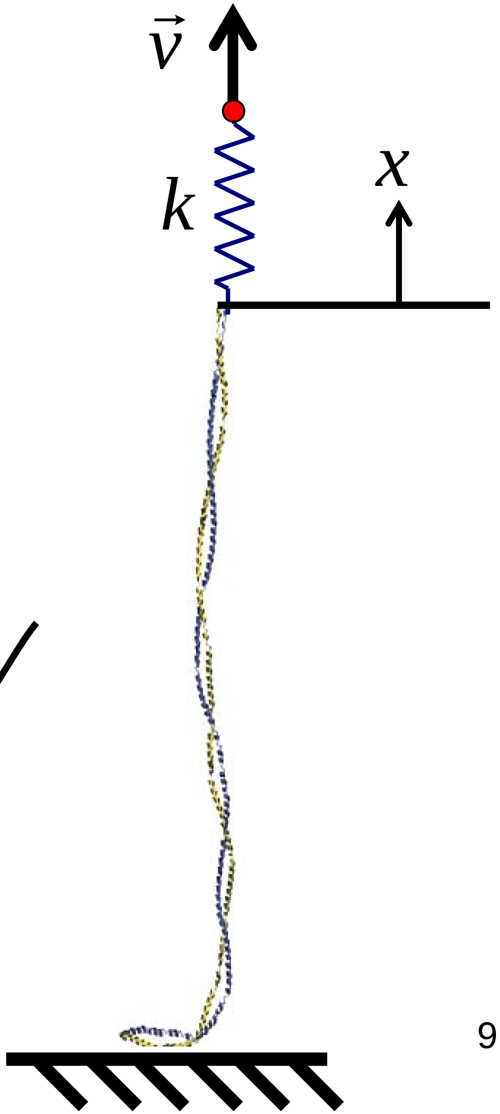
SMD mimics AFM single molecule experiments

Atomic force microscope

pset #3





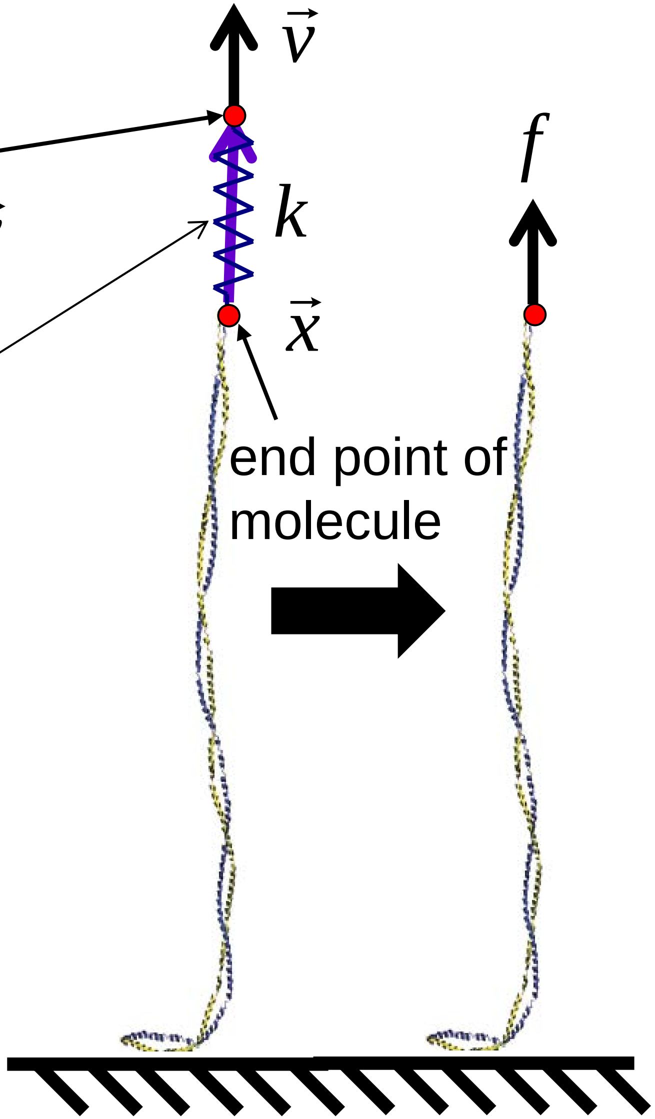


Steered molecular dynamics (SMD)

pset #3

Steered molecular dynamics used to apply forces to protein structures

Virtual atom moves w/ velocity $\vec{v}$



end point of molecule

$$f = k(v \cdot t - x)$$

$$\vec{v} \cdot t - \vec{x}$$

SMD spring constant

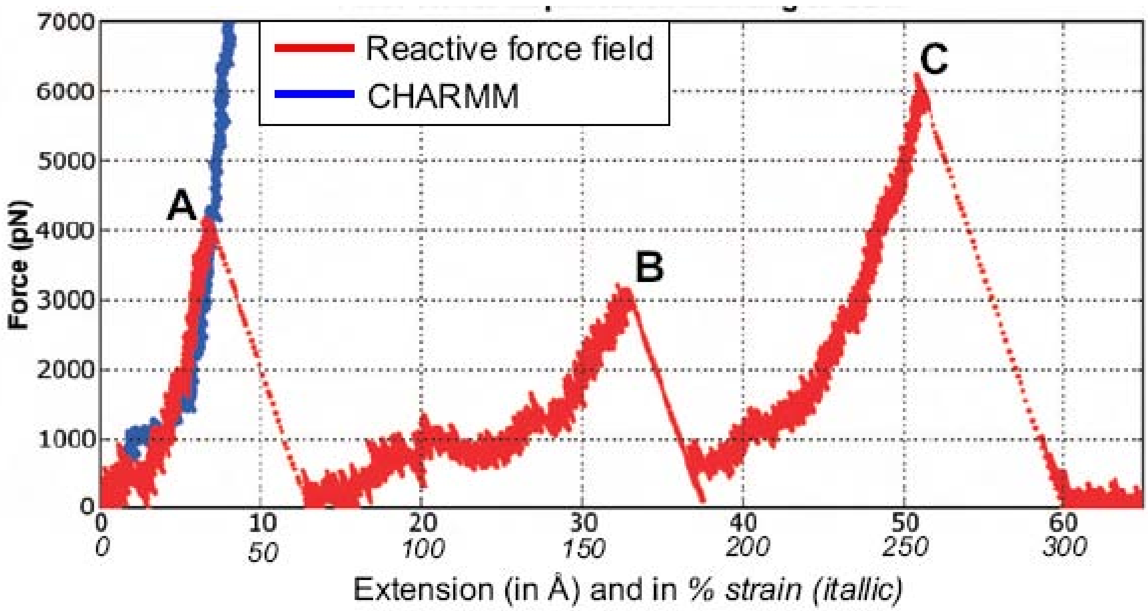
$$\vec{f} = k(\vec{v} \cdot t - \vec{x})$$

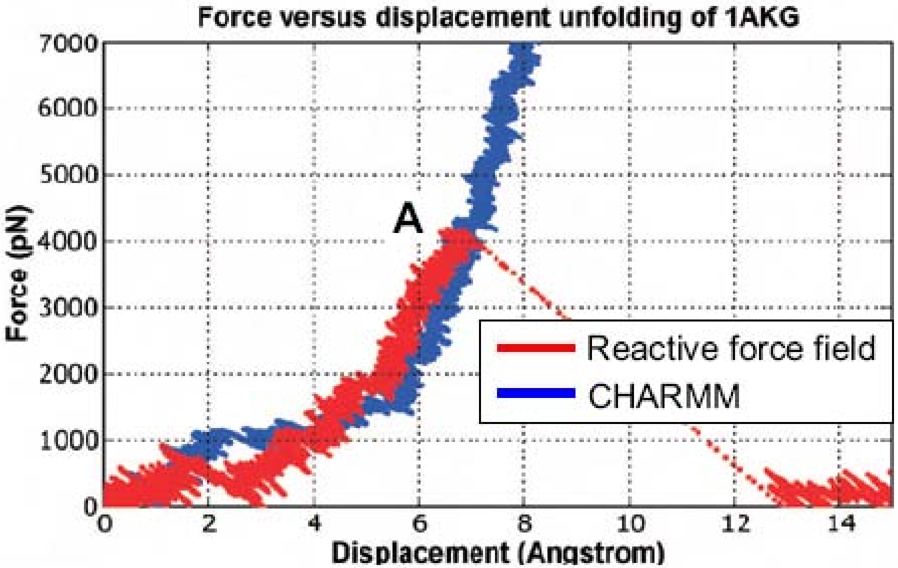
SMD deformation speed vector

time

Distance between end point of molecule and virtual atom

Comparison – CHARMM vs. ReaxFF





Covalent bonds never break in CHARMM

M. Buehler, *JoMMS*, 2007

1.1 Atomistic and molecular simulation algorithms

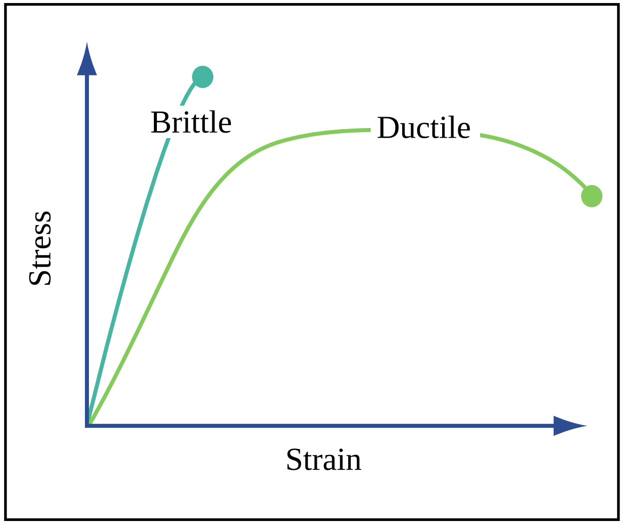
1.2 Property calculation

1.3 Potential/force field models

1.4 Applications

Goals: Select applications of MD to address questions in materials science (ductile versus brittle materials behavior); observe what can be done with MD

Application – mechanics of materials tensile test of a wire



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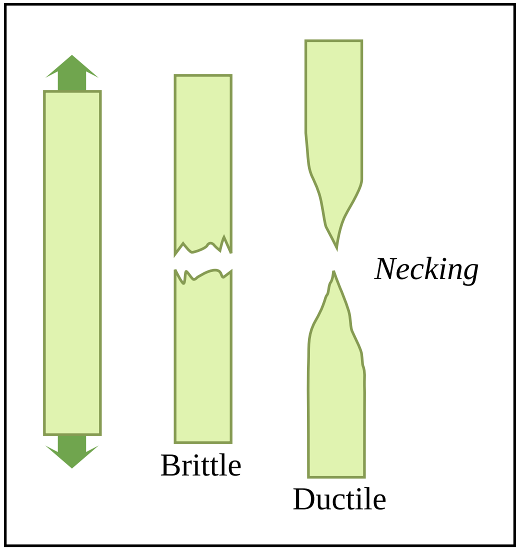
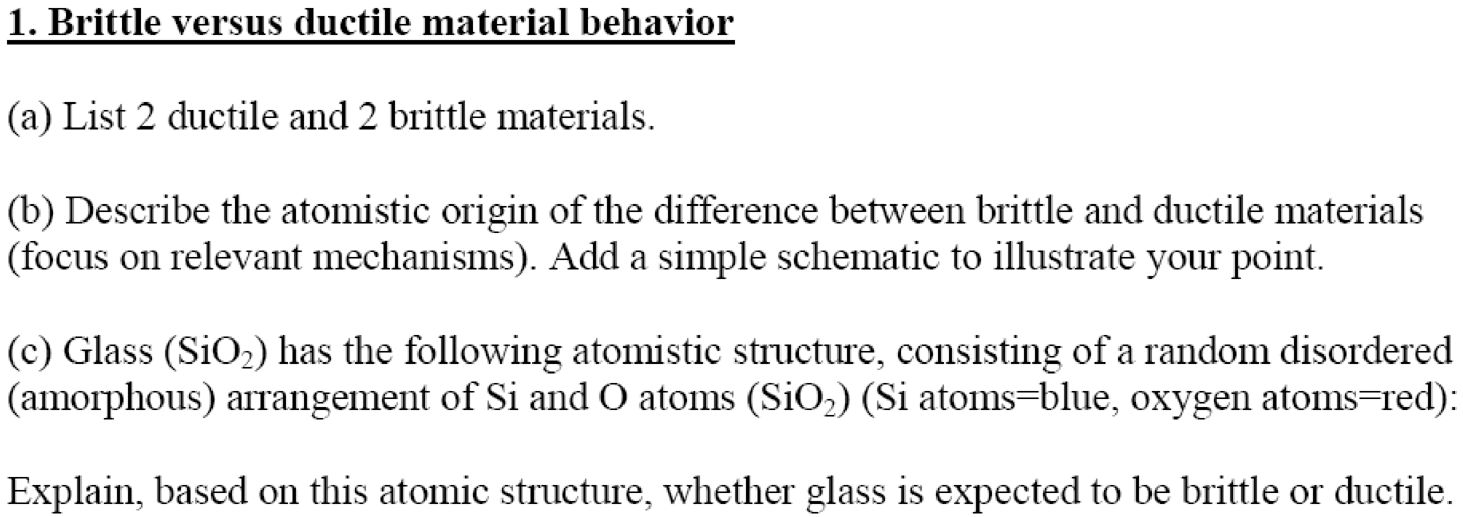


Image by MIT OpenCourseWare.

Brittle versus ductile materials behavior



1. Brittle versus ductile material behavior

(a) List 2 ductile and 2 brittle materials.

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Explain, based on this atomic structure, whether glass is expected to be brittle or ductile.

Ductile versus brittle materials

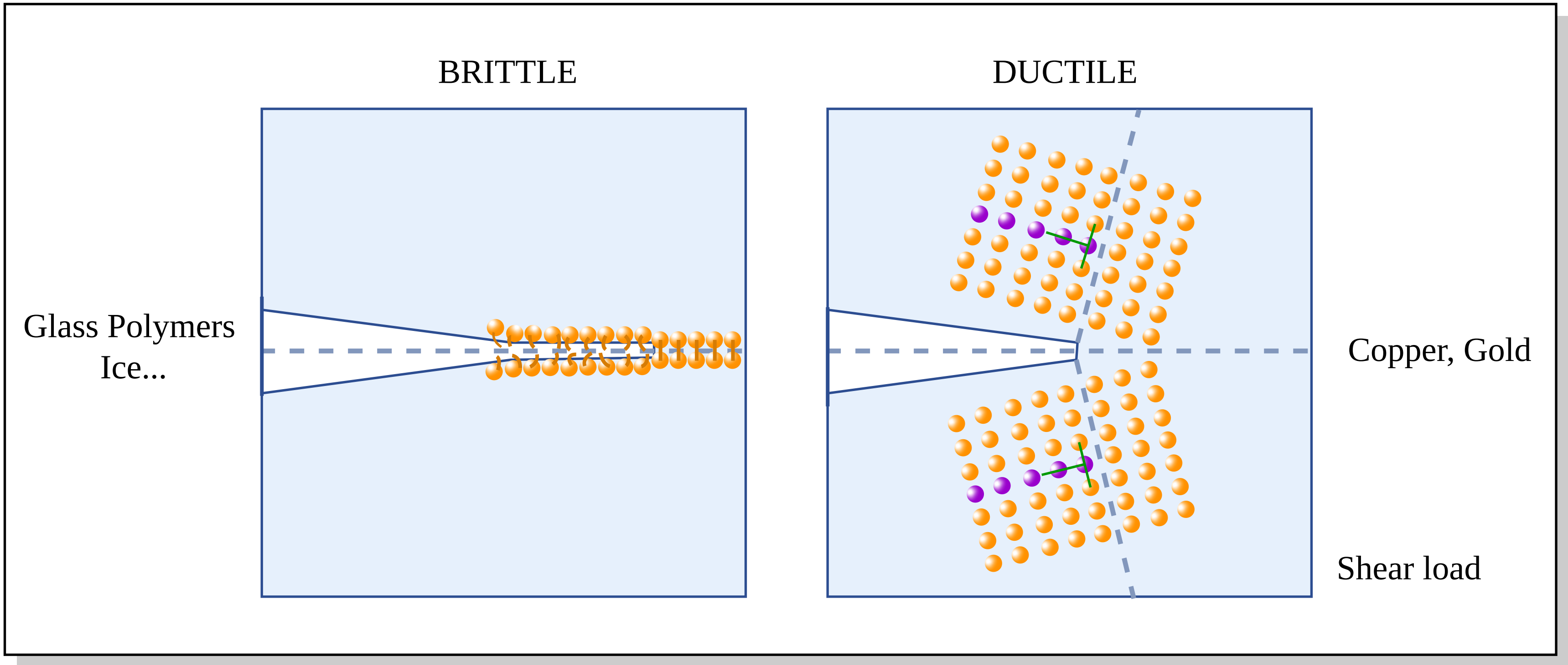
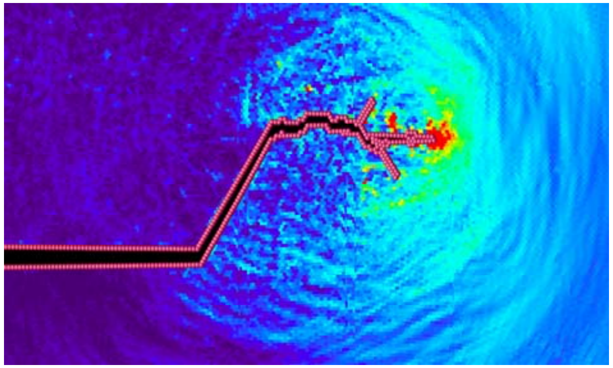
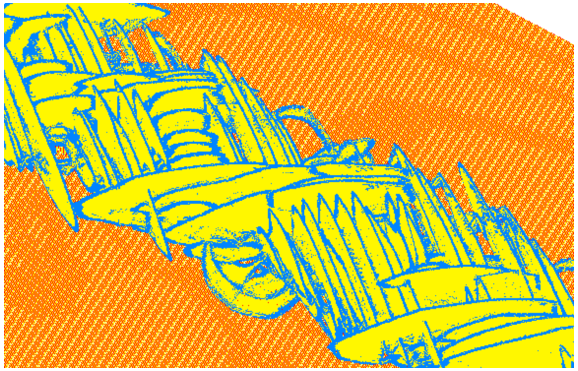


Image by MIT OpenCourseWare.

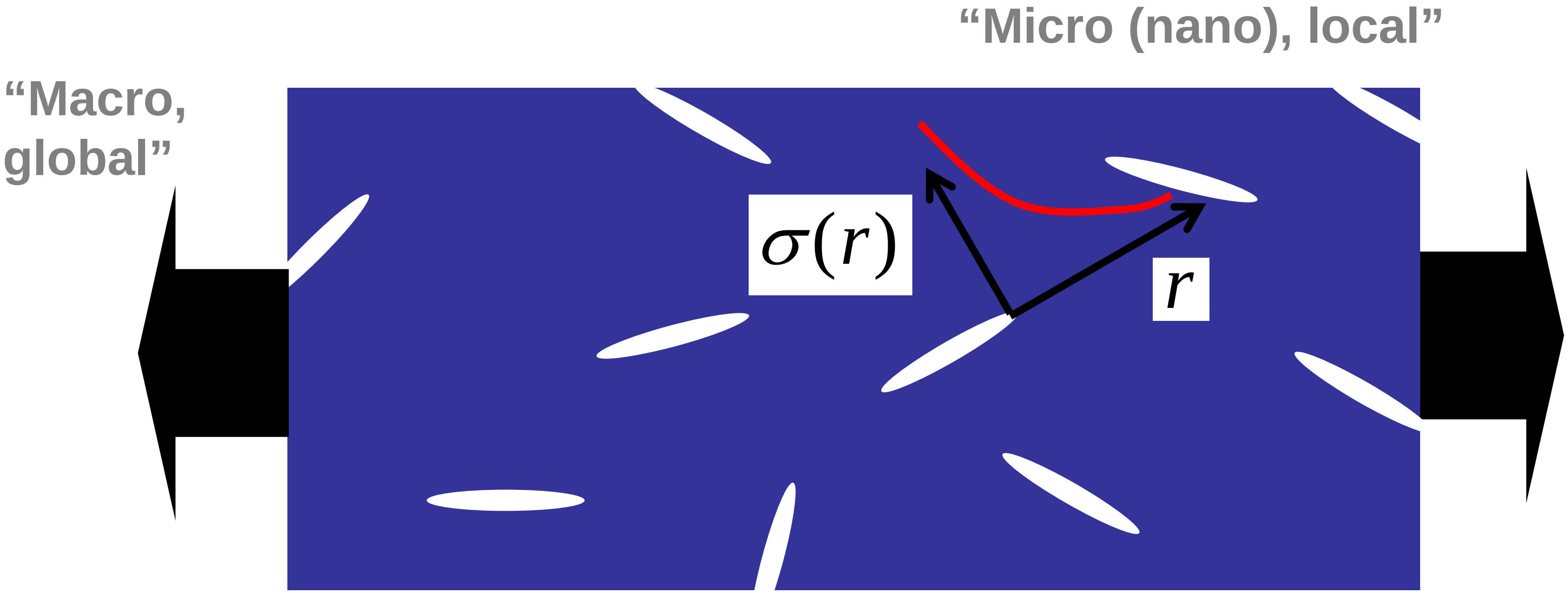
Difficult to deform, breaks easily

Easy to deform hard to break





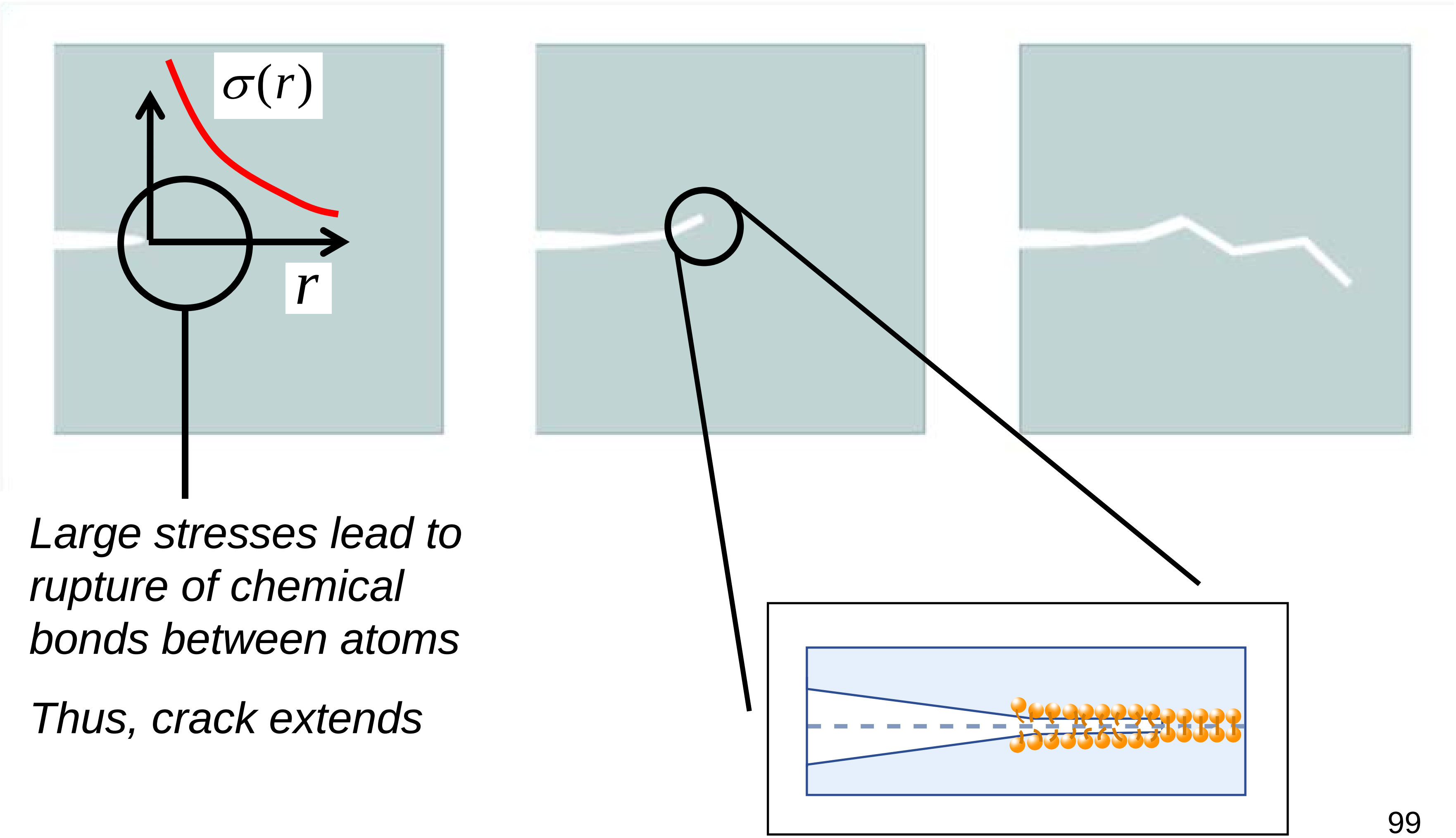
Deformation of materials:
Nothing is perfect, and flaws or cracks matter



Failure of materials initiates at cracks

Griffith, Irwine and others: Failure initiates at defects, such as cracks, or grain boundaries with reduced traction, nano-voids, other imperfections

Crack extension: brittle response

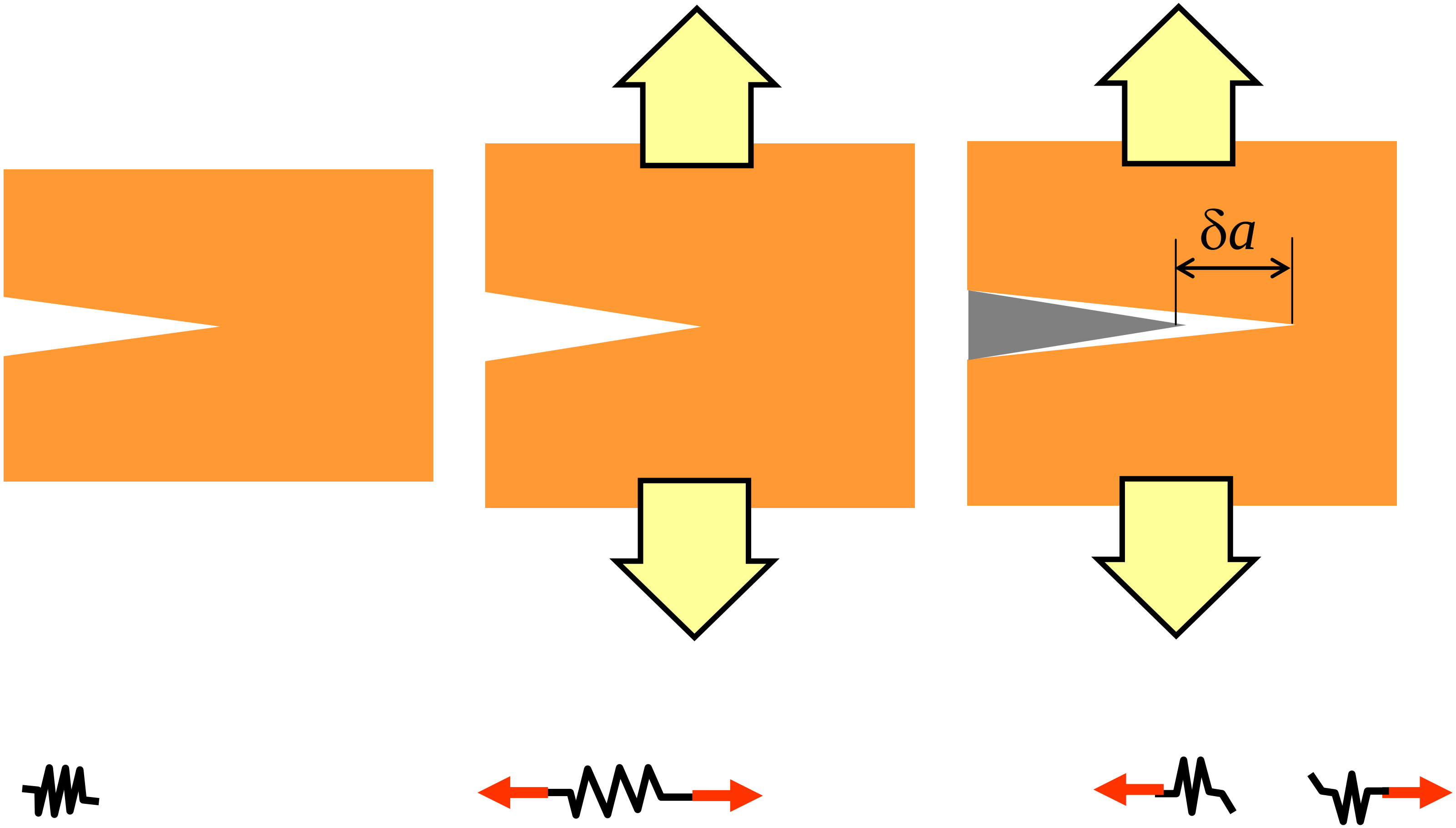


Large stresses lead to rupture of chemical bonds between atoms

Thus, crack extends

Image by MIT OpenCourseWare.

Basic fracture process: dissipation of elastic energy



Undeformed

Stretching=store elastic energy

Release elastic energy dissipated into breaking chemical bonds

Limiting speeds of cracks: linear elastic continuum theory

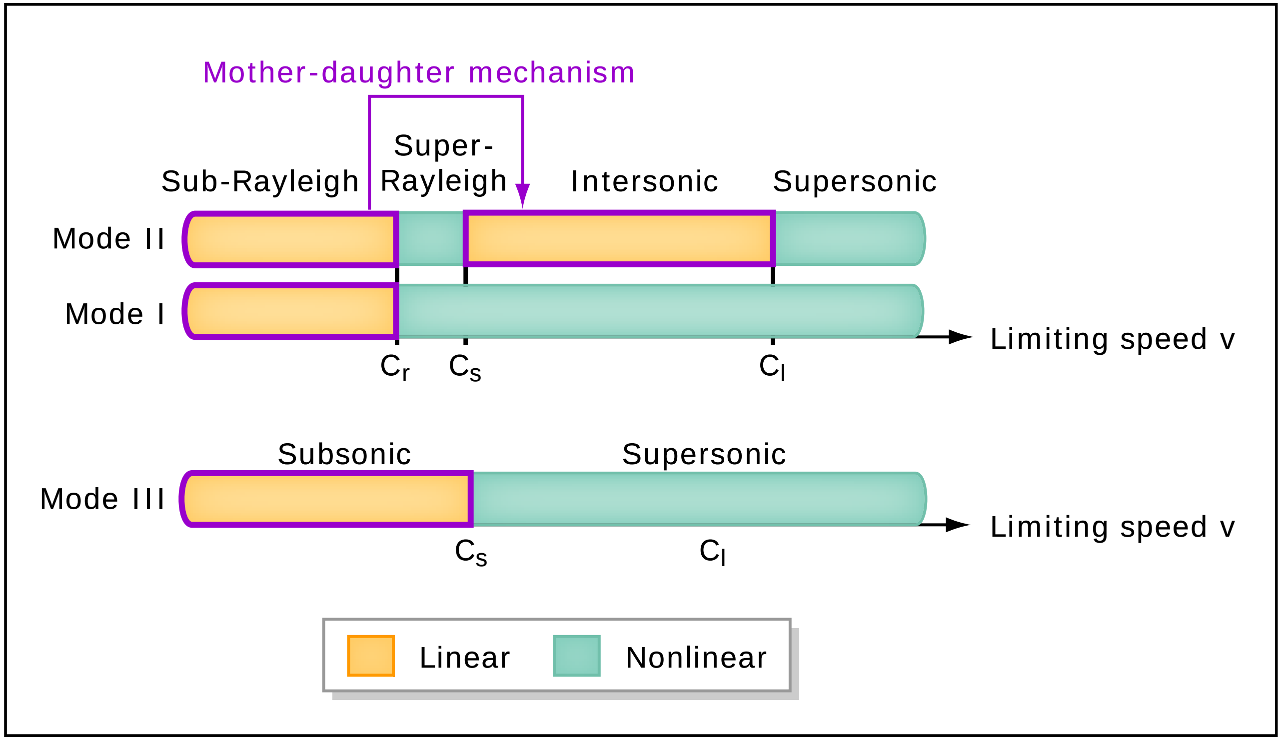


Image by MIT OpenCourseWare.

- Cracks **can not exceed** the limiting speed given by the corresponding wave speeds **unless material behavior is nonlinear**
- Cracks that exceed limiting speed would produce energy (physically impossible - ***linear elastic continuum theory***)

Summary: mixed Hamiltonian approach

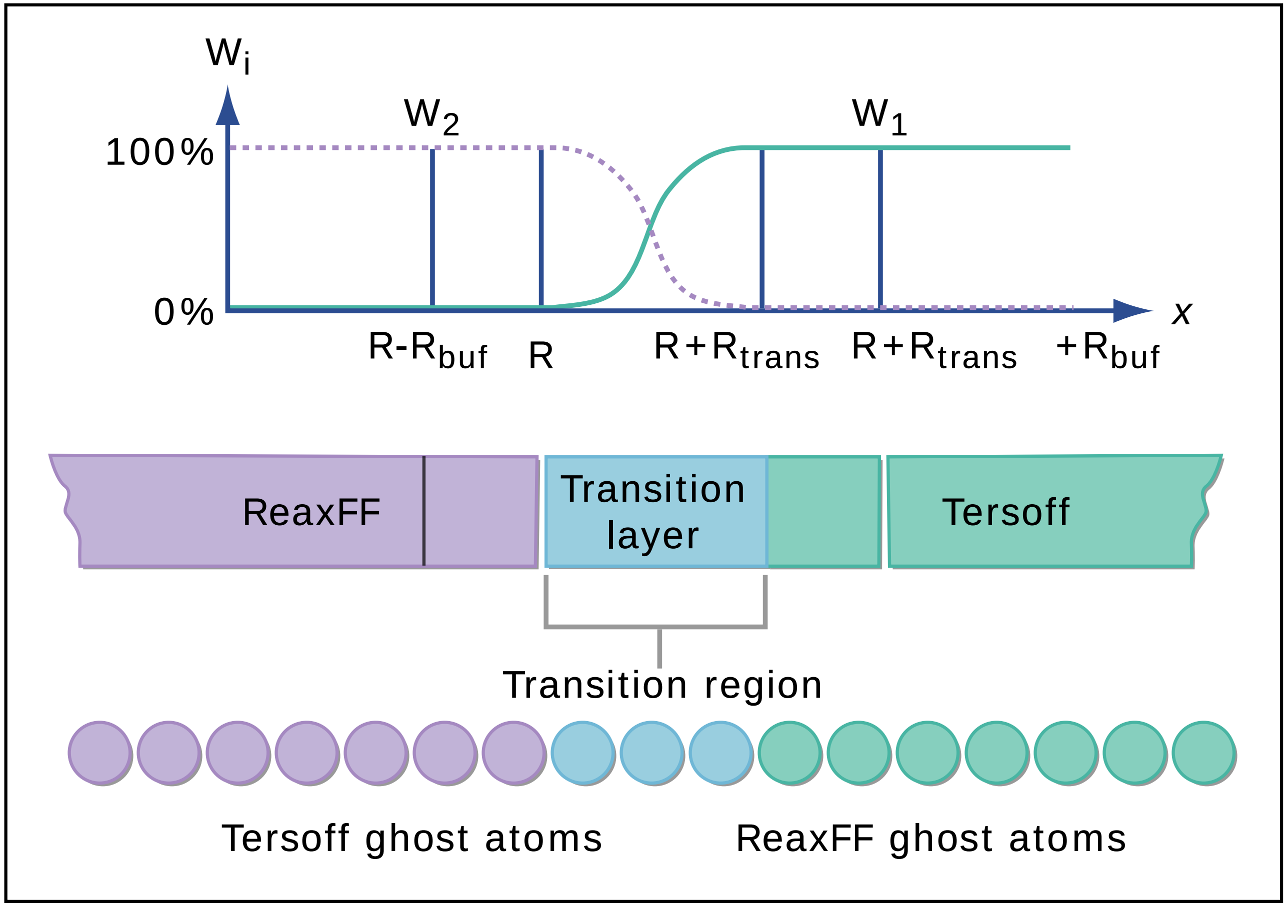
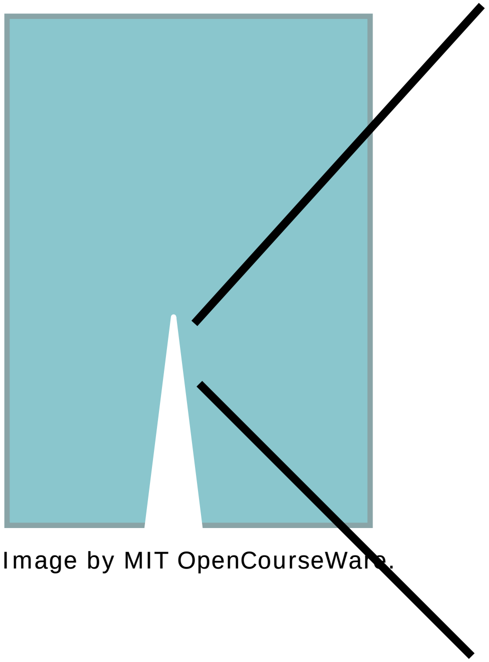


Image by MIT OpenCourseWare.

$$F_{\text{ReaxFF}-\text{Tersoff}} = \left(w_{\text{ReaxFF}}(x)F_{\text{ReaxFF}} + (1 - w_{\text{ReaxFF}})F_{\text{Tersoff}}\right)$$

$$w_{\text{ReaxFF}}(x) + w_{\text{Tersoff}}(x) = 1 \qquad \forall x$$

Atomistic fracture mechanism



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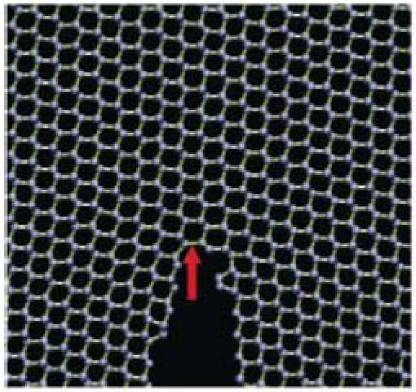
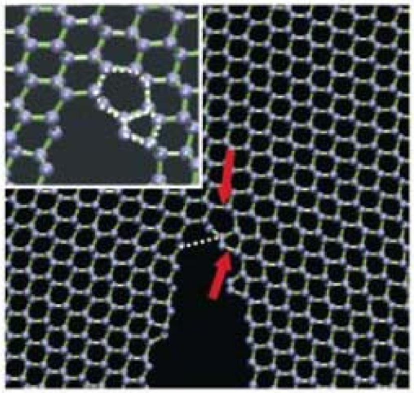
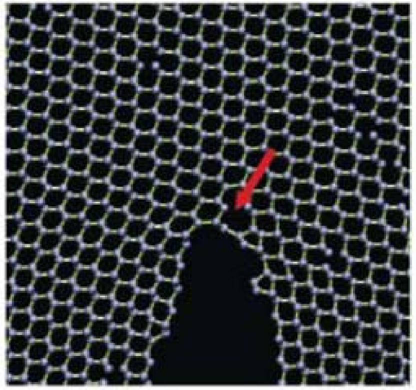


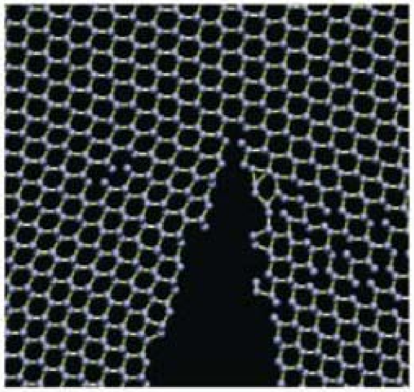
Initial crack



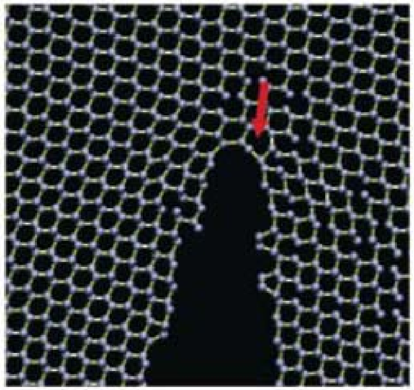
Formation of 7-5 ring defect



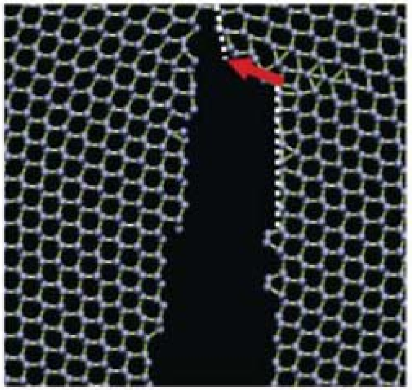
Rupture ahead of 7 membered ring



Crack propagation (smooth surface)



Formation of another 7-5 ring defect



7-5 ring leads to change in crack direction
Creates surface step

Lattice shearing: ductile response

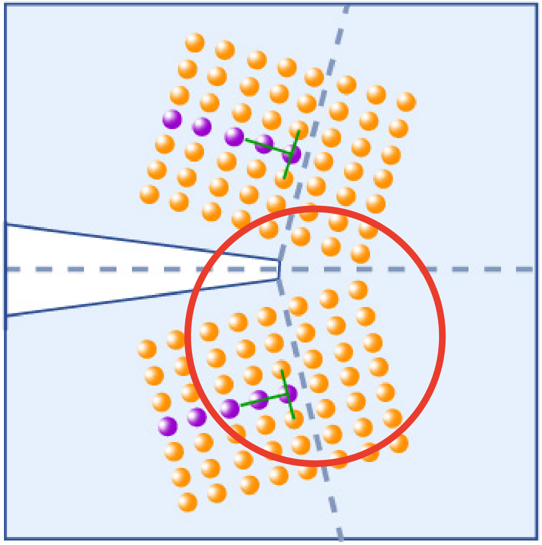


Image by MIT OpenCourseWare.

- Instead of crack extension, induce shearing of atomic lattice
- Due to large shear stresses at crack tip
- Lecture 9

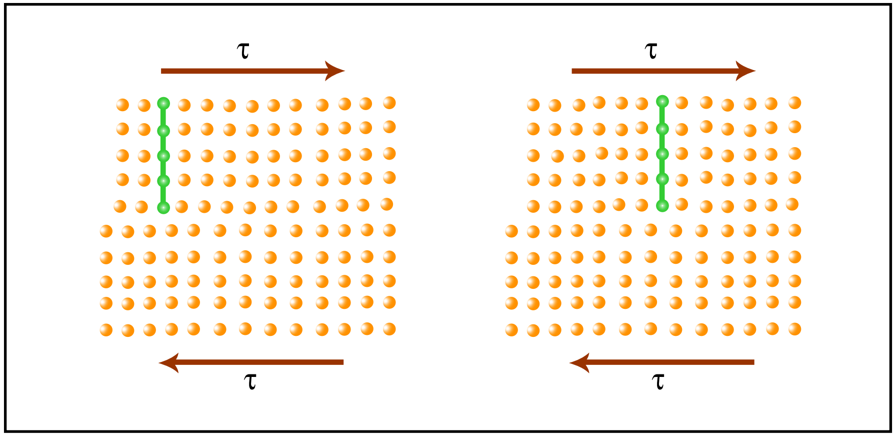
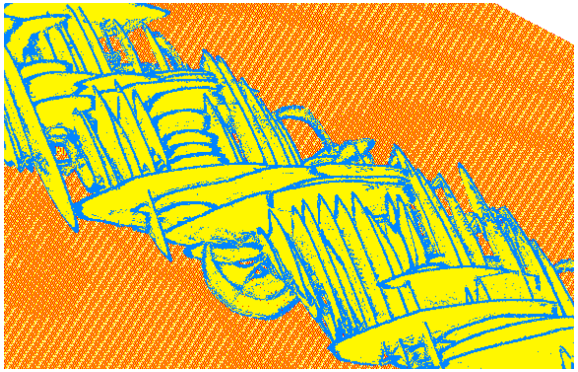


Image by MIT OpenCourseWare.



Concept of dislocations

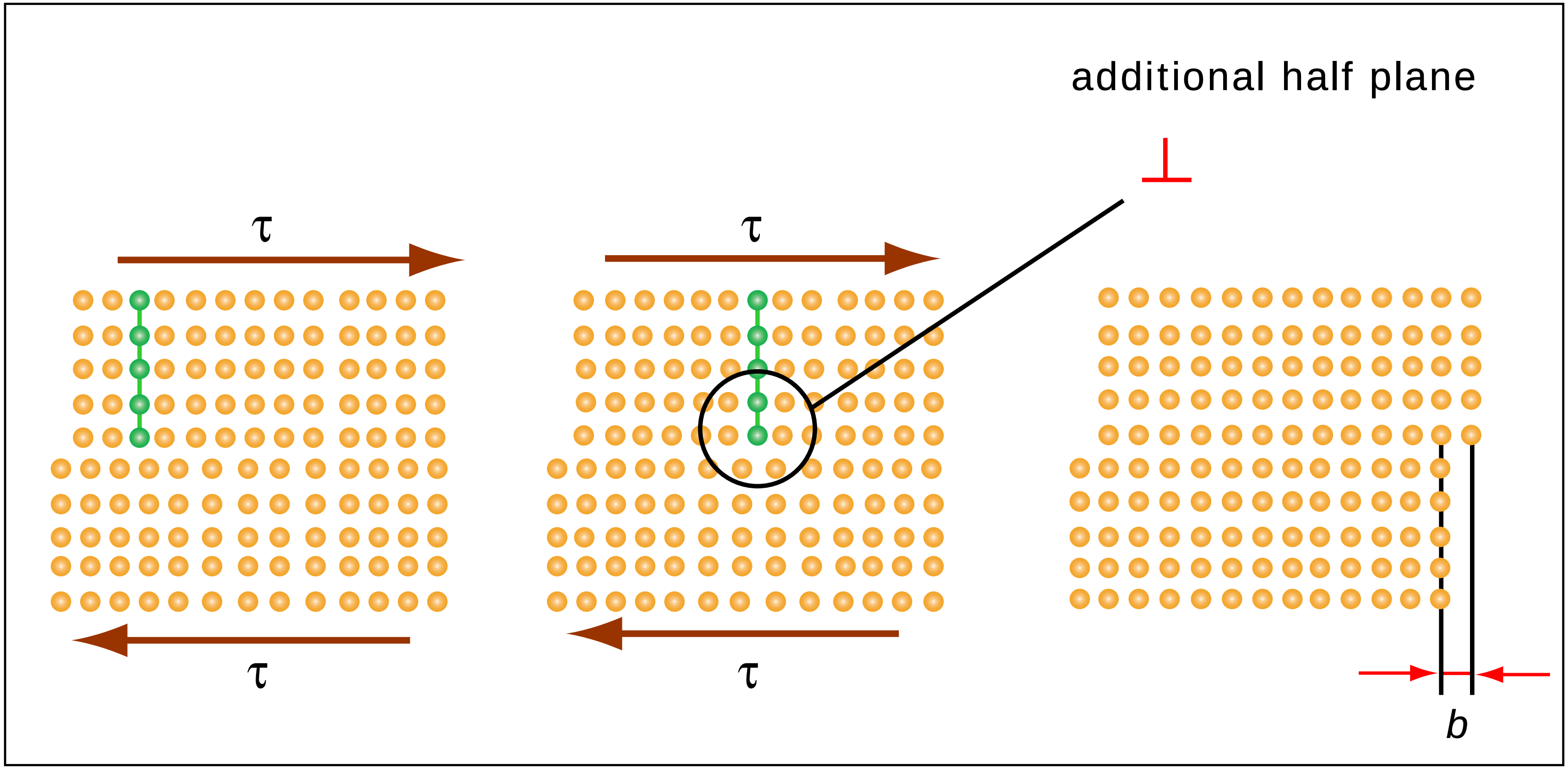


Image by MIT OpenCourseWare.

Localization of shear rather than homogeneous shear that requires **cooperative motion**

“size of single dislocation” = b, Burgers vector

Final sessile structure – “brittle”

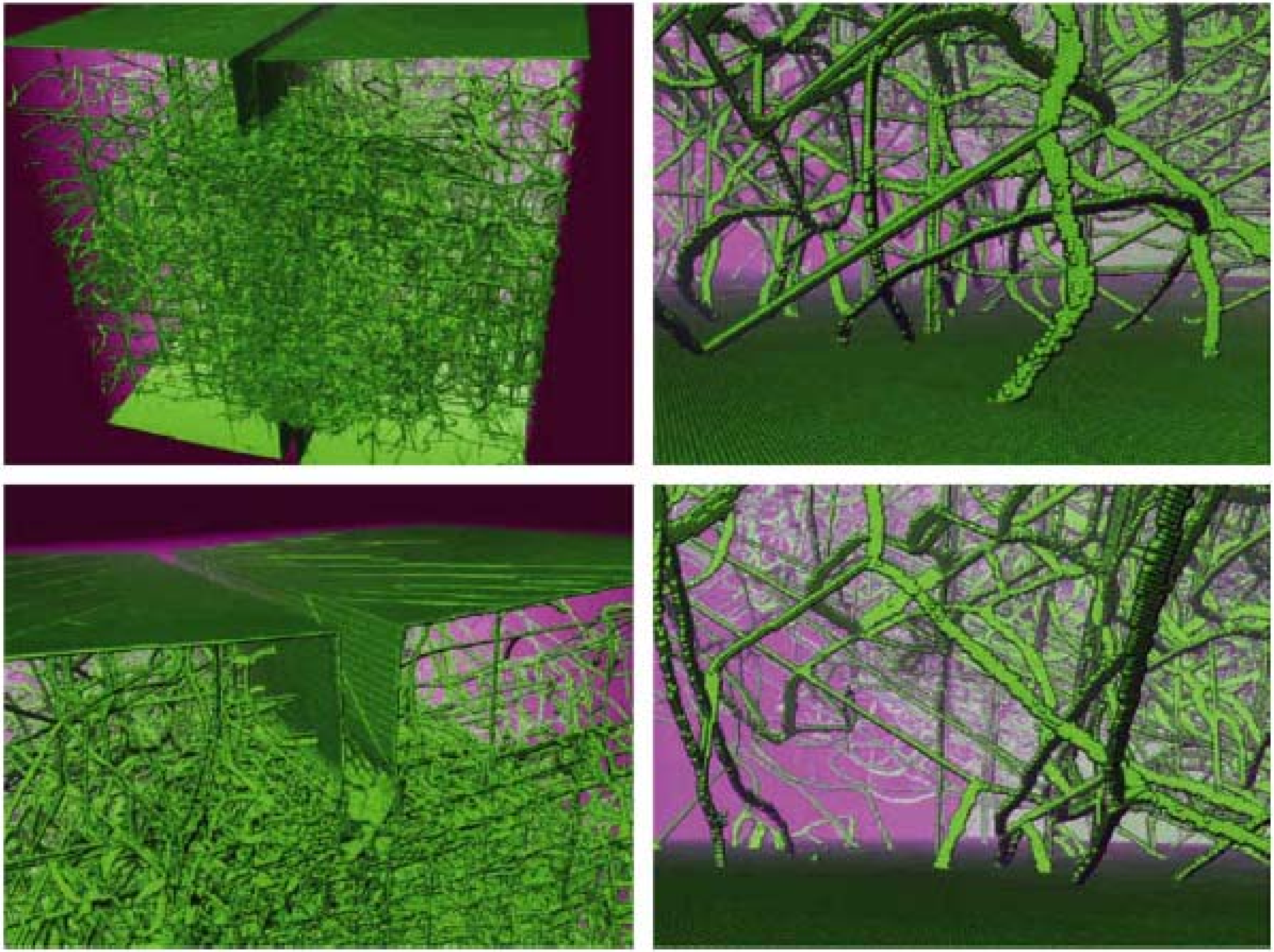


Fig. 1 c from Buehler, M., et al. "The Dynamical Complexity of Work-Hardening: A Large-Scale Molecular Dynamics Simulation." *Acta Mech Sinica* 21 (2005): 103-11.

Brittle versus ductile materials behavior

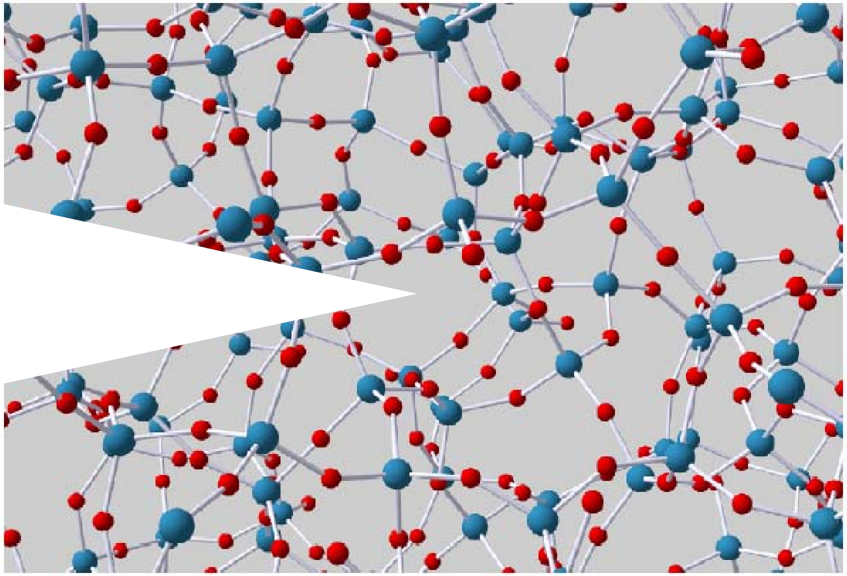
1. Brittle versus ductile material behavior

(a) List 2 ductile and 2 brittle materials. Copper, nickel (ductile) and glass, silicon (brittle)

(b) Describe the atomistic origin of the difference between brittle and ductile materials (focus on relevant mechanisms). Add a simple schematic to illustrate your point.

(c) Glass (SiO_2) has the following atomistic structure, consisting of a random disordered (amorphous) arrangement of Si and O atoms (SiO_2) (Si atoms=blue, oxygen atoms=red):

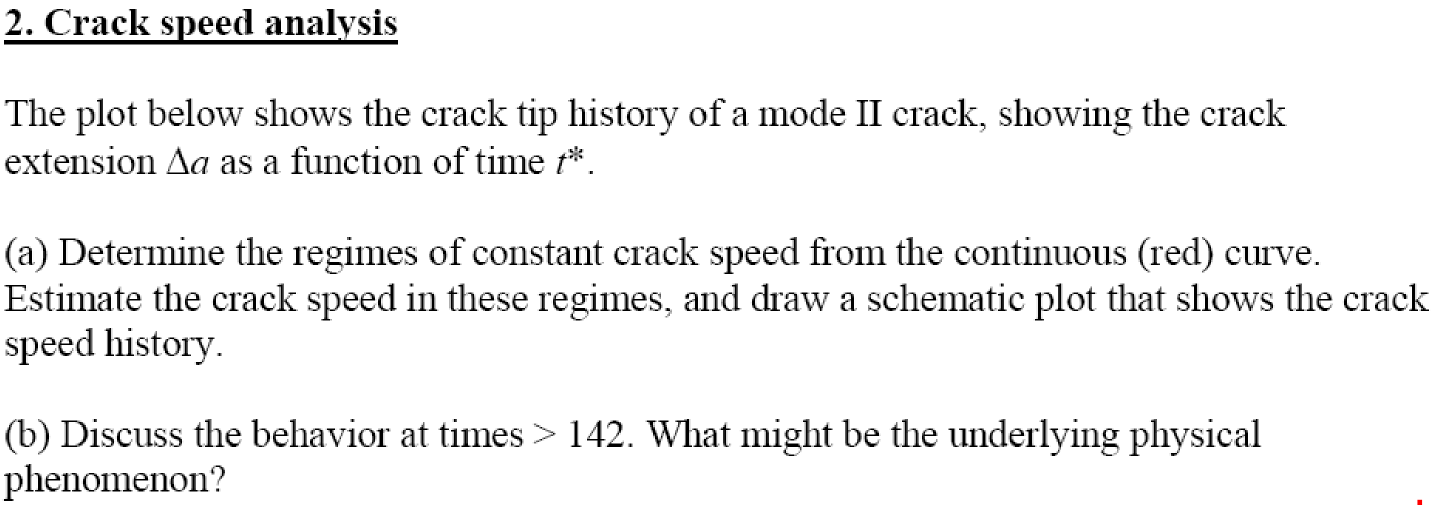
Explain, based on this atomic structure, whether glass is expected to be brittle or ductile.



For a material to be ductile, require dislocations, that is, shearing of lattices

Not possible here (disordered)

Crack speed analysis

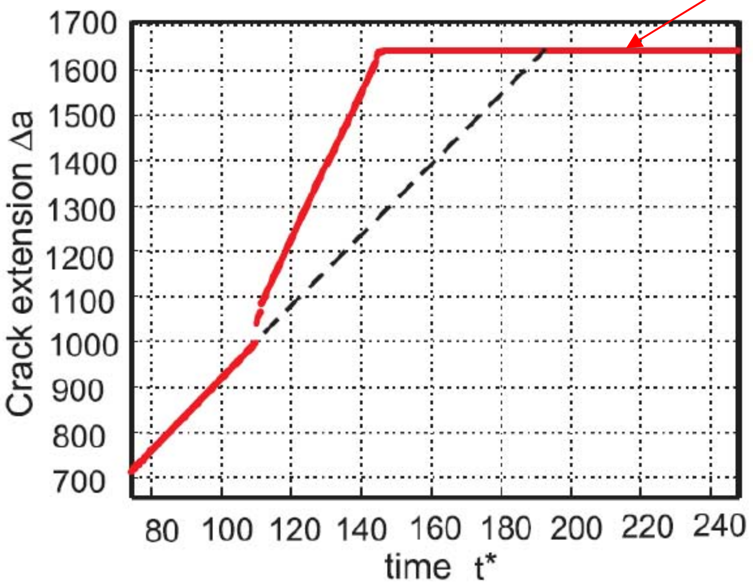


2. Crack speed analysis

The plot below shows the crack tip history of a mode II crack, showing the crack extension Δa as a function of time t^*.

(a) Determine the regimes of constant crack speed from the continuous (red) curve. Estimate the crack speed in these regimes, and draw a schematic plot that shows the crack speed history.

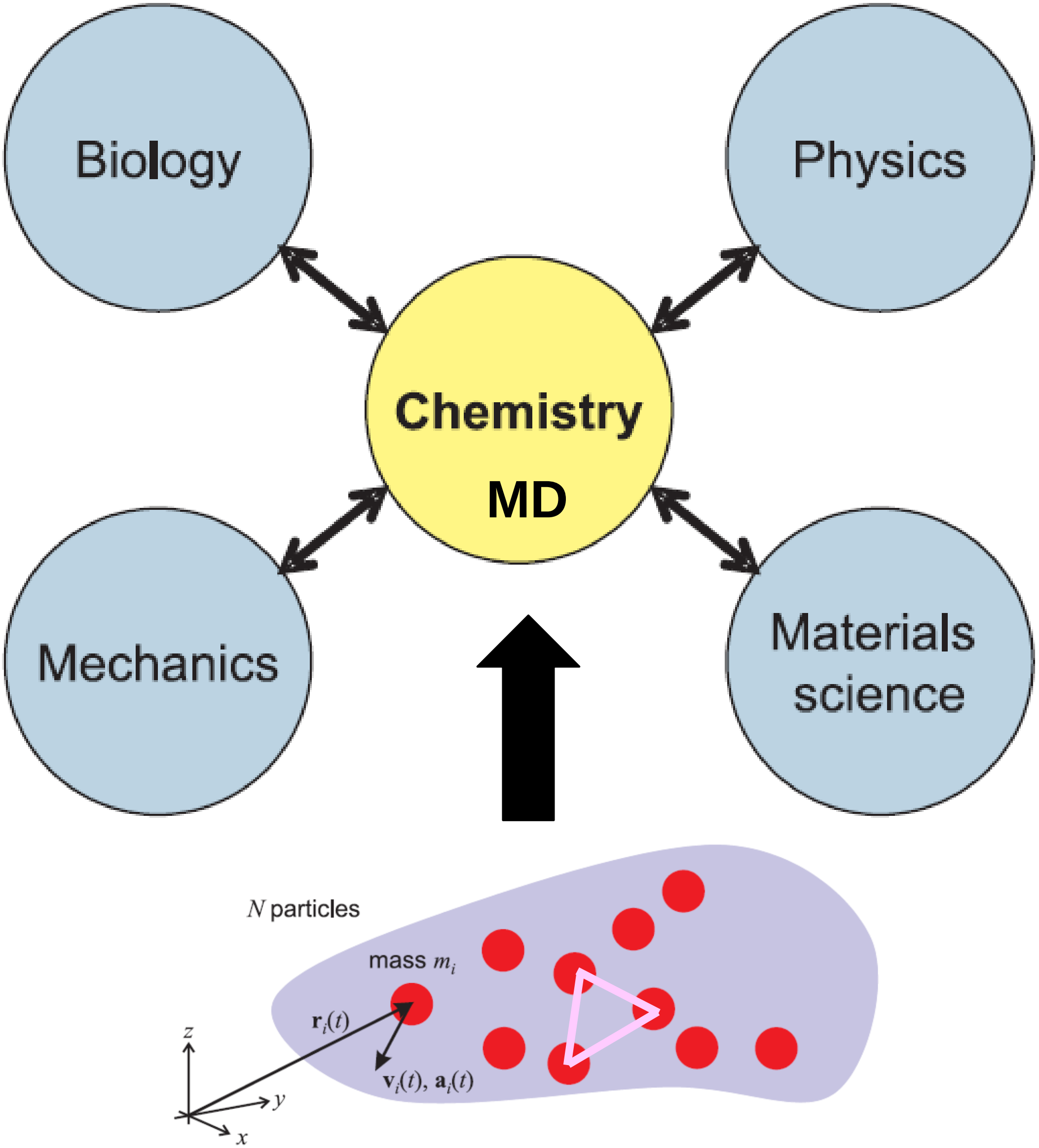
(b) Discuss the behavior at times > 142. What might be the underlying physical phenomenon?



crack has stopped

slope=equal to crack speed

MD simulation: chemistry as bridge between disciplines



Biology

Physics

Chemistry

MD

Mechanics

Materials science

Application – protein folding

ACGT

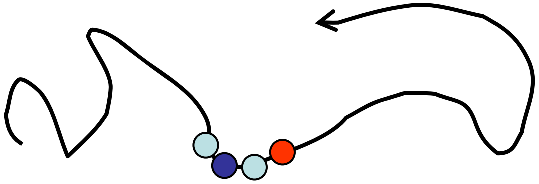
Four letter code “DNA”

Combination of 3 DNA letters equals a amino acid

E.g.: Proline –

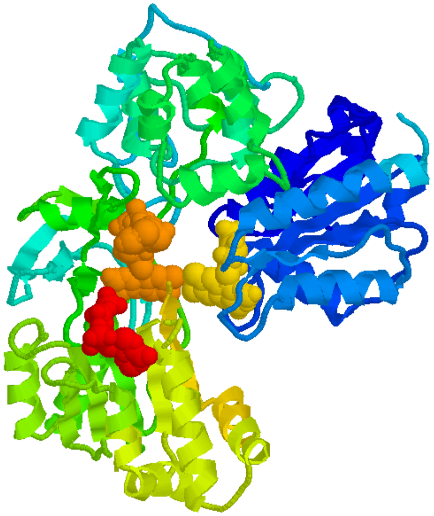
CCT, CCC, CCA, CCG

Transcription/ translation



.. - Proline - Serine – Proline - Alanine - ..

Sequence of amino acids “polypeptide” (1D structure)



Folding (3D structure)

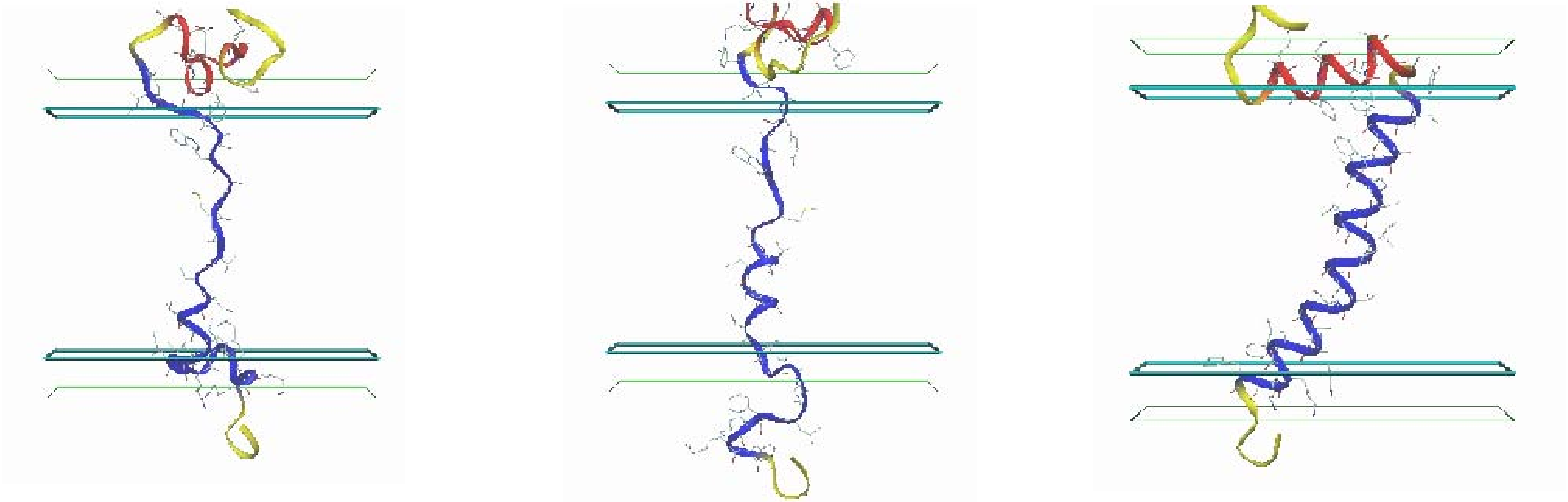
Goal of protein folding simulations:

Predict folded 3D structure based on polypeptide sequence

Movie: protein folding with CHARMM

- *de novo* Folding of a *Transmembrane fd Coat Protein*
  http://www.charmm-gui.org/?doc=gallery&id=23

Polypeptide chain



Quality of predicted structures quite good

Confirmed by comparison of the **MSD deviations** of a room temperature ensemble of conformations from the replica-exchange simulations and **experimental structures** from both **solid-state NMR** in lipid bilayers and solution-phase NMR on the protein in micelles)

2. Important terminology and concepts

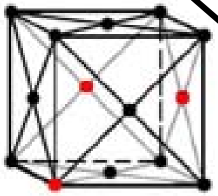
Important terminology and concepts

- Force field
- Potential / interatomic potential
- Reactive force field / nonreactive force field
- Chemical bonding (covalent, metallic, ionic, H-bonds, vdW..)
- Time step
- Continuum vs. atomistic viewpoints
- Monte Carlo vs. Molecular Dynamics
- Property calculation (temperature, pressure, diffusivity [transport properties]-MSD, structural analysis-RDF)
- Choice of potential for different materials (pair potentials, chemical complexity)
- MD algorithm: how to calculate forces, energies
- MC algorithm (Metropolis-Hastings)
- Applications: brittle vs. ductile, crack speeds, data analysis

3. Continuum vs. atomistic approaches

Relevant scales in materials

$\lambda(\text{atom}) \quad << \quad \xi(\text{crystal}) \quad << \quad d(\text{grain}) \quad << \quad dx, dy, dz \quad << \quad H, W, D$



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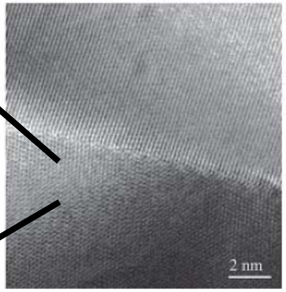

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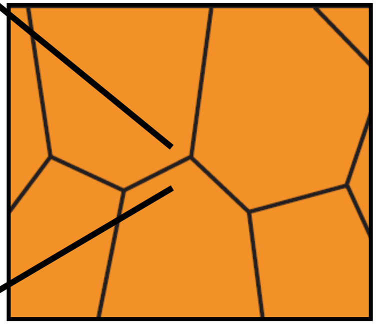

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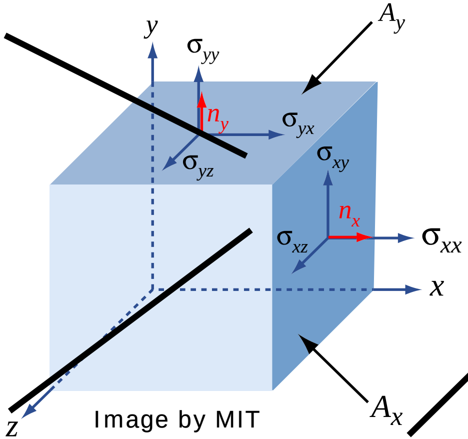

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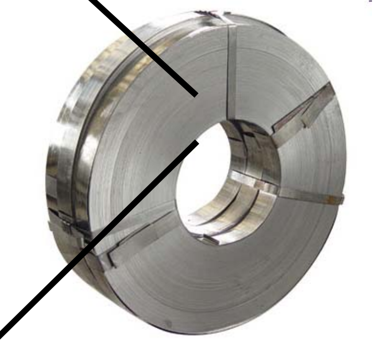


Bottom-up → ← **Top-down**

Atomistic viewpoint:

- Explicitly consider discrete atomistic structure
- Solve for atomic trajectories and infer from these about material properties & behavior
- Features internal length scales (atomic distance)

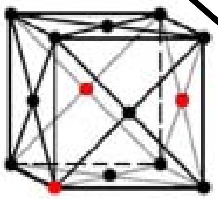
"Many-particle system with statistical properties"

Relevant scales in materials

Separation of scales

RVE

$$\lambda(\text{atom}) \quad << \quad \xi(\text{crystal}) \quad << \quad d(\text{grain}) \quad << \quad dx, dy, dz \quad << \quad H, W, D$$



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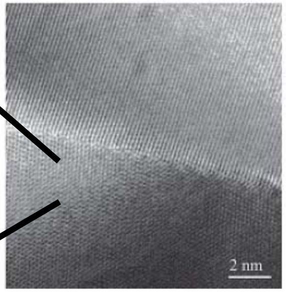

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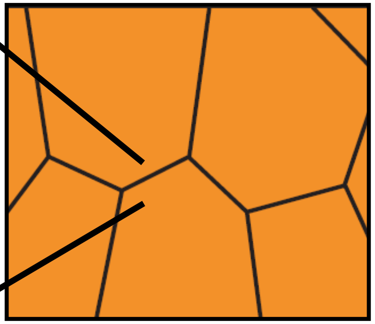

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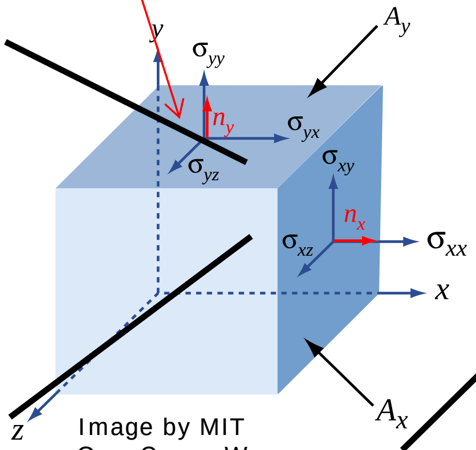

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Top-down

Continuum viewpoint:

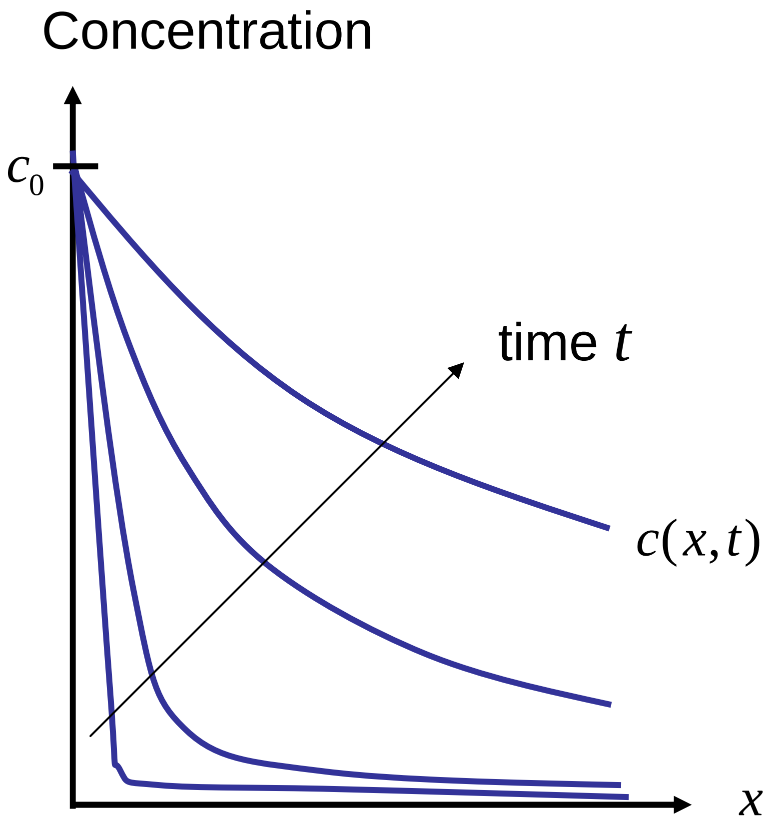
- Treat material as matter with no internal structure
- Develop mathematical model (governing equation) based on representative volume element (RVE, contains “enough” material such that internal structure can be neglected
- Features no characteristic length scales, provided RVE is large enough

“PDE with parameters”

Example – diffusion

Example solution – 2nd Fick's law

$$\frac{\partial c}{\partial t} = \boxed{D}\frac{d^2 c}{dx^2}$$



BC: $c\ (x = 0) = c_0$
IC: $c\ (x > 0, t = 0) = 0$

Need diffusion coefficient to solve for distribution!

2. Finite difference method

How to solve a PDE

$$\frac{\partial c}{\partial t} = D\frac{d^2c}{dx^2}$$

+ BCs, ICs

Note: Flux $J = -D\frac{dc}{dx}$

Finite difference method

$$\frac{\partial c}{\partial t} = D\frac{d^2 c}{dx^2}$$

discrete grid
(space and time)

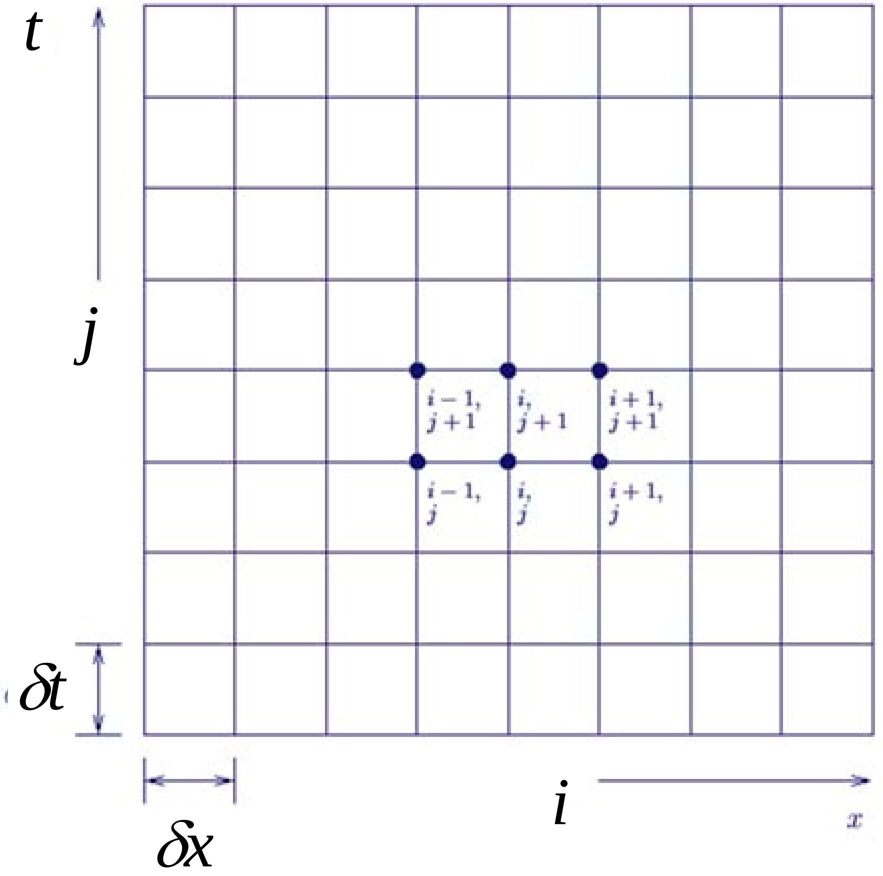
Idea: Instead of solving for continuous field $c(t,x)$

solve for $c(t_i, x_j)$

$i =$ space

$j =$ time

$$c(t_i, x_j) = c_{i,j}$$



$i = 1..N_x$

Finite difference method

$$\frac{\partial c}{\partial t} = D\frac{d^2 c}{dx^2}$$

Idea: Instead of solving for continuous field $c(t, x)$

solve for $c(t_i, x_j)$

Approach: Express continuous derivatives as discrete differentials

$$\frac{\partial c}{\partial t} \approx \frac{\Delta c}{\Delta t}$$

Finite difference method

$$\frac{\partial c}{\partial t} = D\frac{d^2c}{dx^2}$$

Idea: Instead of solving for continuous field $c(t,x)$

solve for $c(t_i, x_j)$

Approach: Express continuous derivatives as discrete differentials

$$\frac{\partial c}{\partial t} \approx \frac{\Delta c}{\Delta t}$$

$$\frac{\partial c}{\partial x} \approx \frac{\Delta c}{\Delta x} \qquad \frac{\partial^2 c}{\partial x^2} \approx \frac{\Delta\left(\frac{\Delta c}{\Delta t}\right)}{\Delta x}$$

Forward, backward and central difference

Forward difference

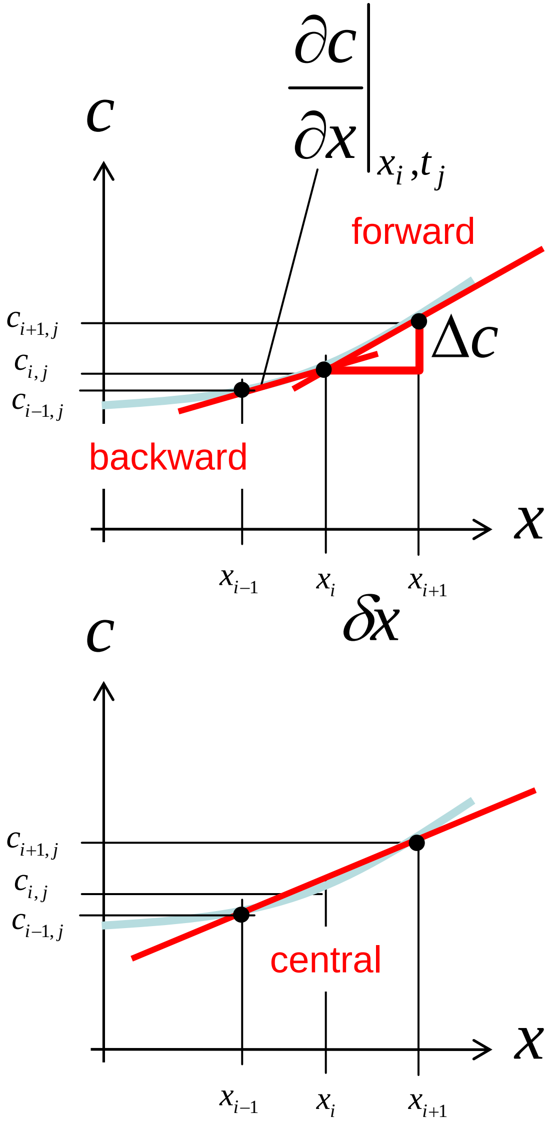
$$\left.\frac{\partial c}{\partial x}\right|_{x_i,t_j} \approx \frac{c_{i+1,j} - c_{i,j}}{x_{i+1} - x_i} = \frac{c_{i+1,j} - c_{i,j}}{\delta x},$$

Backward difference

$$\left.\frac{\partial c}{\partial x}\right|_{x_i,t_j} \approx \frac{c_{i,j} - c_{i-1,j}}{x_i - x_{i-1}} = \frac{c_{i,j} - c_{i-1,j}}{\delta x},$$

Central difference

$$\left.\frac{\partial c}{\partial x}\right|_{x_i,t_j} \approx \frac{c_{i+1,j} - c_{i-1,j}}{x_{i+1} - x_{i-1}} = \frac{c_{i+1,j} - c_{i-1,j}}{2\delta x}.$$

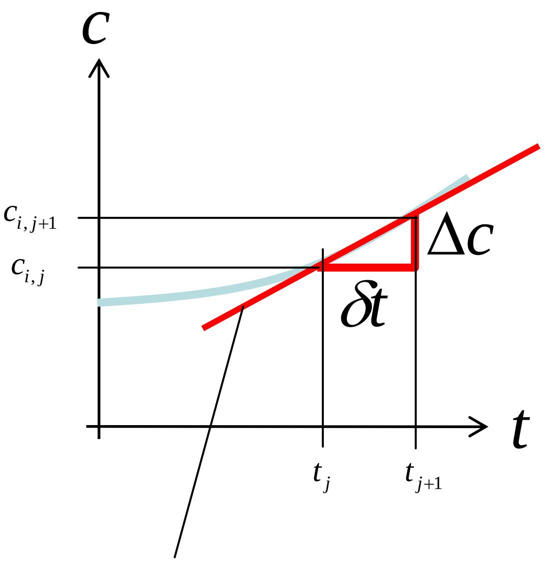


How to calculate derivatives with discrete differentials

$$\boxed{\frac{\partial c}{\partial t}} = D\frac{d^2c}{dx^2}$$

$$\frac{\partial c}{\partial t} \approx \frac{\Delta c}{\Delta t}$$

$$\boxed{\left.\frac{\partial c}{\partial t}\right|_{x_i,t_j} \approx \frac{c_{i,j+1} - c_{i,j}}{t_{j+1} - t_j} = \frac{c_{i,j+1} - c_{i,j}}{\delta t} \qquad (1)}$$



$$\left.\frac{\partial c}{\partial t}\right|_{x_i,t_j}$$

δt discrete time step

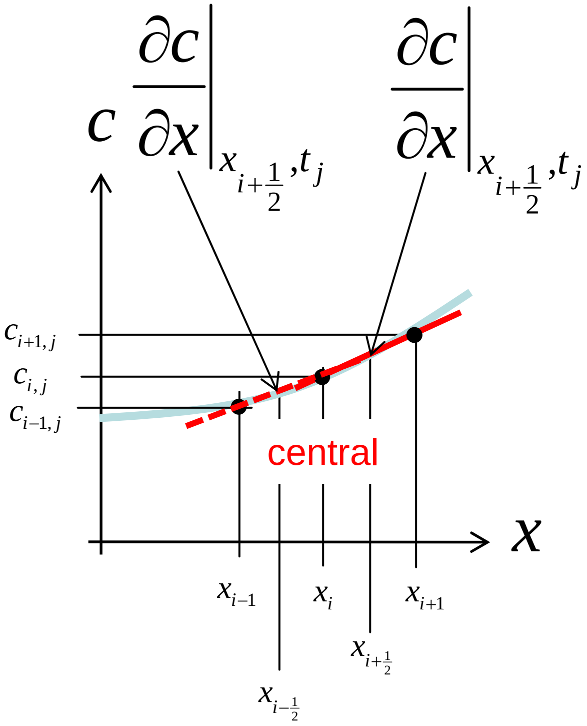
How to calculate derivatives with discrete differentials

$$\frac{\partial c}{\partial t} = \boxed{D\frac{d^2 c}{dx^2}}$$

$$\frac{\partial c}{\partial x} \approx \frac{\Delta c}{\Delta x} \qquad \frac{\partial^2 c}{\partial x^2} \approx \frac{\Delta\left(\frac{\Delta c}{\Delta t}\right)}{\Delta x}$$

$$\left.\frac{\partial c}{\partial x}\right|_{x_{i+\frac{1}{2}},t_j} \approx \frac{c_{i+1,j}-c_{i,j}}{x_{i+1}-x_i} = \frac{c_{i+1,j}-c_{i,j}}{\delta x}$$

$$\left.\frac{\partial c}{\partial x}\right|_{x_{i-\frac{1}{2}},t_j} \approx \frac{c_{i,j}-c_{i-1,j}}{x_i-x_{i-1}} = \frac{c_{i,j}-c_{i-1,j}}{\delta x}$$

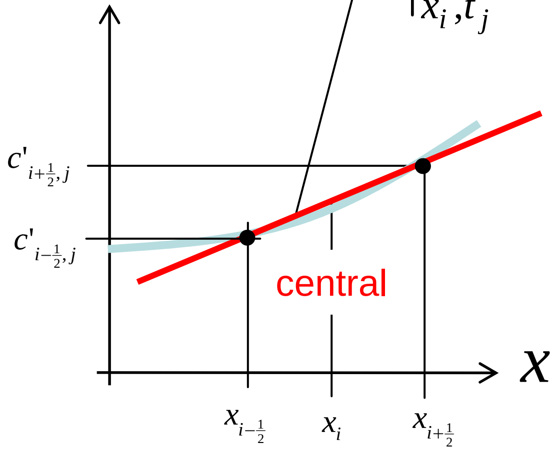


How to calculate derivatives with discrete differentials

$$\frac{\partial c}{\partial t} = \boxed{D\frac{d^2 c}{dx^2}}$$

$$\frac{\partial c}{\partial x} \approx \frac{\Delta c}{\Delta x} \qquad \frac{\partial^2 c}{\partial x^2} \approx \frac{\Delta\left(\frac{\partial c}{\partial x}\right)}{\Delta x}$$

$$\left.\frac{\partial c}{\partial x}\right|_{x_i, t_j} \qquad \left.\frac{\partial^2 c}{\partial x^2}\right|_{x_i, t_j}$$



$$\left.\frac{\partial c}{\partial x}\right|_{x_{i+\frac{1}{2}}, t_j} \approx \frac{c_{i+1,j} - c_{i,j}}{x_{i+1} - x_i} = \frac{c_{i+1,j} - c_{i,j}}{\delta x}$$

$$\left.\frac{\partial c}{\partial x}\right|_{x_{i-\frac{1}{2}}, t_j} \approx \frac{c_{i,j} - c_{i-1,j}}{x_i - x_{i-1}} = \frac{c_{i,j} - c_{i-1,j}}{\delta x}$$

Apply central difference method again…

$$\left.\frac{\partial^2 c}{\partial x^2}\right|_{x_i, t_j} \approx \frac{\left.\frac{\partial c}{\partial x}\right|_{x_{i+\frac{1}{2}}, t_j} - \left.\frac{\partial c}{\partial x}\right|_{x_{i-\frac{1}{2}}, t_j}}{x_{i+\frac{1}{2}} - x_{i-\frac{1}{2}}} = \frac{c_{i+1,j} - c_{i,j} - \left(c_{i,j} - c_{i-1,j}\right)}{\delta x^2} = \frac{c_{i+1,j} - 2c_{i,j} - c_{i-1,j}}{\delta x^2} \tag{2}$$

Complete finite difference scheme

$$\frac{\partial c}{\partial t} = D\frac{d^2 c}{dx^2}$$

$$\begin{cases} \left.\dfrac{\partial^2 c}{\partial x^2}\right|_{x_i,t_j} \approx \dfrac{c_{i+1,j} - 2c_{i,j} - c_{i-1,j}}{\delta x^2} \\ \\ \left.\dfrac{\partial c}{\partial t}\right|_{x_i,t_j} \approx \dfrac{c_{i,j+1} - c_{i,j}}{\delta t} \end{cases}$$

$$\Big\downarrow$$

$$\frac{c_{i,j+1} - c_{i,j}}{\delta t} = D\left(\frac{c_{i+1,j} - 2c_{i,j} - c_{i-1,j}}{\delta x^2}\right)$$

Complete finite difference scheme

$$\frac{\partial c}{\partial t} = D\frac{d^2 c}{dx^2}$$

$$\left\{ \begin{array}{l} \left.\dfrac{\partial^2 c}{\partial x^2}\right|_{x_i,t_j} \approx \dfrac{c_{i+1,j} - 2c_{i,j} - c_{i-1,j}}{\delta x^2} \\[2em] \left.\dfrac{\partial c}{\partial t}\right|_{x_i,t_j} \approx \dfrac{c_{i,j+1} - c_{i,j}}{\delta t} \end{array}\right.$$

$$\Big\downarrow$$

Want

$$\frac{\bigcirc\!\!\!\!\!\!\!\!\;\; c_{i,j+1} - c_{i,j}}{\delta t} = D\left(\frac{c_{i+1,j} - 2c_{i,j} - c_{i-1,j}}{\delta x^2}\right)$$

$$\boxed{c_{i,j+1} = c_{i,j} + \frac{\delta t}{\delta x^2} D\left(c_{i+1,j} - 2c_{i,j} - c_{i-1,j}\right)}$$

Complete finite difference scheme

$$\frac{\partial c}{\partial t} = D\frac{d^2 c}{dx^2}$$

$i =$ space

$j =$ time

Concentration at i
at old time

$$c_{i,j+1} = c_{i,j} + \frac{\delta t}{\delta x^2} D\left(c_{i+1,j} - 2c_{i,j} - c_{i-1,j}\right)$$

"explicit" numerical scheme (new concentration directly from concentration at earlier time)

Concentration at i
at old time

Concentration at i-1
at old time

Concentration at i
at new time

Concentration at $i+1$
at old time

Summary

- Developed finite difference approach to solve for diffusion equation

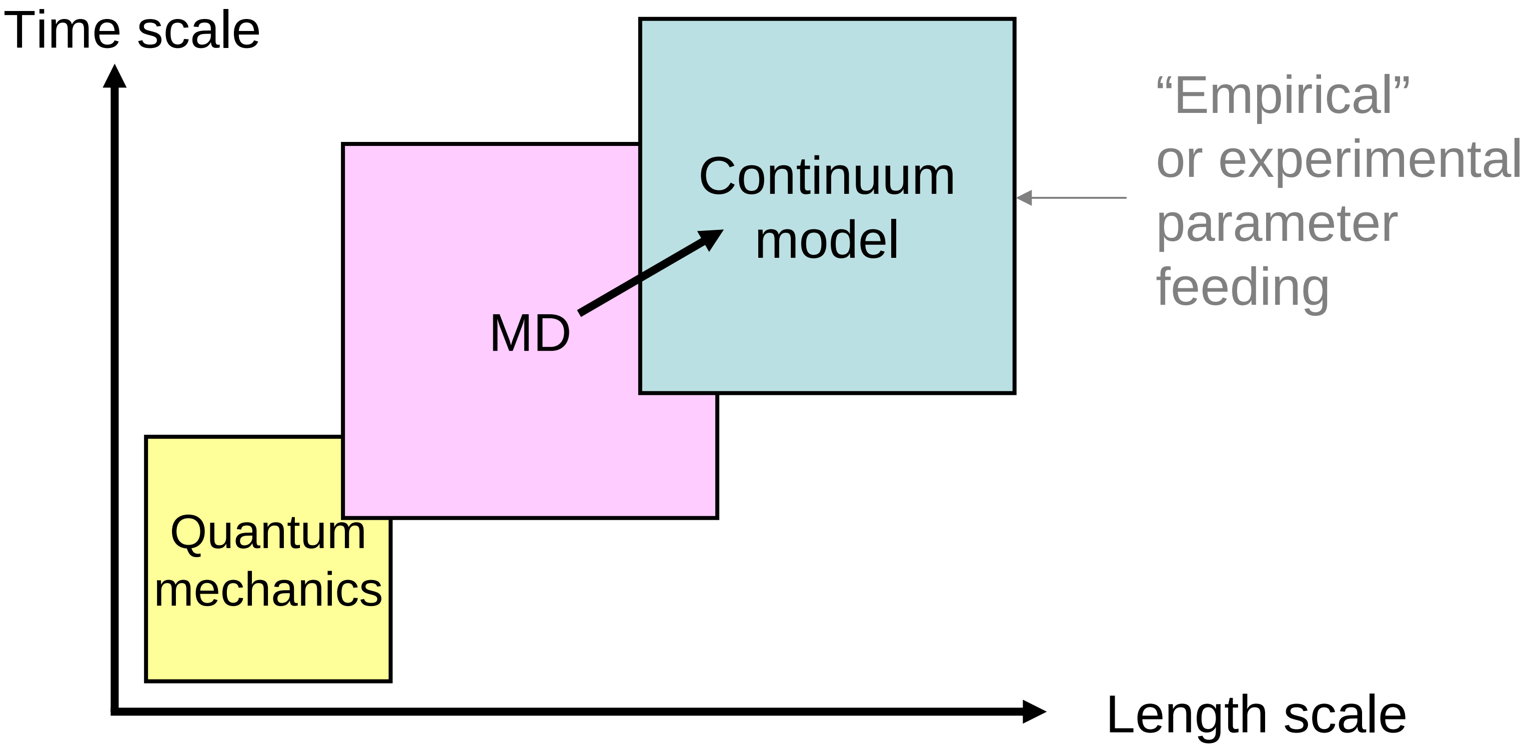
- Use parameter (D), e.g. calculated from molecular dynamics, and solve “complex” problem at continuum scale

- Do not consider “atoms” or “particles”

Summary

Multi-scale approach:

Feed parameters from atomistic simulations to continuum models



“Empirical”
or experimental
parameter
feeding

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Spring 2012