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

Part I – Continuum and particle methods

Property calculation II

Lecture 4

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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** (Advanced property calculation, introduction to chemical interactions, Monte Carlo methods)

Lecture 4: Property calculation II

Outline:

1. Advanced analysis methods: Radial distribution function (RDF)
2. Introduction: How to model chemical interactions
    2.1 How to identify parameters in a Lennard-Jones potential
3. Monte-Carlo (MC) approach: Metropolis-Hastings algorithm
    3.1 Application to integration
    3.2 Metropolis-Hastings algorithm

Goal of today's lecture:

- Learn how to analyze structure of a material based on atomistic simulation result (solid, liquid, gas, different crystal structure, etc.)
- Introduction to potential or force field (Lennard-Jones)
- Present details of MC algorithm – background and implementation

1. Advanced analysis methods: Radial distribution function (RDF)

Goals

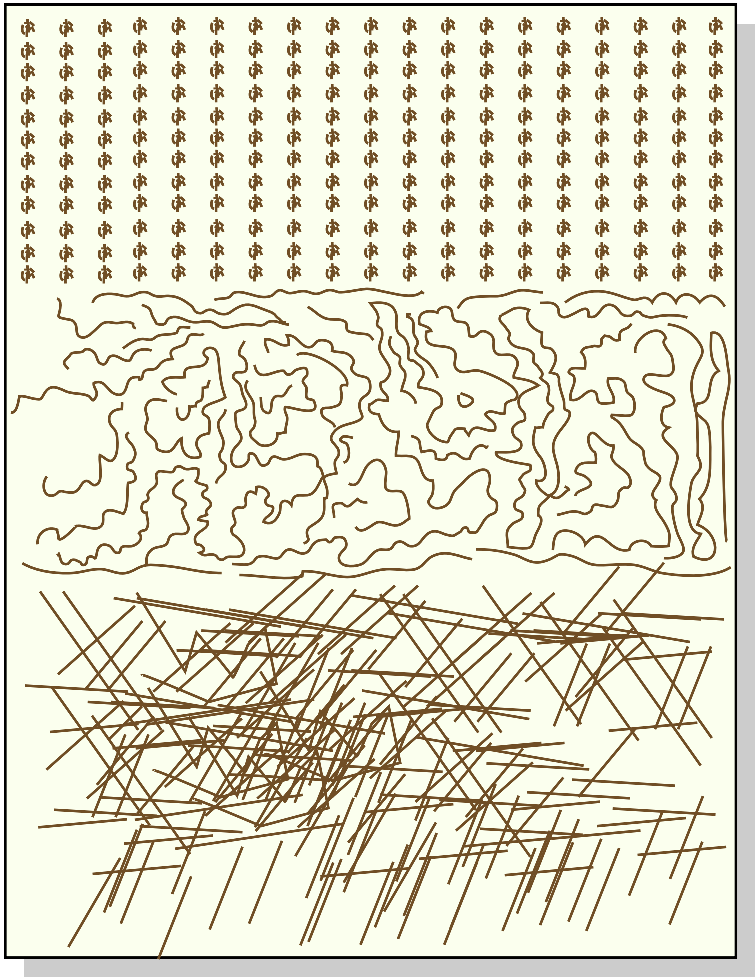
- ***Define algorithms that enable us to "make sense" of positions, velocities etc. and time histories to relate with experimentally measurable quantities***

- So far: temperature, MSD (mean square displacement function)

- Here: extend towards other properties

MD modeling of crystals – solid, liquid, gas phase

- Crystals: Regular, ordered structure
- The corresponding particle motions are small-amplitude vibrations about the lattice site, diffusive movements over a local region, and long free flights interrupted by a collision every now and then.
- Liquids: Particles follow Brownian motion (collisions)
- Gas: Very long free paths



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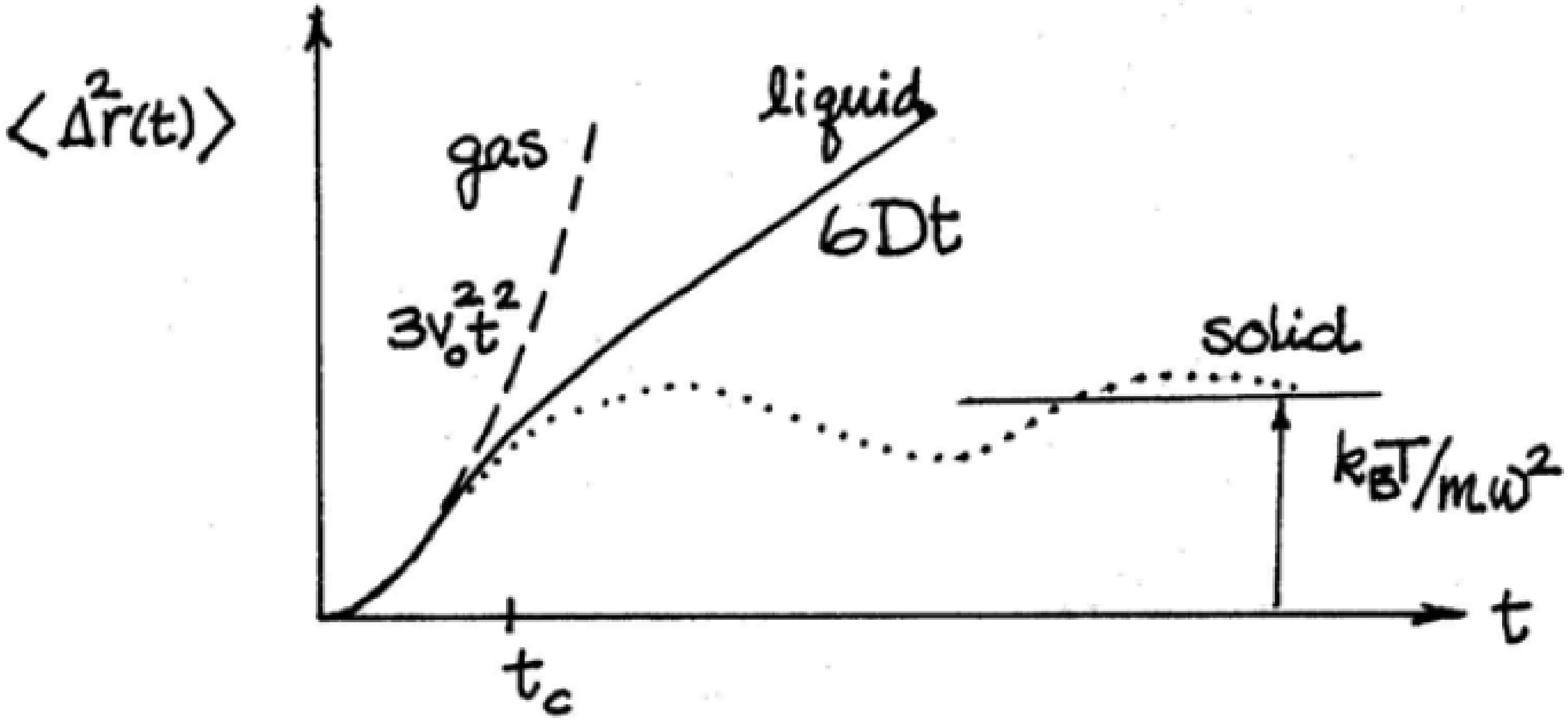
Atomistic trajectory – through MSD



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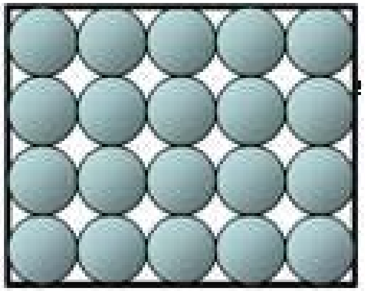
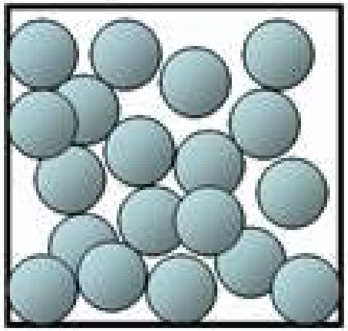
Need positions over time – **what if not available?**

How to characterize material state (solid, liquid, gas)

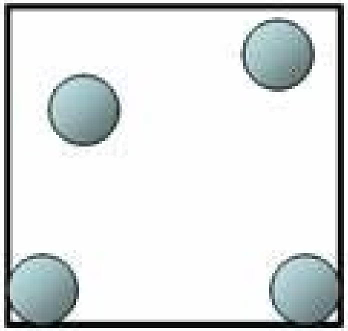
- Application: Simulate phase transformation (melting)



Solid State
Ordered and dense
Has a definite
shape and volume.
Solids are very slightly
compressible.



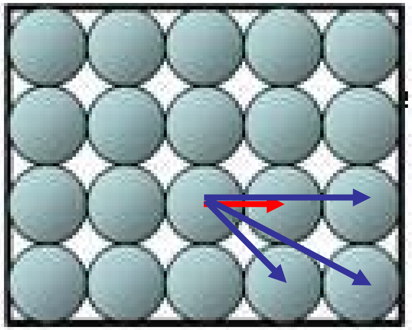
Liquid State
Disordered and usually
slightly less dense.
Has a definite volume
and takes the shape of
the container.
Liquids are slightly
compressible.



Gas State
Disordered and
much lower density
than crystal or liquid.
Does not have
definite shape and
volume.
Gases are highly
compressible.

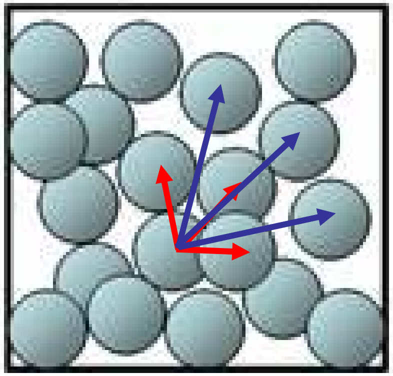
http://www.t2i2edu.com/WebMovie/1Chap1_files/image002.jpg

How to characterize material state (solid, liquid, gas)



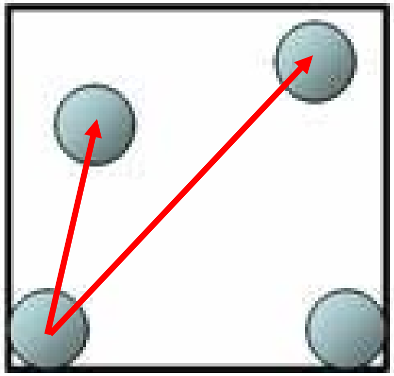
Regular spacing

Neighboring particles found at characteristic distances



Irregular spacing

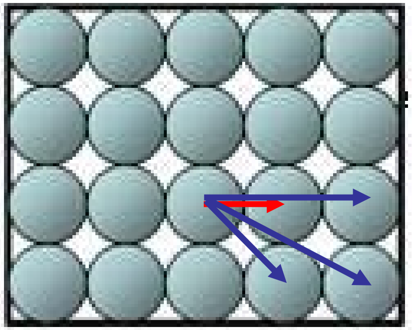
Neighboring particles found at approximate distances (smooth variation)



More irregular spacing

More random distances, less defined

How to characterize material state (solid, liquid, gas)



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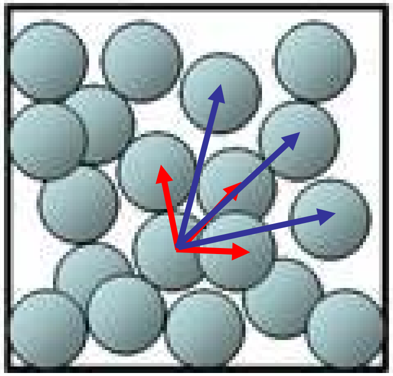

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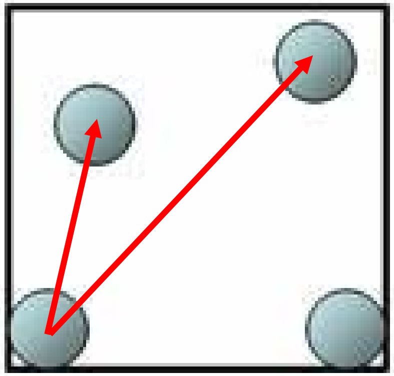


More irregular spacing

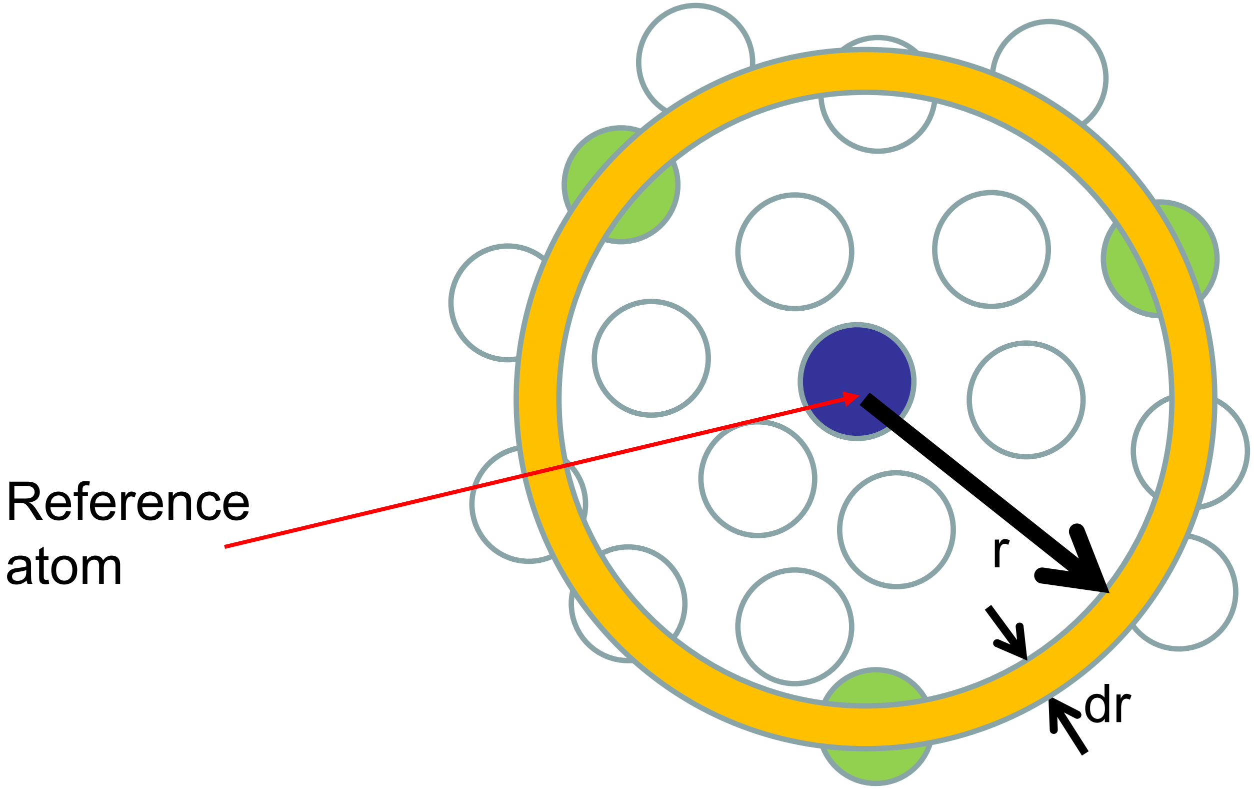
More random distances, less defined

Concept:

- Measure distance of particles to their neighbors
- Average over large number of particles
- Average over time (MD) or iterations (MC)

Formal approach: Radial distribution function (RDF)

Ratio of density of atoms at distance r (in control area dr) by overall density = relative density of atoms as function of radius



$$g(r) = \rho(r) / \rho$$

Formal approach: Radial distribution function (RDF)

The radial distribution function is defined as

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

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

Formal approach: Radial distribution function (RDF)

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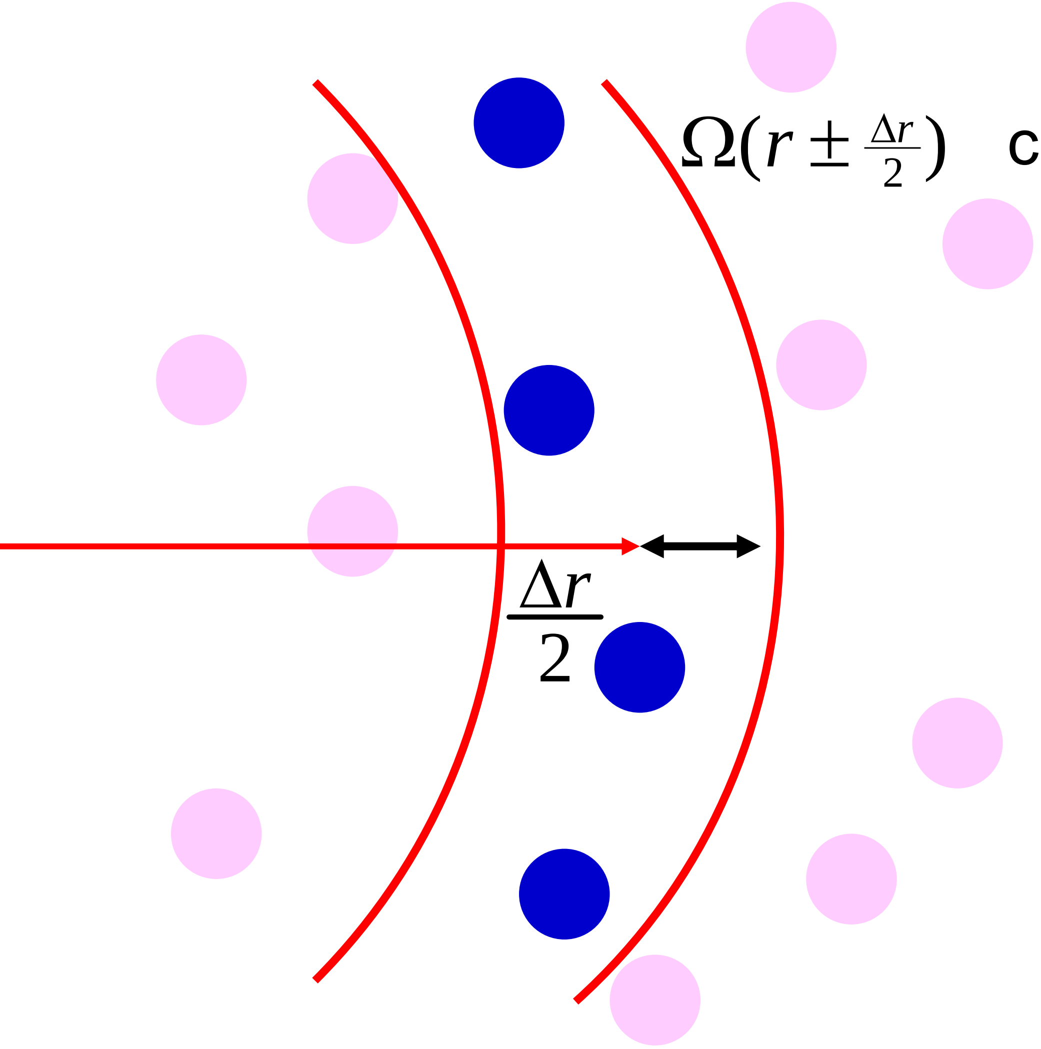
Discrete:

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

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

Radial distribution function



$\Omega(r \pm \frac{\Delta r}{2})$ considered volume

$$g(r) = \frac{N(r \pm \frac{\Delta r}{2})}{\Omega(r \pm \frac{\Delta r}{2})\rho}$$

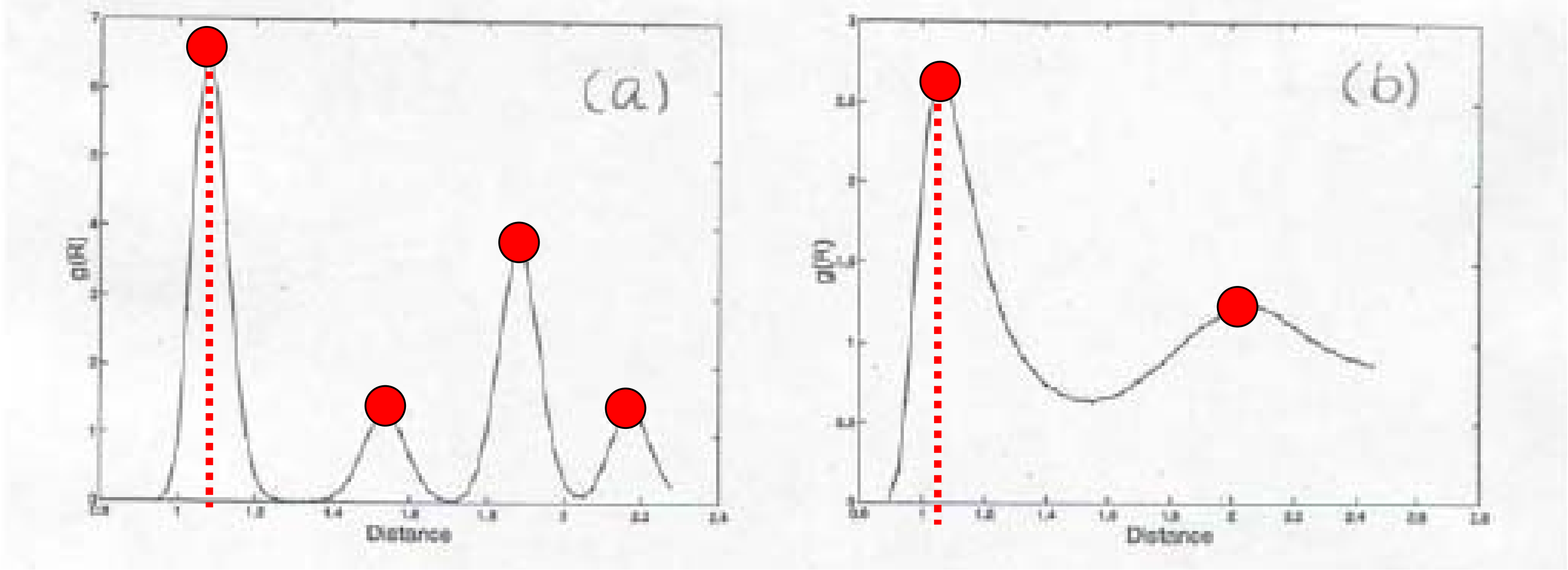
Density

$$\rho = N / V$$

Note: RDF can be measured experimentally using x-ray or neutron-scattering techniques

Radial distribution function:

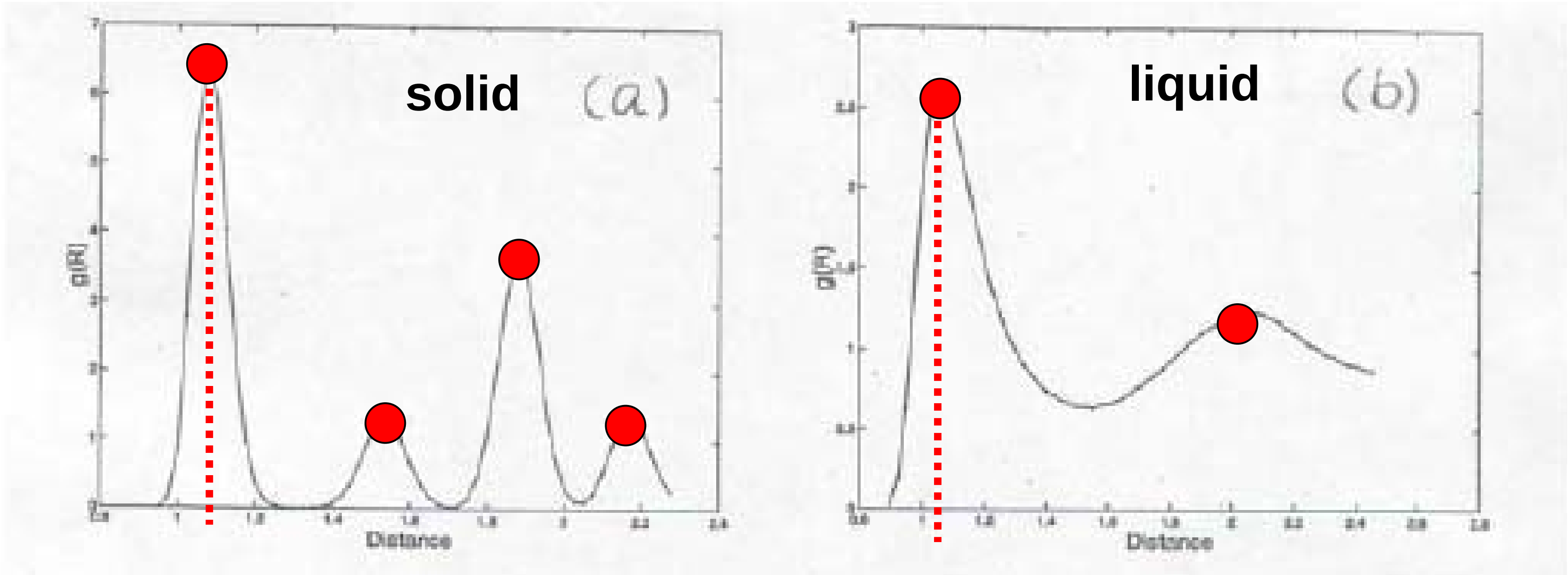
Which one is solid / liquid?



Interpretation: A peak indicates a particularly favored separation distance for the neighbors to a given particle Thus, RDF reveals details about the atomic structure of the system being simulated

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

Radial distribution function



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

Radial distribution function: JAVA applet

Java applet:

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

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Screenshot of the radial distribution function Java applet.

Radial distribution function: Solid versus liquid versus gas

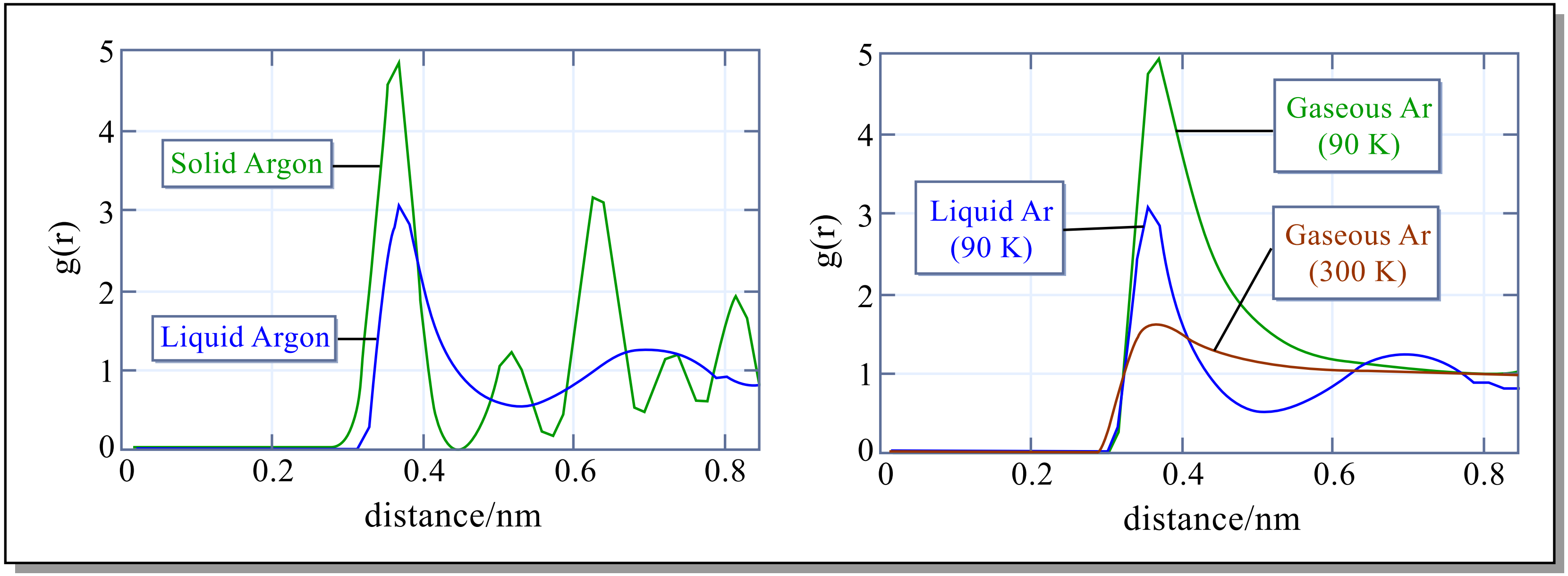

Image by MIT OpenCourseWare.

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

Notes: Radial distribution function (RDF)

- Pair correlation function (consider only pairs of atoms)
- Provides structural information
- Can provide information about dynamical change of structure, but not about transport properties (how fast atoms move)

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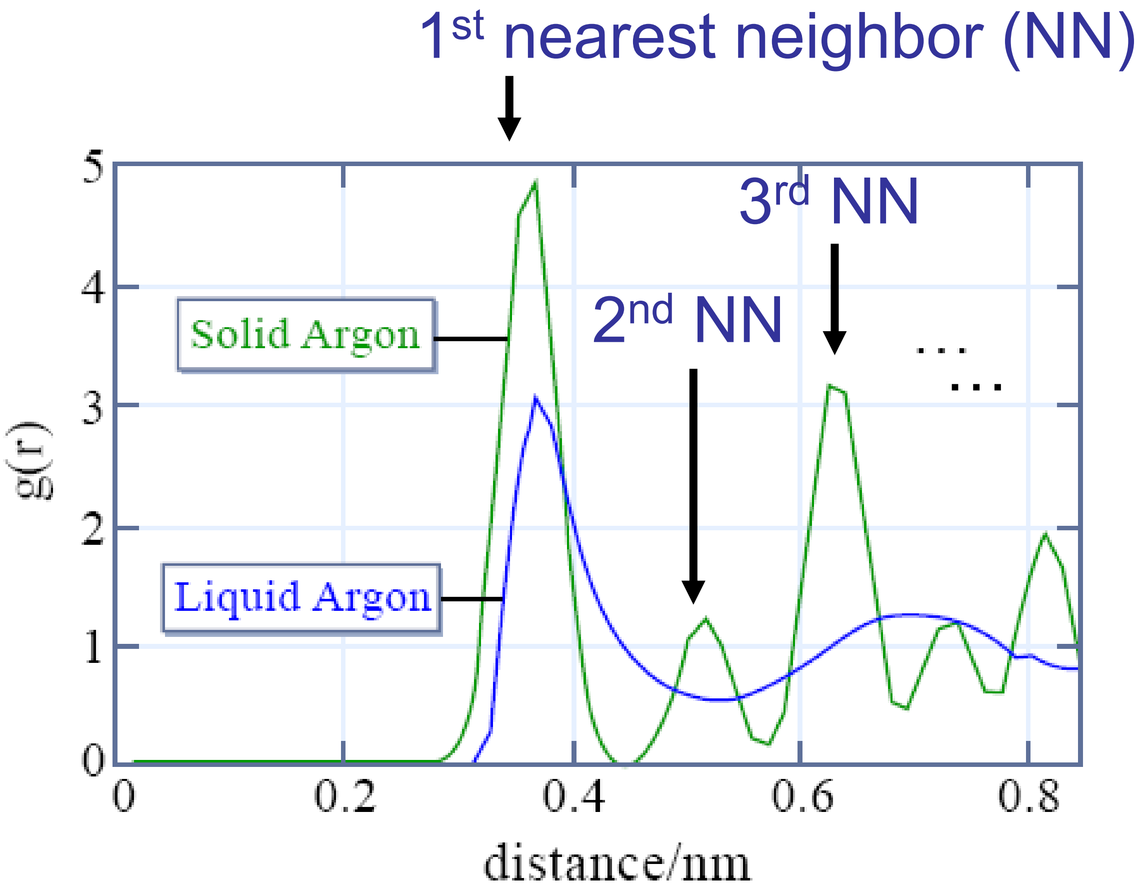
- Pair correlation function (consider only pairs of atoms)
- Provides structural information
- Can provide information about dynamical change of structure, but not about transport properties (how fast atoms move)

Additional comments:

- Describes how - on average - atoms in a system are radially packed around each other
- Particularly effective way of describing the structure of disordered molecular systems (liquids)
- In liquids there is continual movement of the atoms and a single snapshot of the system shows only the instantaneous disorder it is extremely useful to be able to deal with the average structure

Example RDFs for several materials

RDF and crystal structure



1^{st} nearest neighbor (NN)

2^{nd} NN

3^{rd} NN

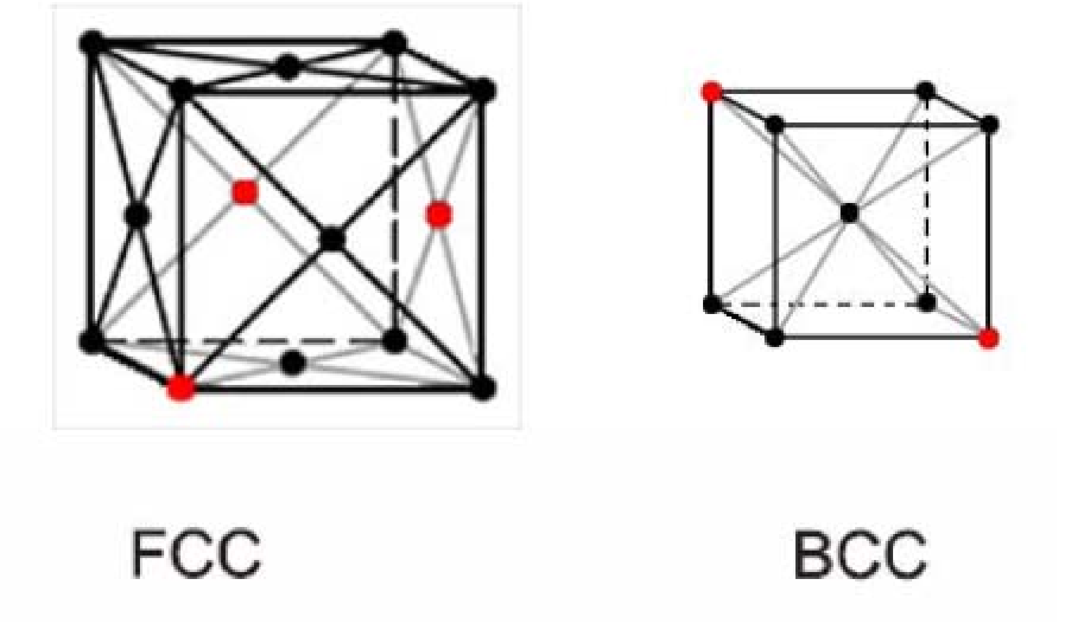
…

…

Image by MIT OpenCourseWare.

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

Face centered cubic (FCC), body centered cubic (BCC)



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Aluminum, NN: 2.863 Å (a_0=4.04 Å)

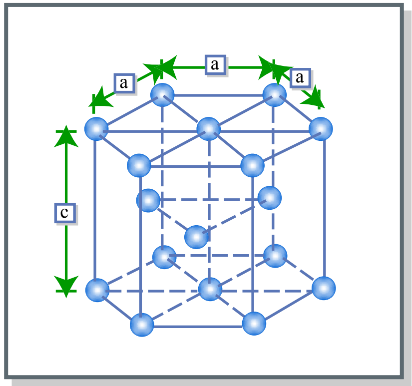
Copper, NN: 2.556 Å (a_0=3.615 Å))

Chromium, NN: 2.498 Å (a_0=2.91 Å)

Iron, NN: 2.482 Å (a_0=2.86 Å)

See also: http://www.webelements.com/

Hexagonal closed packed (HCP)



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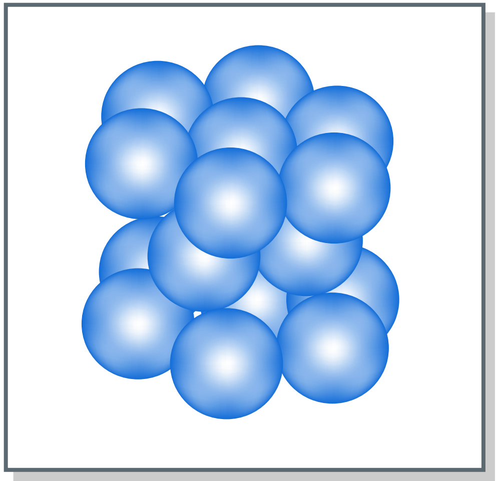

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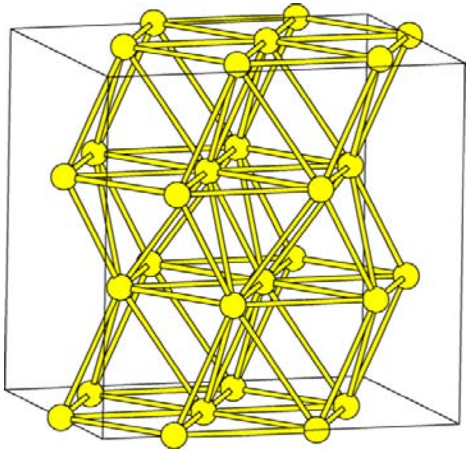

Image courtesy of the U.S. Navy.

Cobalt
a: 250.71 pm
b: 250.71 pm
c: 406.95 pm
α: 90.000°
β: 90.000°
γ: 120.000°
NN: 2.506 Å

Zinc
a: 266.49 pm
b: 266.49 pm
c: 494.68 pm
α: 90.000°
β: 90.000°
γ: 120.000°
NN: 2.665 Å

Graphene/carbon nanotubes

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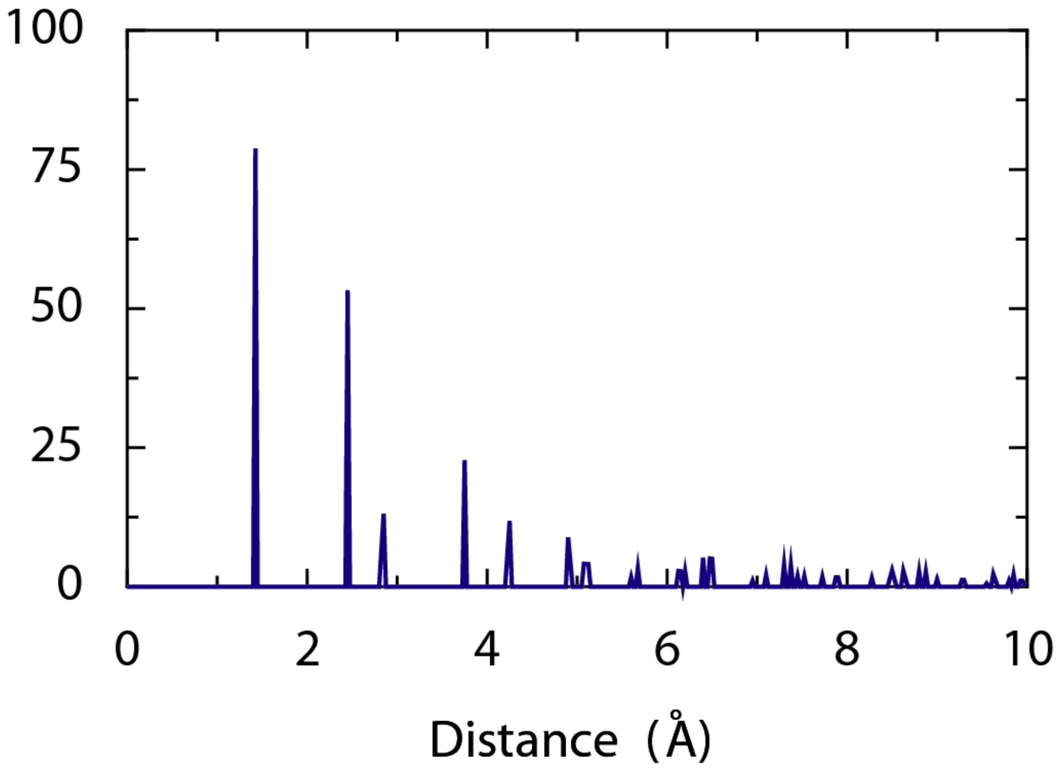
Please see: http://weblogs3.nrc.nl/techno/wp-content/uploads/080424_Grafeen/Graphene_xyz.jpg
http://depts.washington.edu/polylab/images/cn1.jpg

RDF



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

Macroscale view of water

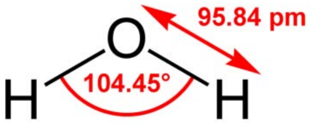
Iceberg

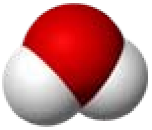
Image courtesy of dnkemontoh.

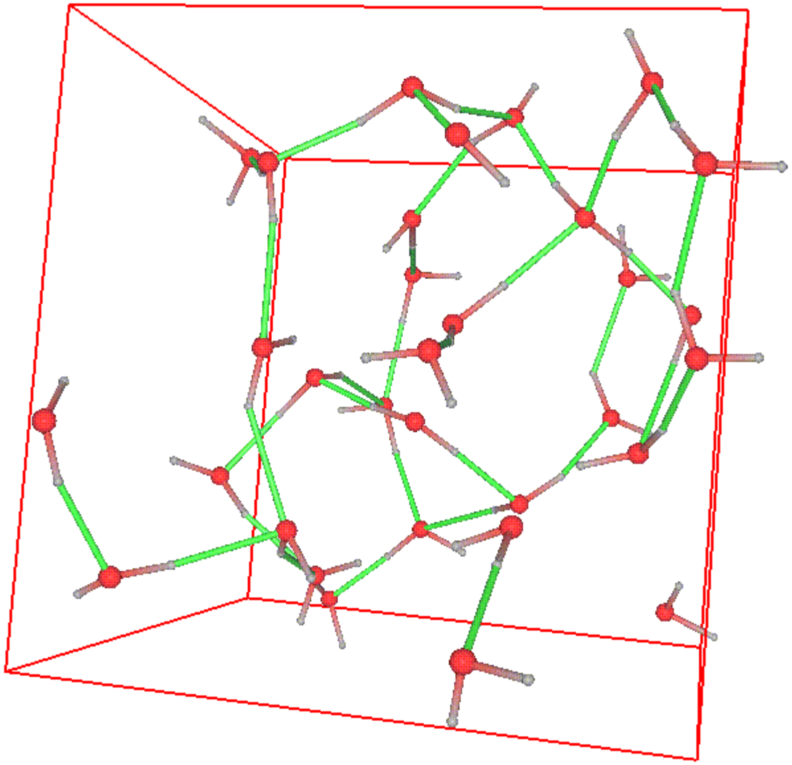
Glacier

Image courtesy of blmiers2.

RDF of water (H_2O)







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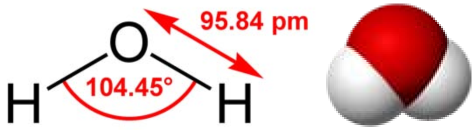
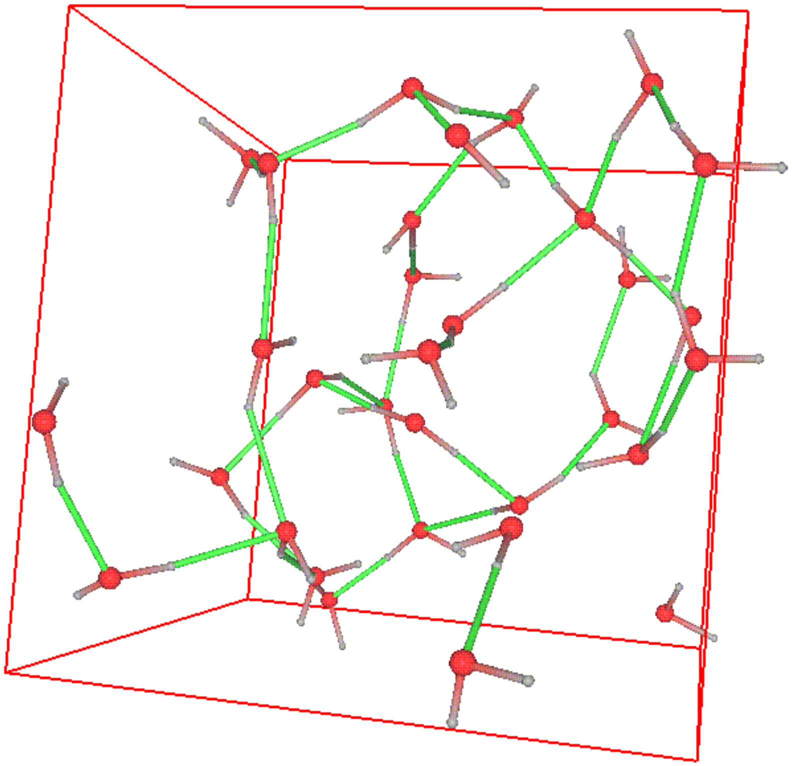
http://www.nyu.edu/classes/tuckerman/stat.mech/lectures/lecture_8/node1.html

RDF of water (H_2O)





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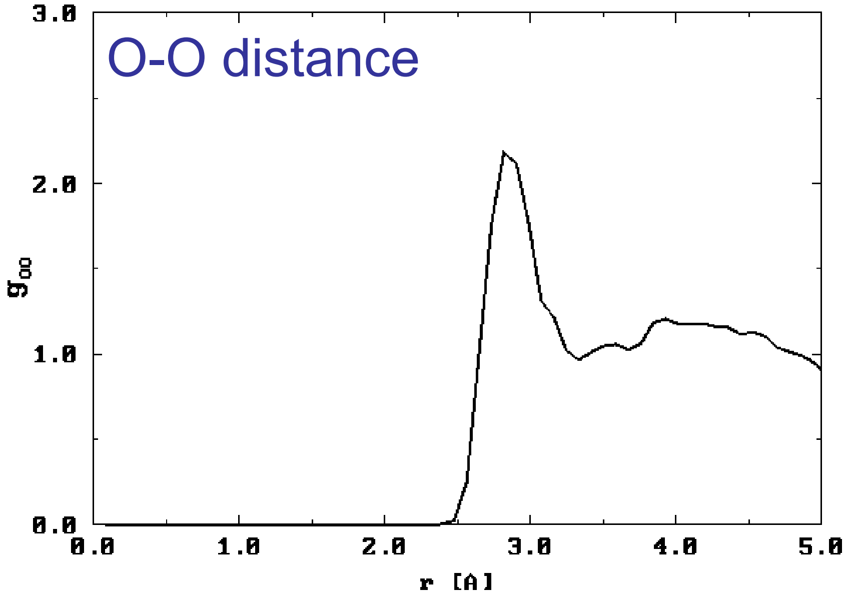
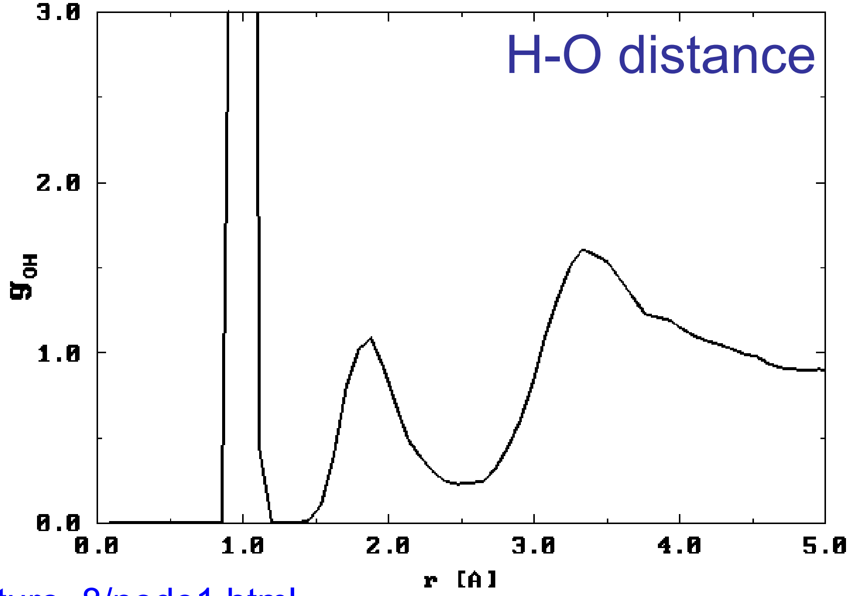
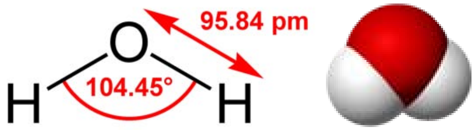
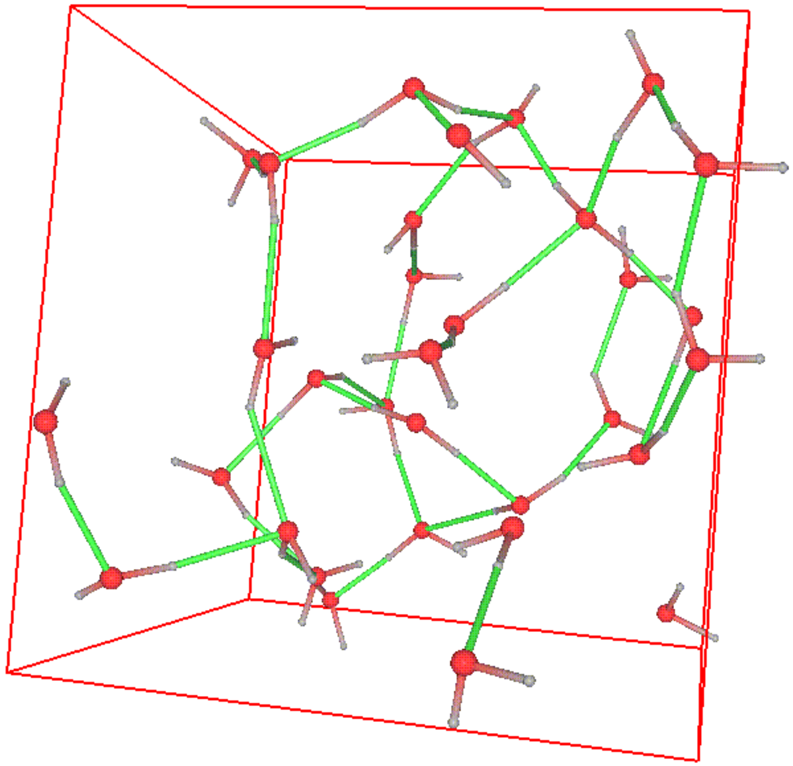




http://www.nyu.edu/classes/tuckerman/stat.mech/lectures/lecture_8/node1.html

RDF of water (H_2O)





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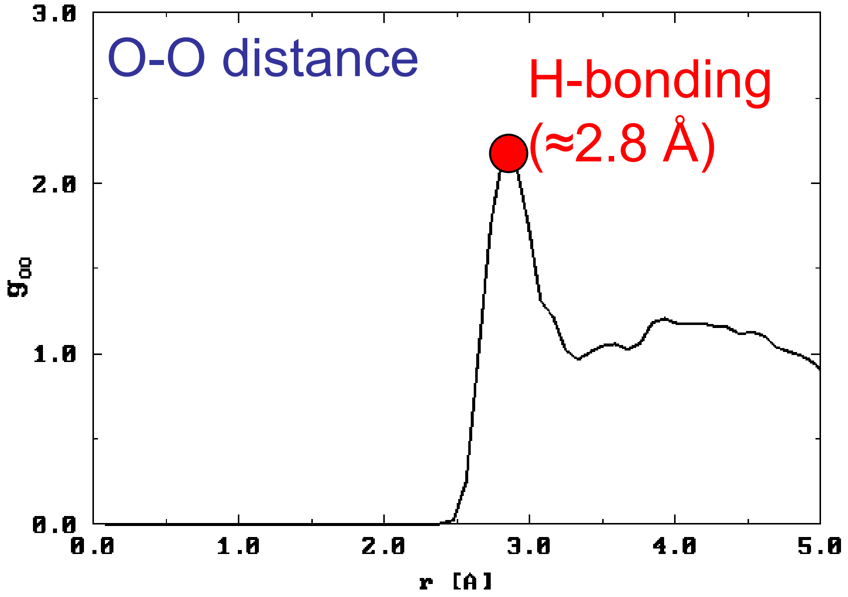
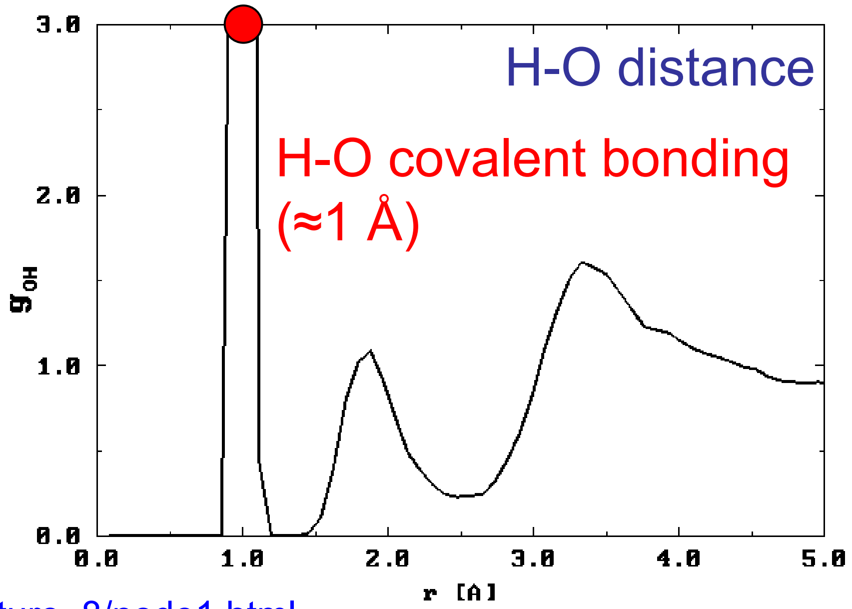


O-O distance

H-bonding (≈2.8 Å)



H-O distance

H-O covalent bonding (≈1 Å)

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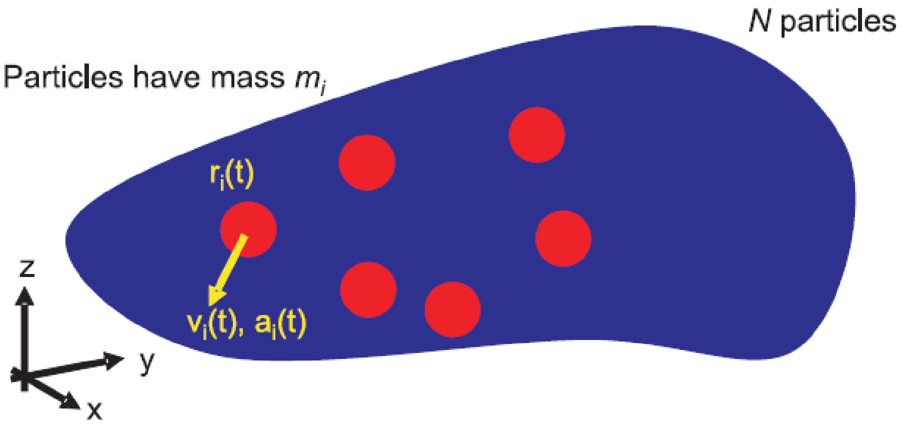
2. Introduction: How to model chemical interactions

Molecular dynamics: A “bold” idea



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

$$a_i = f_i / m$$

Forces between atoms… how to obtain?

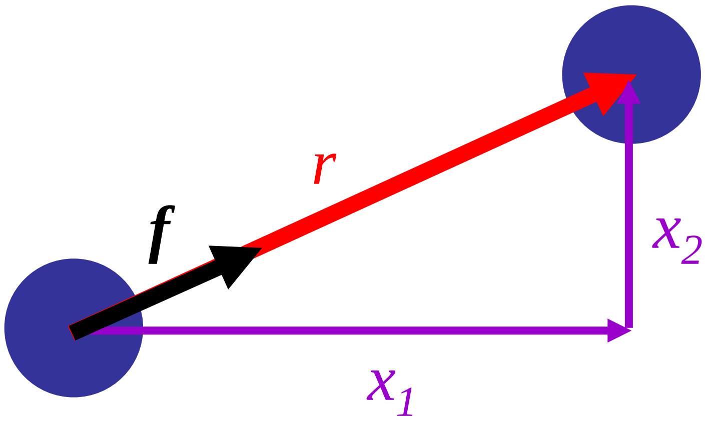
How are forces calculated?

Force magnitude: Derivative of potential energy with respect to atomic distance

$$f = -\frac{\mathrm{d}U(r)}{\mathrm{d}r}$$

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

$$\boxed{f_i = f\,\frac{x_i}{r}}$$



Often: Assume pair-wise interaction between atoms

Atomic interactions – quantum perspective

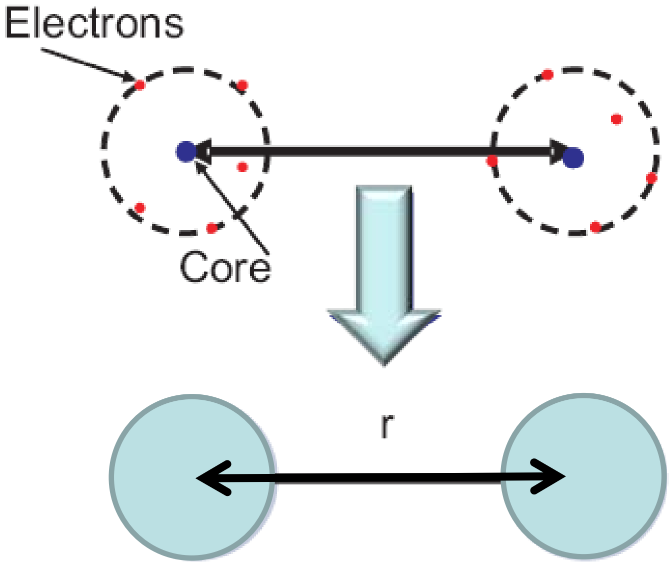
How electrons from different atoms interact defines nature of chemical bond

Density distribution of electrons around a H-H molecule

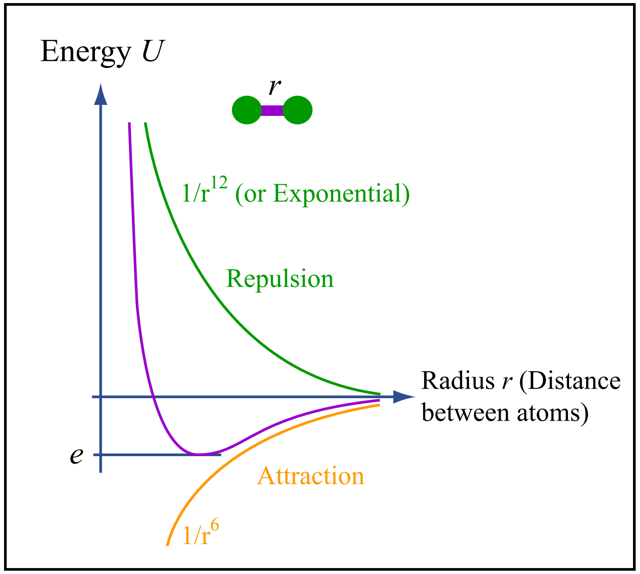
Image removed due to copyright restrictions. Please see the animation of hydrogen bonding orbitals at http://winter.group.shef.ac.uk/orbitron/MOs/H2/1s1s-sigma/index.html

Much more about it in part II

Concept: Interatomic potential



"point particle" representation



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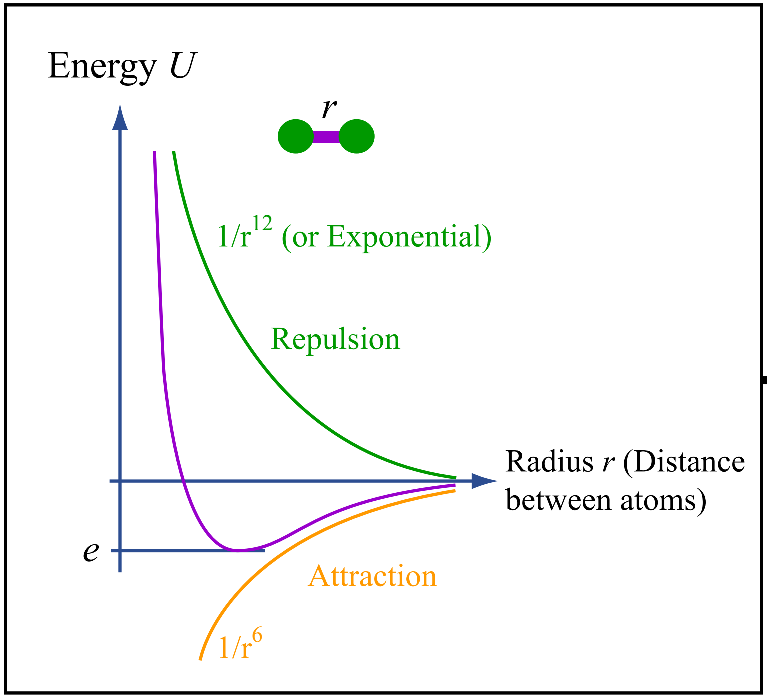
Attraction: Formation of chemical bond by sharing of electrons
Repulsion: Pauli exclusion (too many electrons in small volume)

Interatomic bond - model



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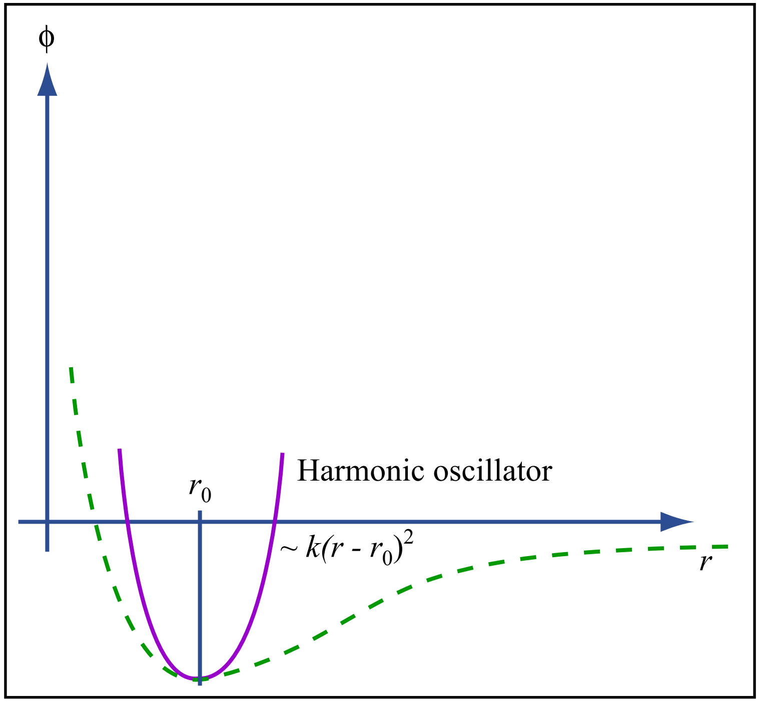

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Attraction: Formation of chemical bond by sharing of electrons
Repulsion: Pauli exclusion (too many electrons in small volume)

Atomic interactions – different types of chemical bonds

- **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)

Difference of material properties originates from different atomic interactions

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

What is the difference between these models?

Shape of potential (e.g. behavior at short or long distances, around equilibrium)

Number of parameters (to fit)

Ability to describe bond breaking

Lennard-Jones potential

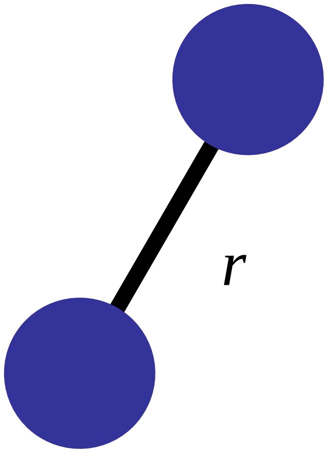
Sir J. E. Lennard-Jones (Cambridge UK)

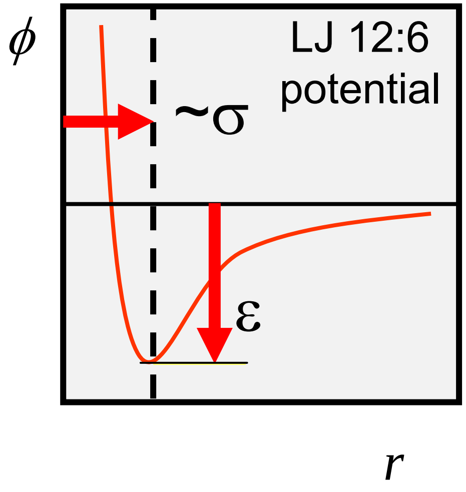
Parameters ε, σ

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

Lennard-Jones 12:6

Lennard-Jones potential: schematic & parameter meaning





ε: well depth (energy stored per bond)

σ: proportional to point where force vanishes (equilibrium distance between atoms)

Lennard-Jones 12:6

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

2.1 How to identify parameters in a Lennard-Jones potential

(=force field training, force field fitting, parameter coupling, etc.)

Parameter identification for potentials

- Typically done based on more accurate (e.g. **quantum mechanical**) results (or experimental measurements, if available)

- Properties used include:

  Lattice constant, cohesive bond energy, elastic modulus (bulk, shear, …), equations of state, phonon frequencies (bond vibrations), forces, stability/energy of different crystal structures, surface energy, RDF, etc.

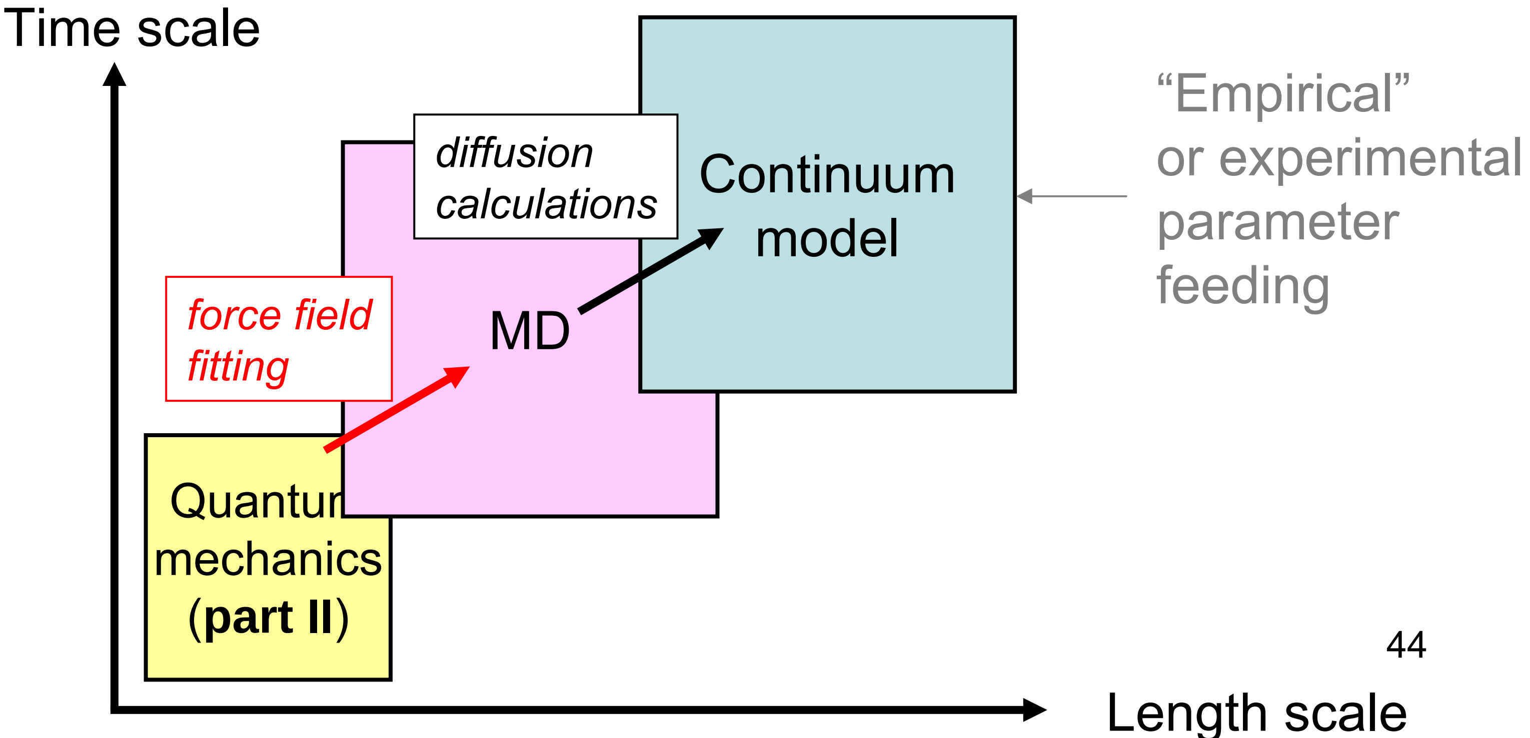
  Potential should closely reproduce these reference values

- **Challenges**: mixed systems, different types of bonds, reactions

Multi-scale paradigm

- Show earlier: molecular dynamics provides a powerful approach to relate the diffusion constant that appears in continuum models to atomistic trajectories

- Force field fitting to identify parameters for potentials (based on quantum mechanical results) is yet another “step” in this multi-scale paradigm



Derivative of LJ potential ~ force

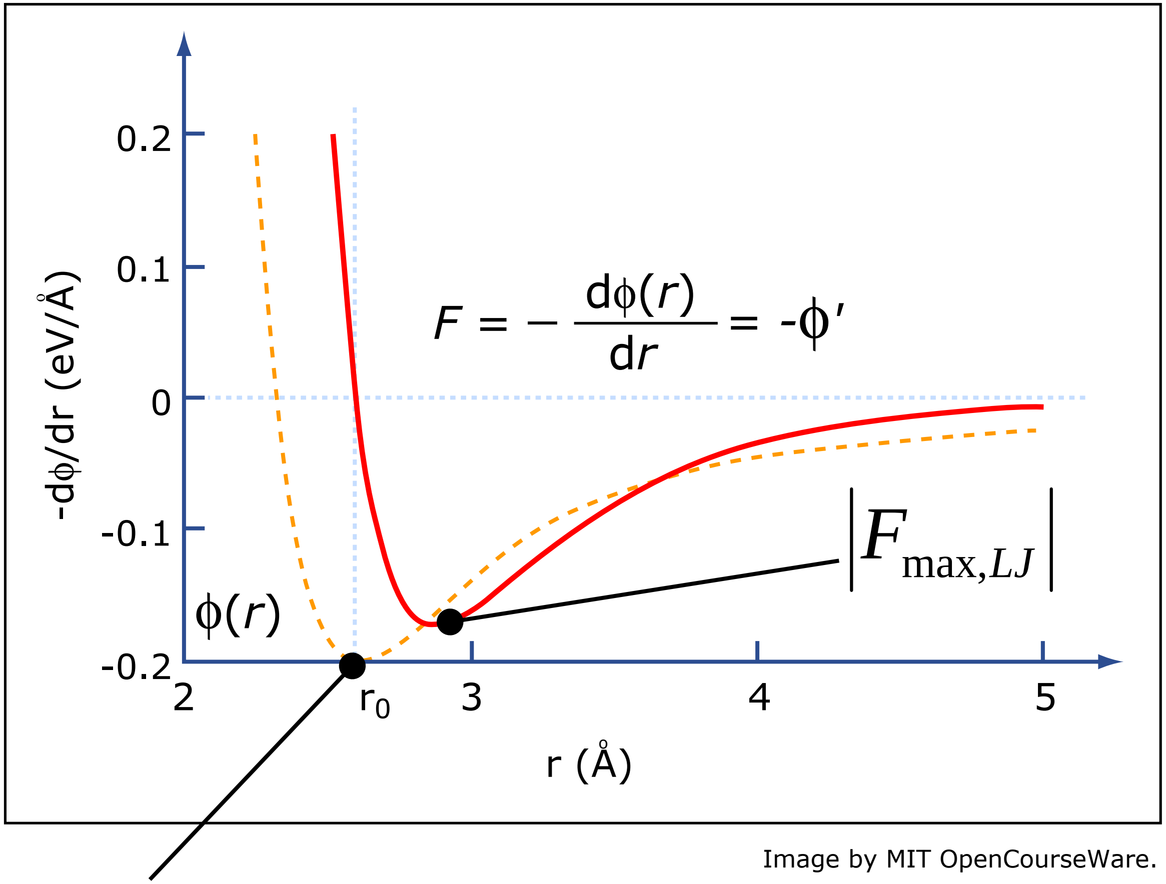


Image by MIT OpenCourseWare.

EQ r_0

relates to equilibrium spacing crystal

Properties of LJ potential as function of parameters ε, σ

Equilibrium distance between atoms r_0 and maximum force

$$\sigma \sqrt[6]{2} = r_0 \qquad F_{\max,LJ} = \frac{2.394\varepsilon}{\sigma}$$

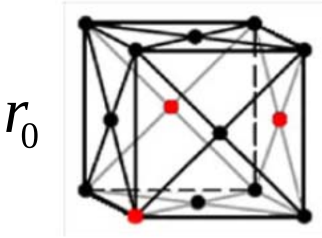
first derivative zero (force)

second derivative zero (=loss of convexity, spring constant=0)

$r_0 =$ distance of nearest neighbors in a lattice

Copper, NN: 2.556 Å (a_0=3.615 Å))

FCC



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Determination of parameters for atomistic interactions

- **Example** (based on elastic properties) of FCC lattice

- **Approach:** Express bulk modulus as function of potential parameters
    - **Second derivative of potential** is related to **spring constant** (=stiffness) of chemical bonds

Young's modulus

$$\nu = 1/4$$

Shear modulus

$$K = E/(3(1-2\nu)) \qquad E = 8/3\mu \qquad \mu = r_0^2 \boxed{k} / 2 / V \qquad V = a_0^3 / 4$$

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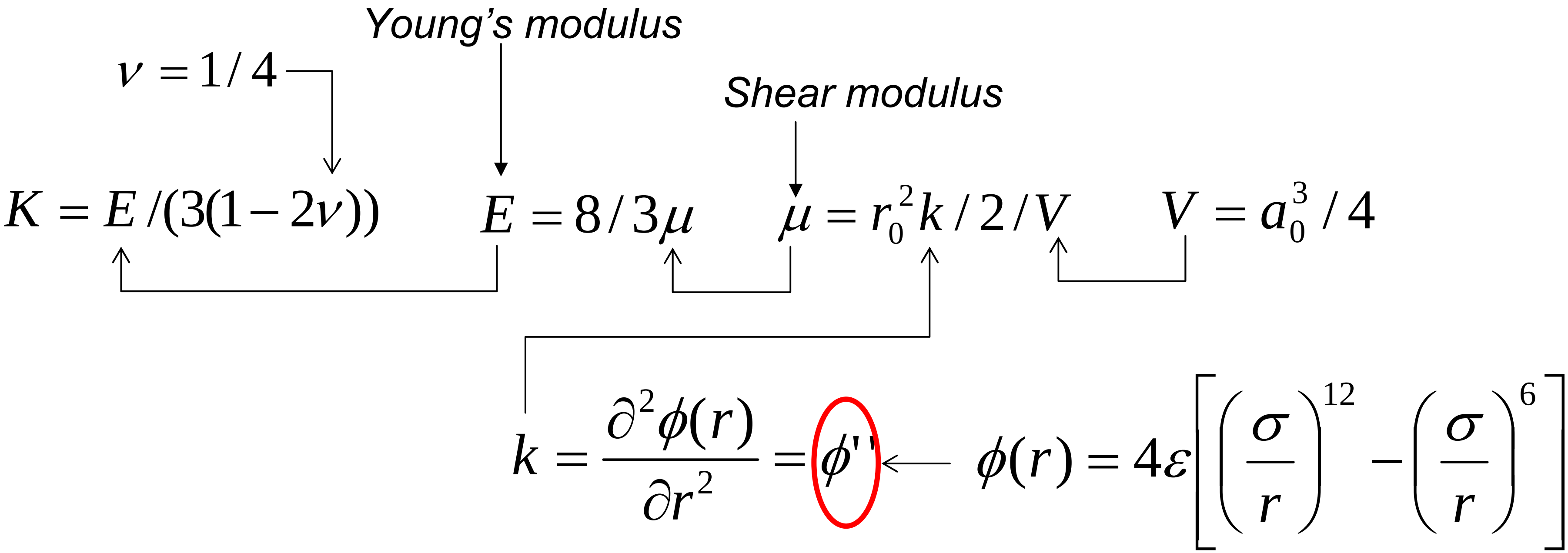

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Shear modulus

$$K = E/(3(1-2\nu)) \qquad E = 8/3\mu \qquad \mu = r_0^2 k/2/V \qquad V = a_0^3/4$$

$$k = \frac{\partial^2 \phi(r)}{\partial r^2} = \boxed{\phi''} \longleftarrow \phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Determination of parameters for atomistic interactions

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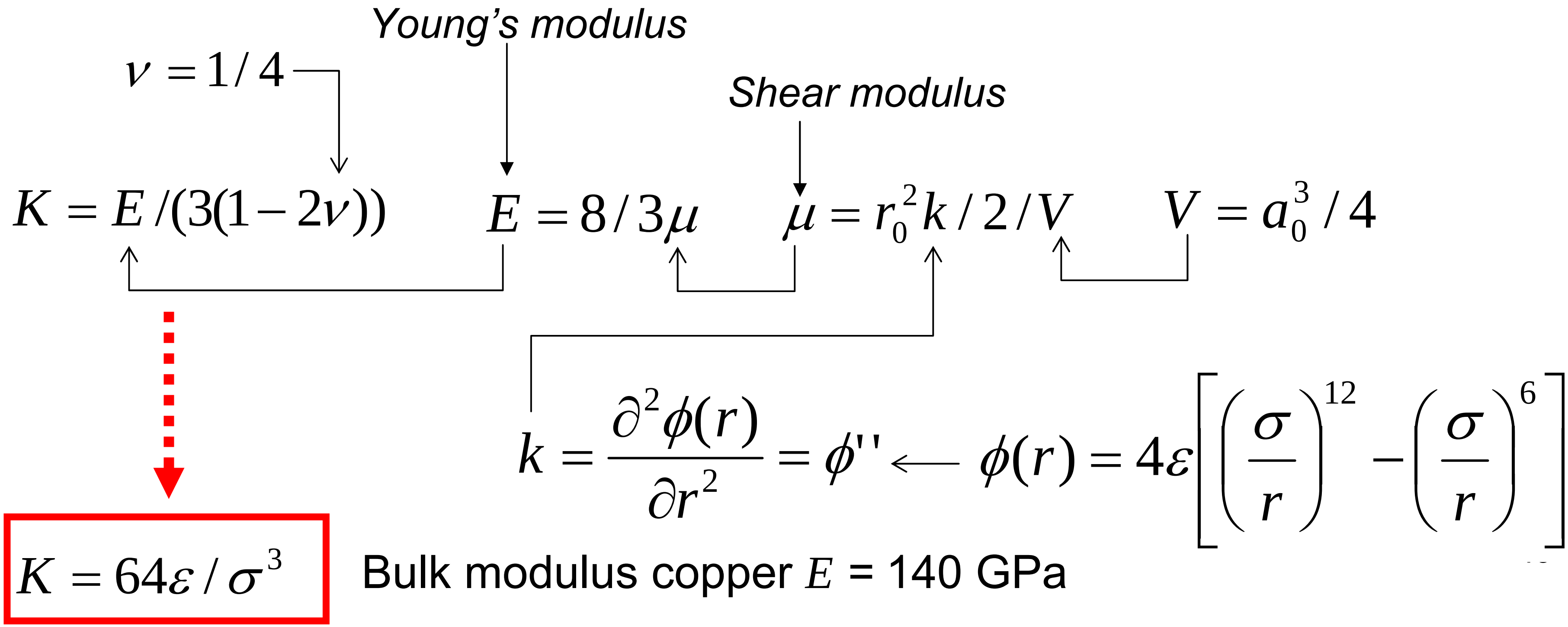

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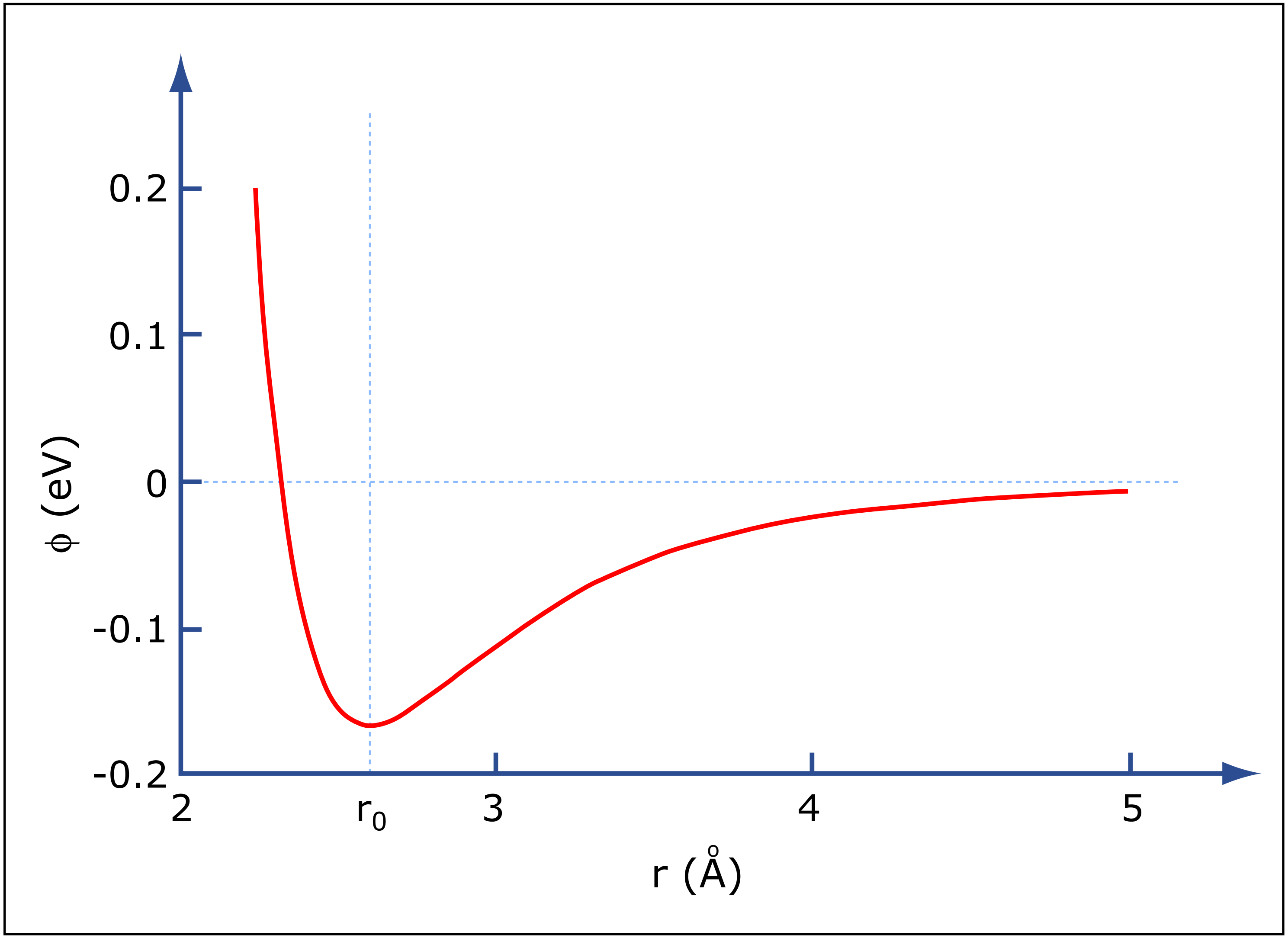
$$\boxed{K = 64\varepsilon/\sigma^3}$$

Bulk modulus copper E = 140 GPa

Lennard-Jones potential – example for copper



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LJ potential – parameters for copper

3. Monte Carlo approaches

How to solve…

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

Probability density distribution

Virtually impossible to carry out analytically

Must know all possible configurations

Therefore: Require numerical simulation

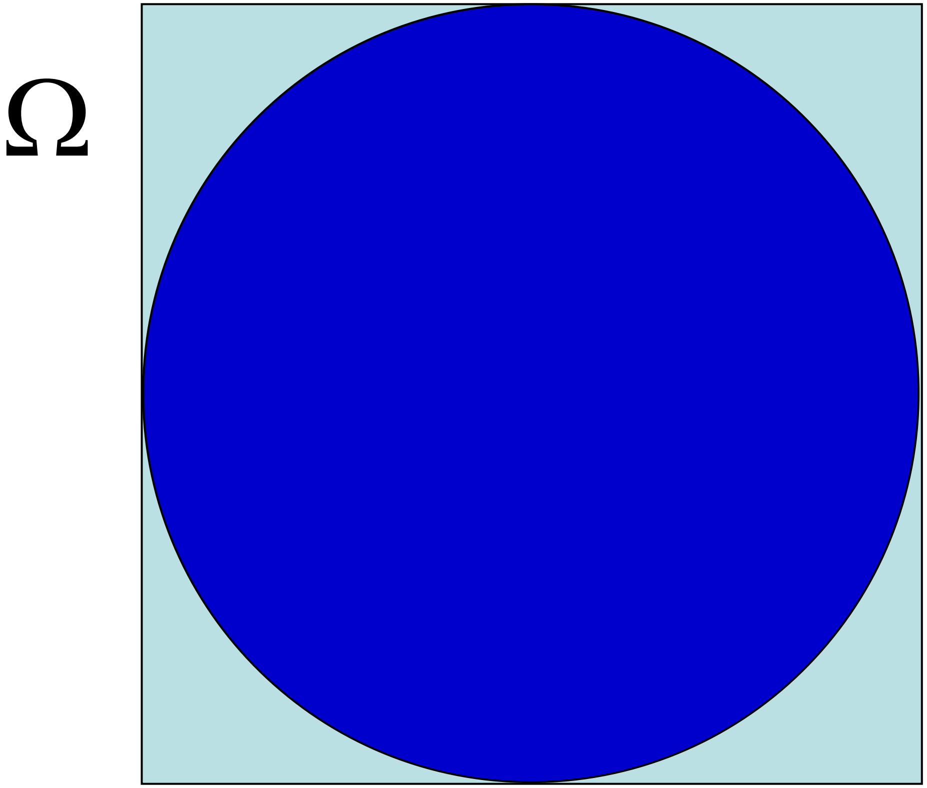
Molecular dynamics OR Monte Carlo

3.1 Application to integration

“Random sampling”

Monte Carlo scheme

Method to carry out integration over "domain"



Want:

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

E.g.: Area of circle (value of π)

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

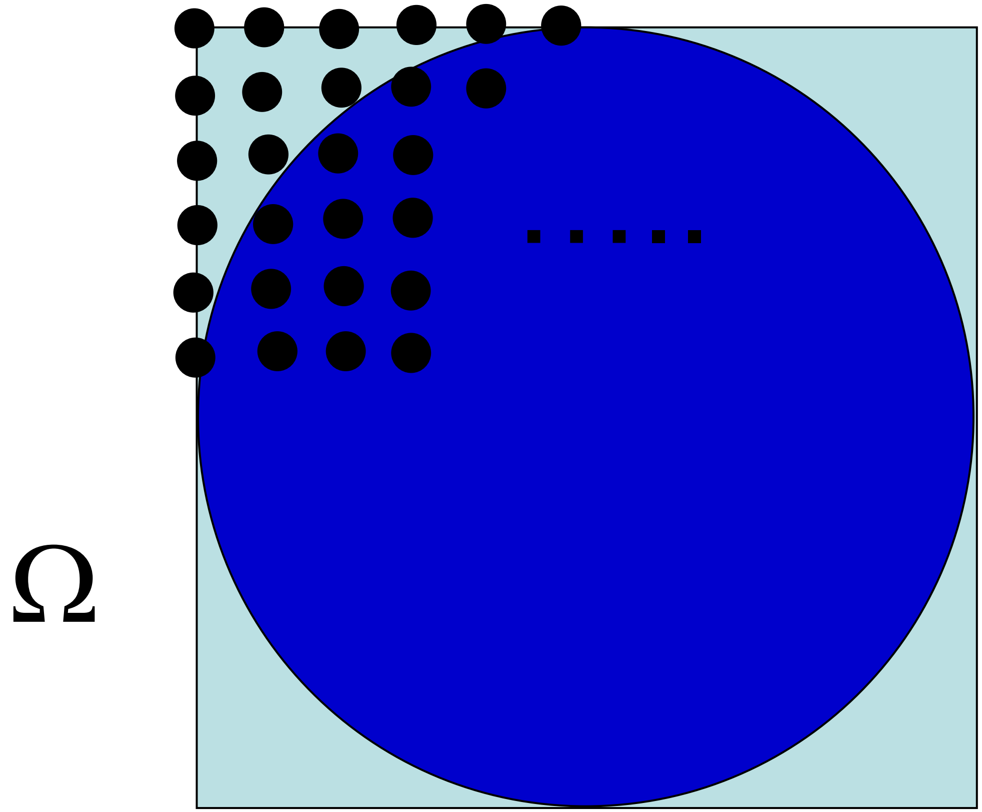
$$\pi = 4A_C$$

$$d = 1$$

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

Conventional way…

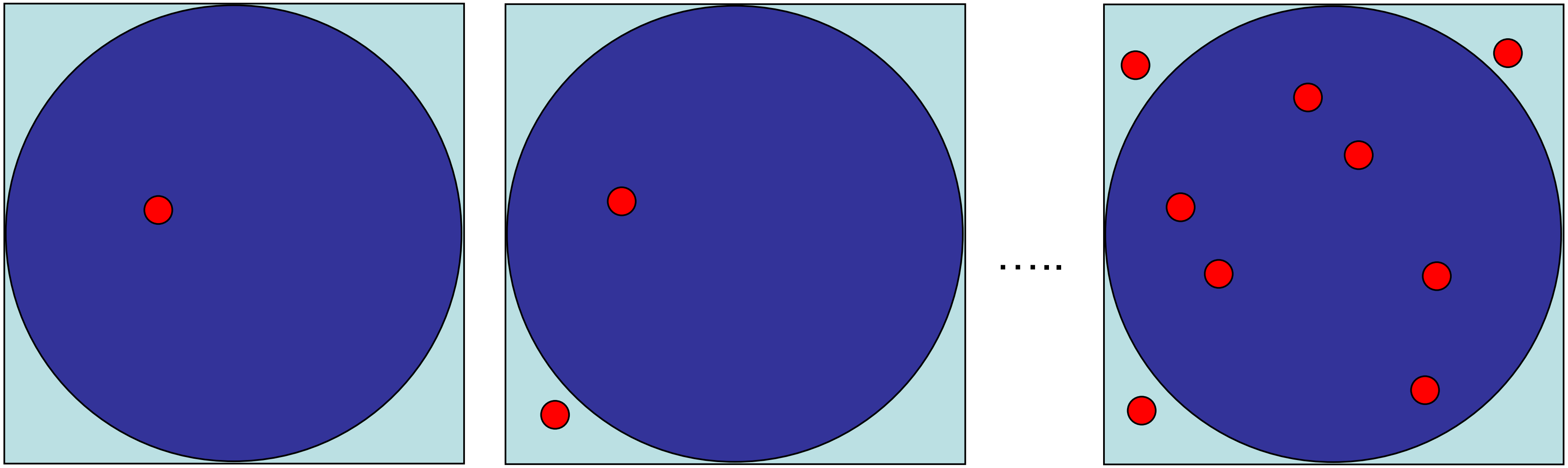
- Evaluate integrand at predetermined values in the domain (e.g. quadratic grid)
- Evaluate integral at discrete points and sum up



What about playing darts..

Public domain image.

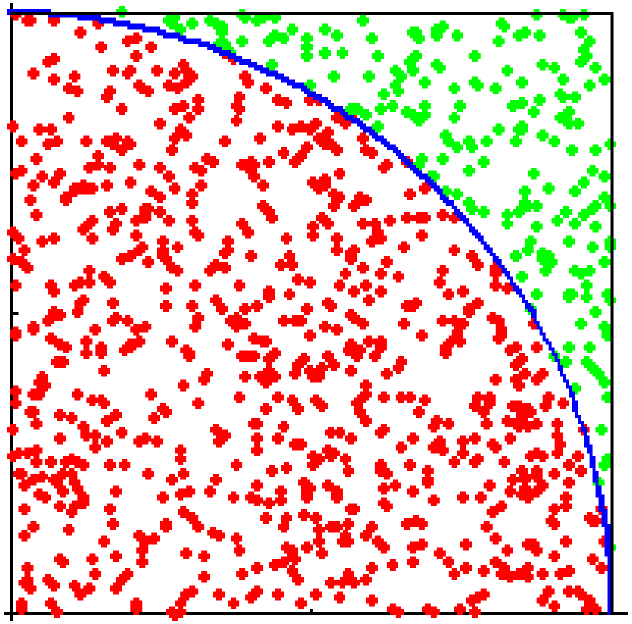
Alternative way: integration through MC



Playing darts: Randomly select point in domain
Evaluate integral a these points
Sum up results to solve integral

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.

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

$$\updownarrow$$

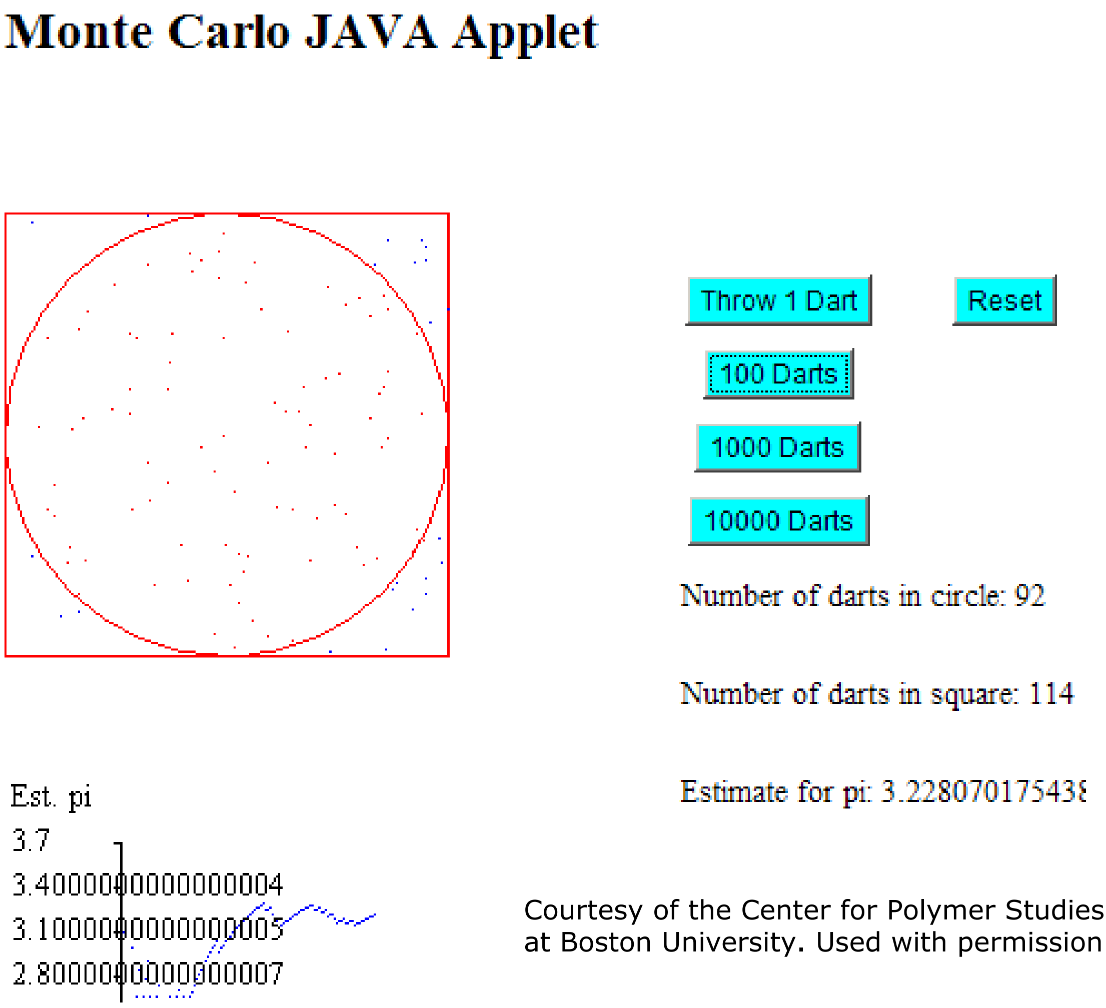
$$\boxed{A_C = \frac{1}{N_A}\sum_i f(\vec{x}_i)}$$

N_A: Attempts made

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

Java applet: how to calculate pi

- http://polymer.bu.edu/java/java/montepi/montepiapplet.html



Monte Carlo JAVA Applet

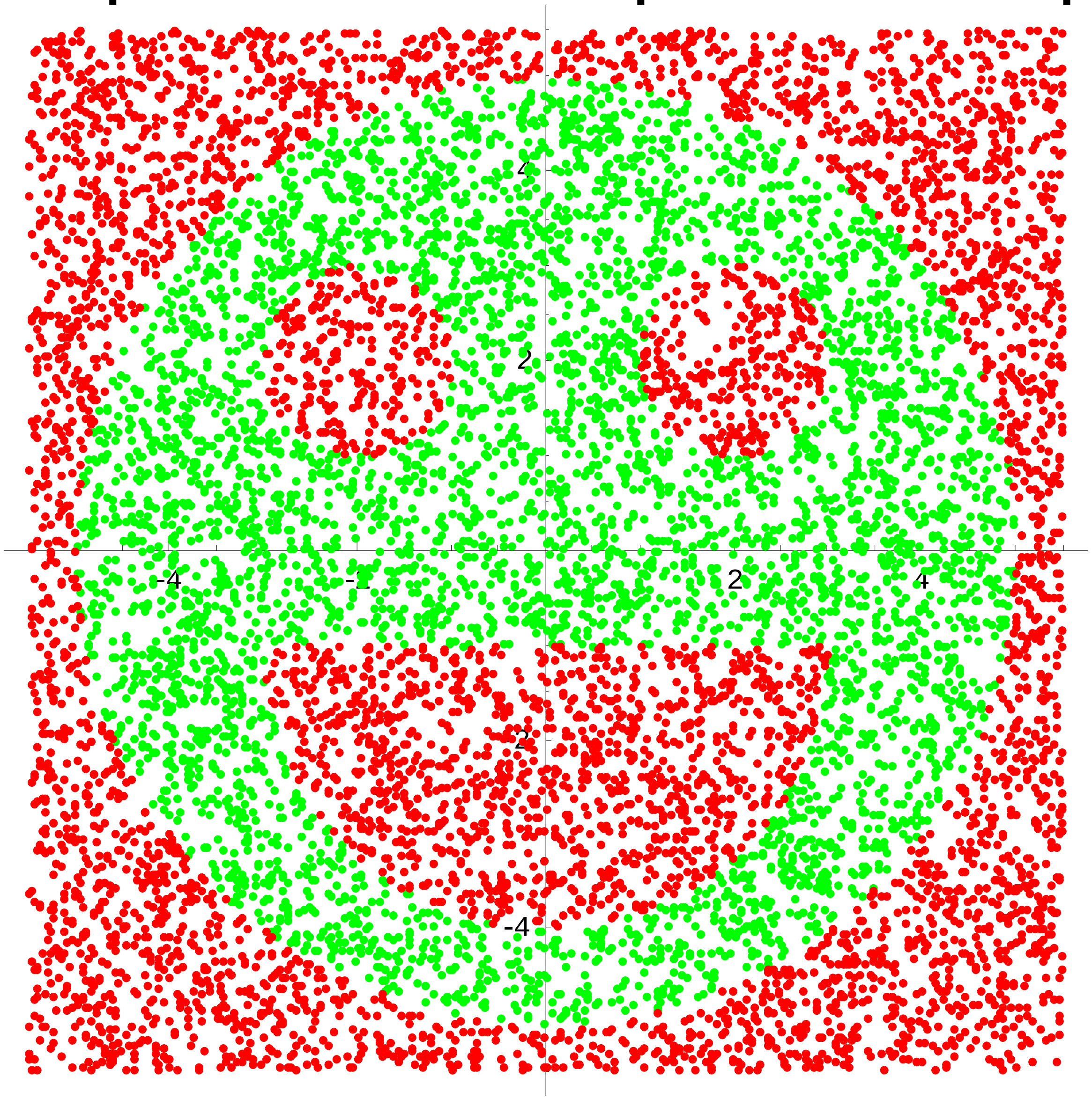
Number of darts in circle: 92

Number of darts in square: 114

Estimate for pi: 3.22807017543

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

Example: more complicated shapes



How to apply to ensemble average?

- Similar method can be used to apply to integrate the ensemble average
- Need more complex iteration scheme (replace "*random sampling*" by "*importance sampling*")

- E.g. Metropolis-Hastings algorithm

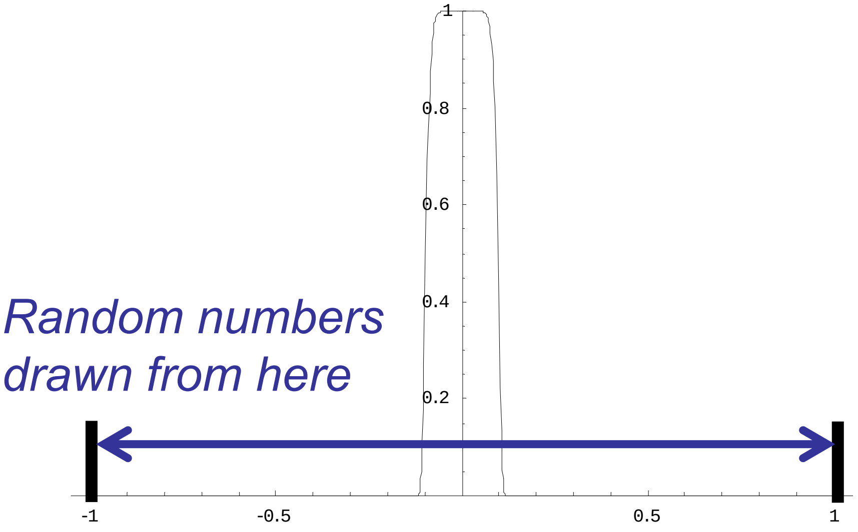
Want:

$$< A >= \int_p \int_r A(p,r)\rho(p,r)drdp \quad \longleftrightarrow \quad \boxed{< A > \frac{1}{N_A}\sum_i A_i}$$

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)

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

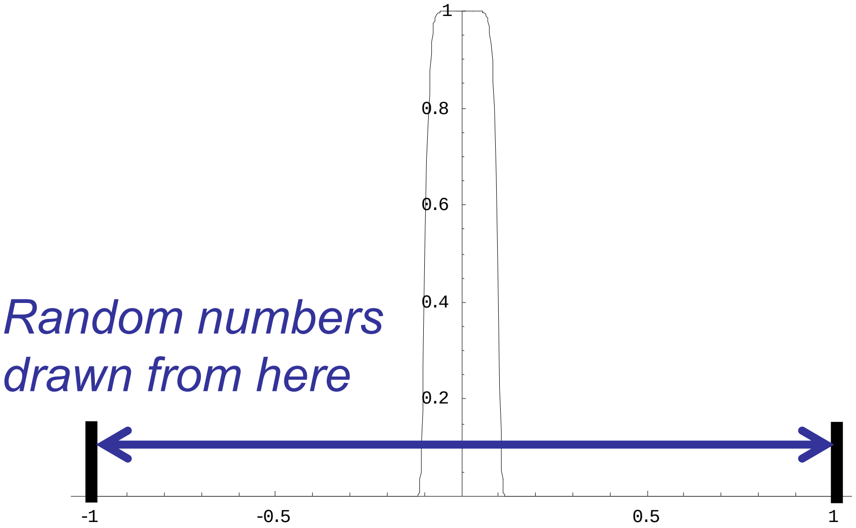


Random numbers drawn from here

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*"

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



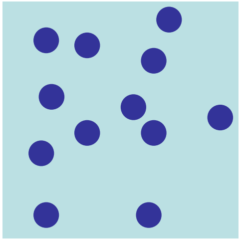
Random numbers drawn from here

3.2 Metropolis-Hastings algorithm

“Importance sampling”

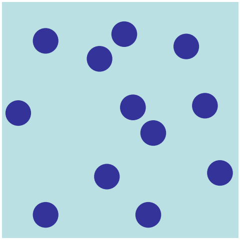
Averaging over the ensemble

Property A_1



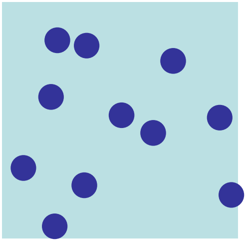
C_1

Property A_2



C_2

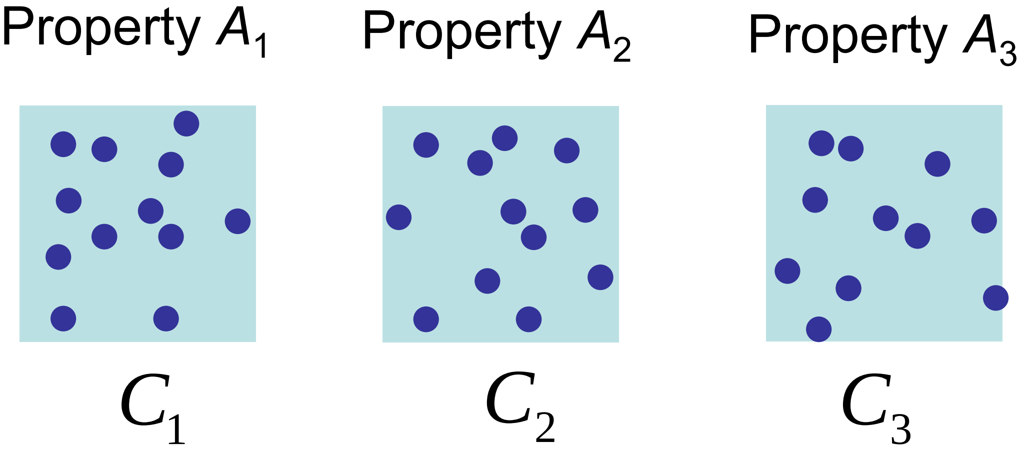
Property A_3



C_3

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

Averaging over the ensemble



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

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)

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

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

Probability to find system in state C_1

How to apply to ensemble average?

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

"discrete"

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

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

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

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*")

Importance sampling

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

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

$$\Big\downarrow$$

$$< A >= \frac{1}{N_A} \sum_{i=1}^{N_A} A(r_A, p_A)$$

Corresponding to…

$$< A >= \frac{1}{3}\left(\rho_1 A_1 + \rho_2 A_2 + \rho_3 A_3\right) \rightarrow < A >= \frac{1}{3}\left(A_1 + A_2 + A_3\right)$$

Importance sampling

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

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

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

Importance sampling: Metropolis algorithm

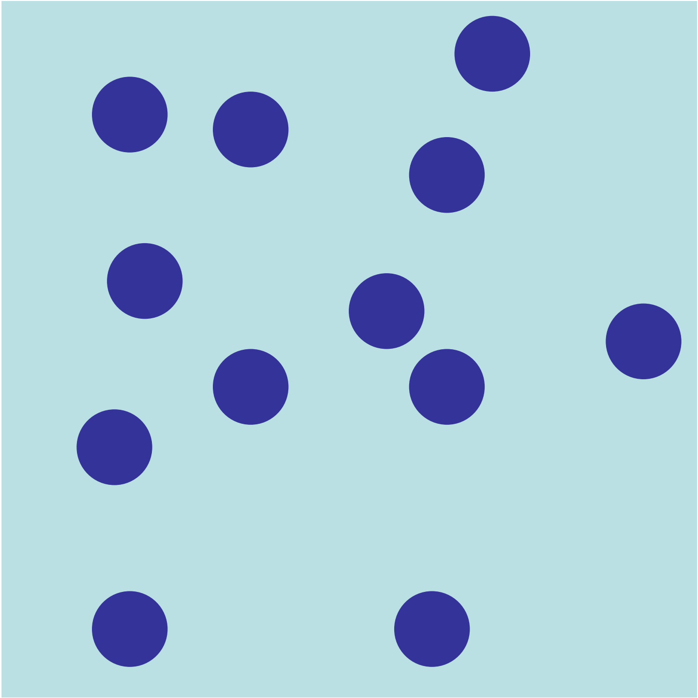
- Leads to an appropriate “chain” of states, visiting each state with **correct probability**

- 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)

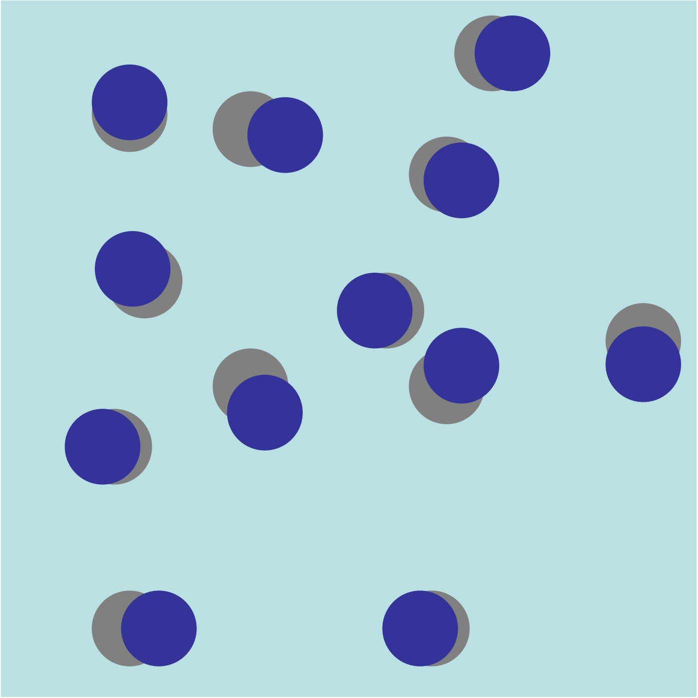
Original reference: *J. Chem. Phys.* **21**,1087, 1953

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** $\boxed{a = 1}$

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 $a = 1$
         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
```

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

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

a=variable either 0 or 1 (used to detect acceptance

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 $a = 1$
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                  else
                          $a = 0$
                  endif
          endif

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

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

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
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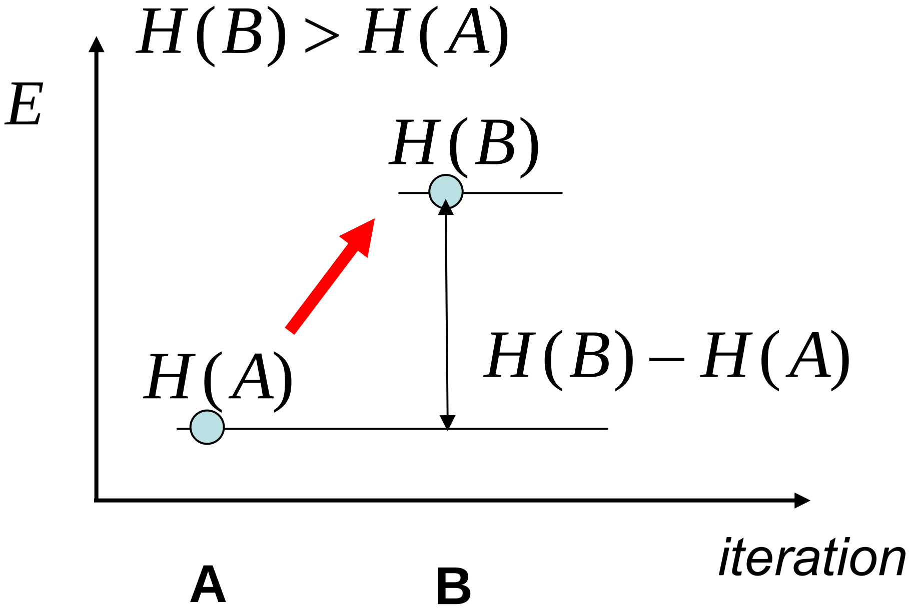
a=variable either 0 or 1
(used to detect acceptance
of state B when a=1)

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

Arrhenius law - explanation



$H(B) > H(A)$

E

$H(B)$

$H(B) - H(A)$

$H(A)$

A

B

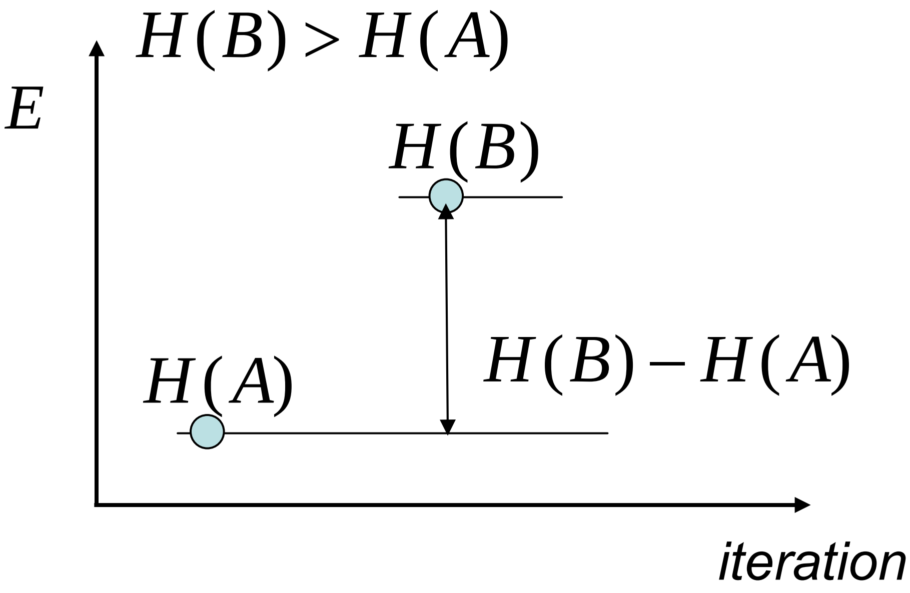
iteration

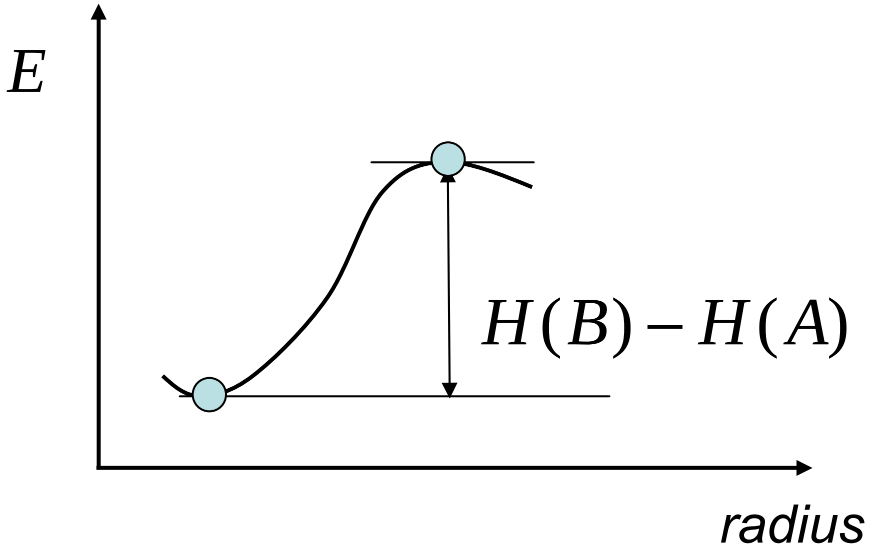
Consider two states, A and B

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

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

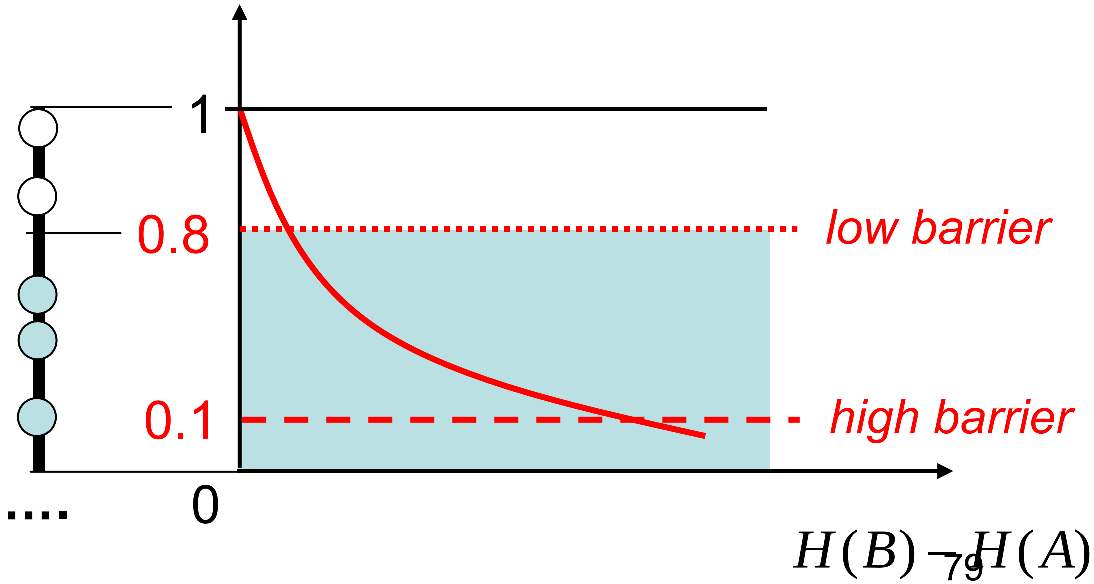
Random number $0 < p < 1$

(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 $p < \exp\left[-\frac{H(B)-H(A)}{k_B T}\right]$   $a = 1$
                 else
                     $a = 0$
                 endif
             endif
    Step 3:  if $a = 1$ then accept state $B$
             endif
```

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

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

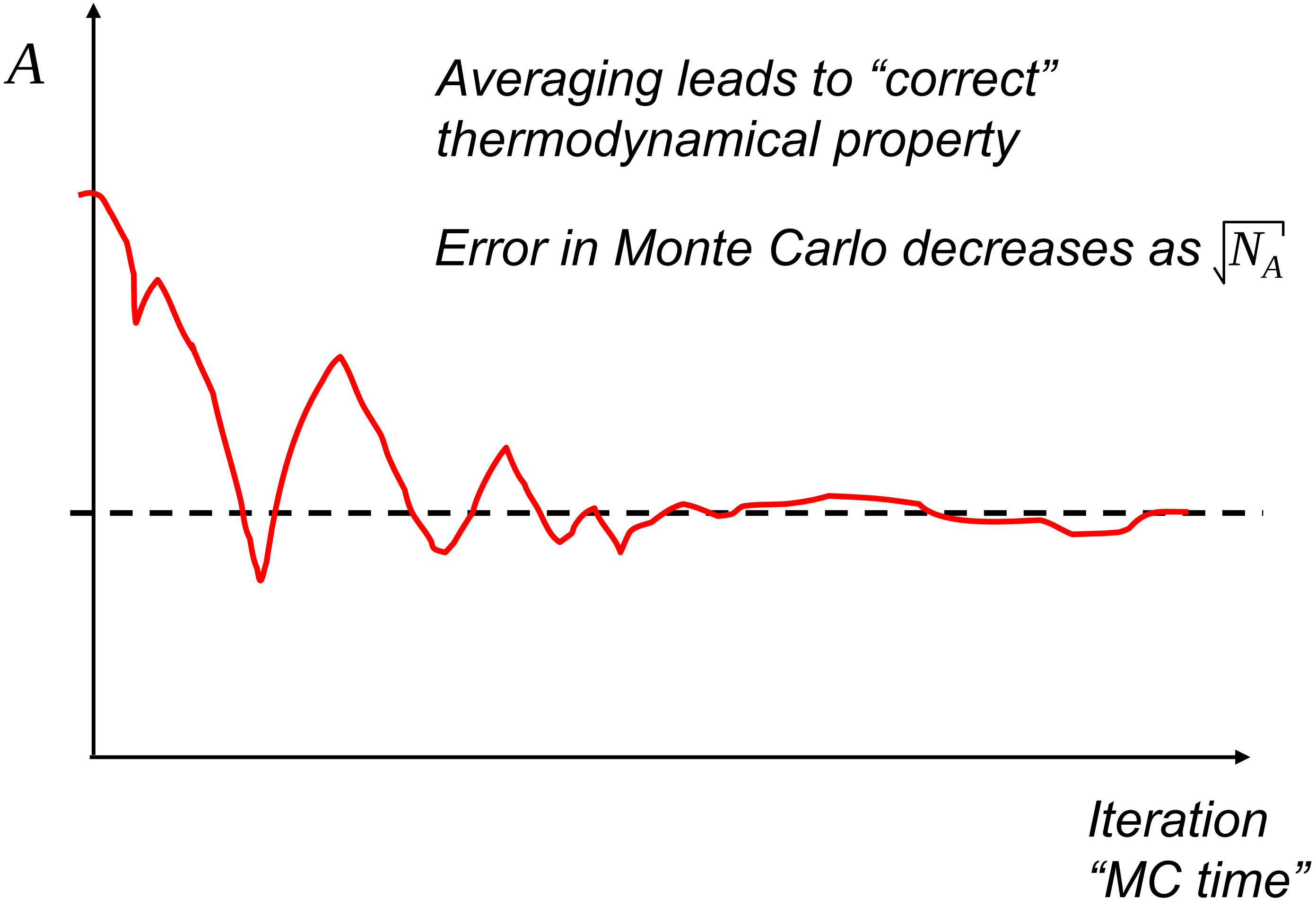
Have achieved:

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

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 $\sqrt{N_A}$

Other ensembles/applications

- Other ensembles carried out by modifying the acceptance criterion (in Metropolis-Hastings algorithm), e.g. *NVT, NPT;* **goal is to reach the appropriate distribution of states according to the corresponding probability distributions**

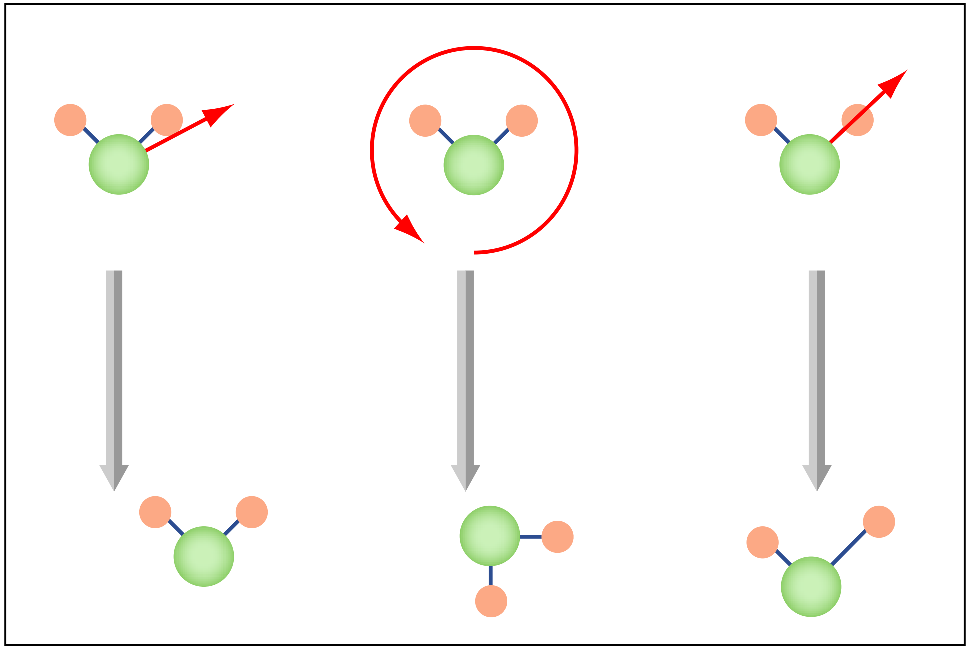
- Move sets can be adapted for other cases, e.g. not just move of particles but also **rotations of side chains** (=rotamers), **torsions**, etc.

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

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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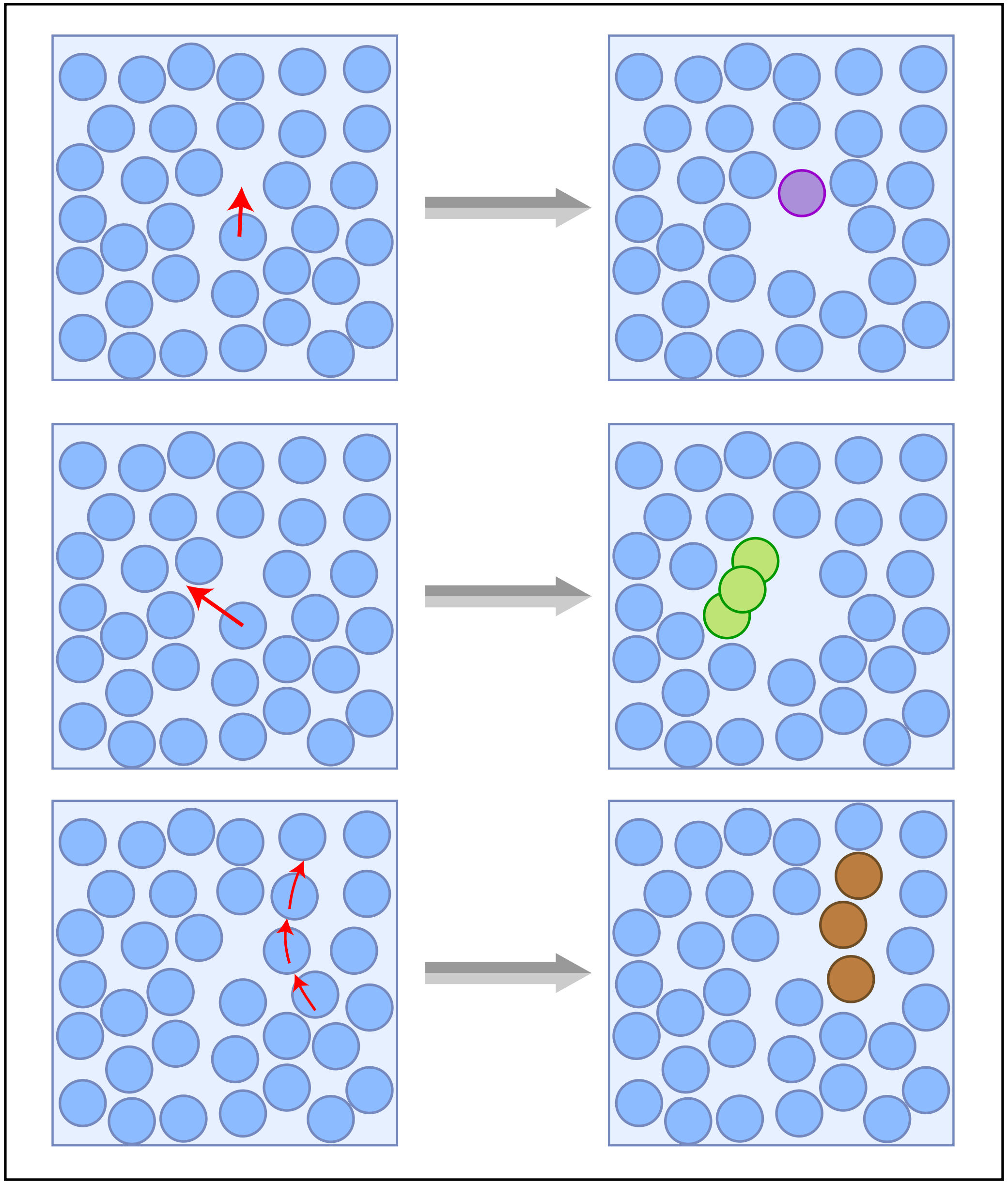
After N. Baker (WUSTL)

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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3.021J / 1.021J / 10.333J / 18.361J / 22.00J Introduction to Modeling and Simulation
Spring 2011