

Purdue MSE597G Lectures on Molecular Dynamics simulations of materials

Lecture 4

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Molecular Dynamics simulations

Introduction

- What is molecular dynamics (MD)? Examples of current research
- Why molecular dynamics?

Part 1: the theory behind molecular dynamics

- Basic ideas & algorithms
- Brief introduction to the physics necessary to run & understand MD

Part 2: total energy and force calculations

- Quantum mechanical origin of atomic interactions
- Inter-atomic potentials: “averaging electrons out”

Part 3: advanced techniques, mesodynamics, verification and validation

- MD in under isothermal and isobaric conditions
- Coarse grain approaches and dynamics with implicit degrees of freedom
- Before you perform production runs

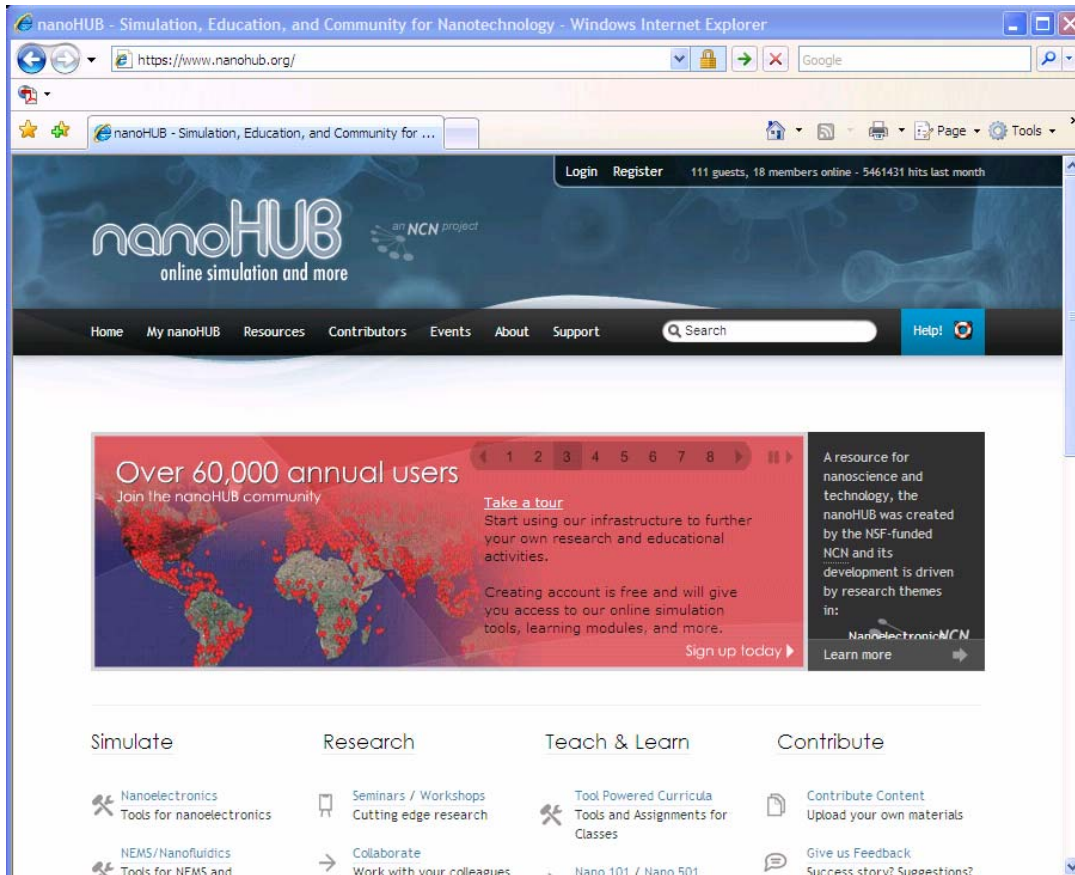
- Tutorial to perform MD simulations using the nanoMATERIALS simulation tool at the nanoHUB
- Homework exercises



Run your own MD simulation

[nanoHUB](http://www.nanohub.org) (*www.nanohub.org*)

- Science portal developed by the Network of Computational Nanotechnology
- Provides services for online education, collaboration and simulation



The screenshot shows the nanoHUB website in a Windows Internet Explorer browser window. The address bar displays <https://www.nanohub.org/>. The website header features the nanoHUB logo, the tagline "online simulation and more", and navigation links for Home, My nanoHUB, Resources, Contributors, Events, About, and Support. A search bar and a Help! button are also present. A prominent banner highlights "Over 60,000 annual users" and encourages users to "Join the nanoHUB community". The banner includes a world map with red dots representing users and a "Sign up today" button. Below the banner, the website is organized into four main sections: Simulate, Research, Teach & Learn, and Contribute. Each section lists various tools and resources available on the platform.

MD simulations in the nanoHUB: nanoMATERIALS simulation tool

Molecular Dynamics simulations

Introduction

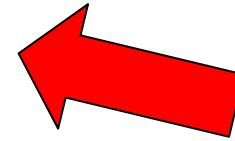
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Pair-wise potentials

Simplest, non-trivial, function

Sum of pair-wise terms

$$V(\{r_i\}) = \sum_{i < j} \phi(|r_i - r_j|)$$

Lennard-Jones (6-12)

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

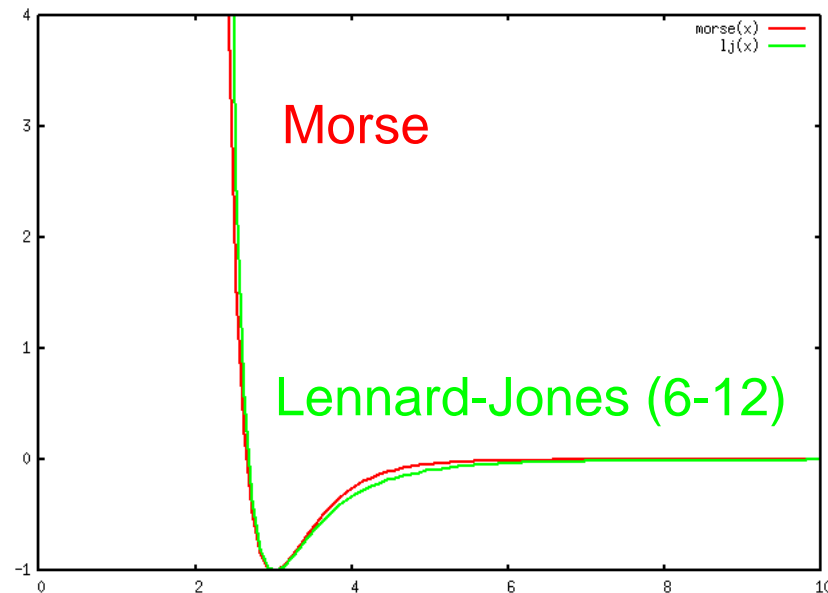
Distance & energy

Exponential-6

$$\phi_{\text{exp-6}}(r) = \varepsilon \left[e^{-\gamma r} - Ar^{-6} \right]$$

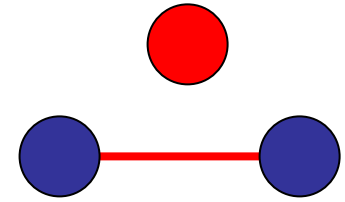
Morse

$$\phi_{\text{Morse}}(r) = \varepsilon \left[\exp\left(\gamma \left(1 - \frac{r}{r_0} \right) \right) - 2 \exp\left(\frac{\gamma}{2} \left(1 - \frac{r}{r_0} \right) \right) \right]$$

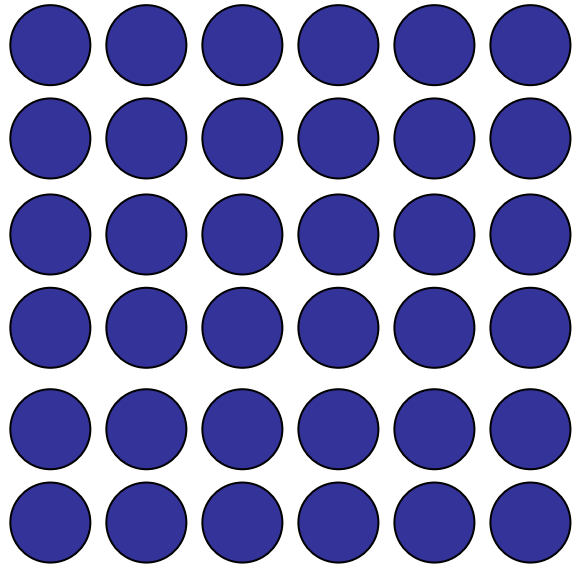


Distance, energy, & curvature

Two-body potentials



Pair-wise interactions: $E(\{r_i\}) = \sum_{i < j} \phi(r_{ij})$



- Vacancy energy in Perfect crystal
 - Coordination number Z
 - Interactions: only first nearest neighbors

$$E_{xtal}(N) = \frac{1}{2} NZE_0$$

- Now let's create a vacancy:

$$E_{vac}(N-1) =$$

$$\varepsilon_{vac} = E_{vac}(N-1) - \frac{N-1}{N} E_{xtal}(N) = \frac{1}{2} NZE_0 - ZE_0 - \frac{1}{2} (N-1)ZE_0 = -\frac{1}{2} ZE_0$$

Vacancy formation energy is equal to cohesive energy

Two-body potentials: limitations

- Two-body potentials: vacancy formation \sim cohesive energy
- Metals: $\epsilon_{\text{vac}} \sim 1/3 E_{\text{coh}}$

	E_{coh} (eV)	E_{vac} (eV)	$E_{\text{vac}}/E_{\text{coh}}$
Al	3.39	0.75	0.22
Ni	3.516	1.6	0.46
Cu	3.615	1.2	0.33
Ag	4.086	1.15	0.28
Pt	3.924	1.4	0.36
Au	4.079	0.95	0.23

- Two-body potentials and elastic constants: $c_{12} = c_{44}$
 - Metals: $c_{12} > c_{44}$
 - Pair potentials can only describe simple non-bond interactions
 - Closed-shell atoms (Ne, Ar, Kr, etc.)
 - Atoms that are fully coordinated (e.g. inter-molecular)
 - Pauli repulsion at short distances
 - London dispersion at longer distances
- } van der Waals

Capturing many-body effects in metals

Embedded atom model (EAM)

Mike Baskes and collaborators 1980's + other groups

$$V = \sum_{i < j} \phi(r_{ij}) + \sum_i F(\rho_i) \quad \rho_i = \sum_{j \neq i} f(r_{ij})$$

Two-body potential

Embedding energy:
Energy to embed atom i in
the electronic density ρ_i

Local electronic density
on atom i contributed
from nearby atoms

Accurate description of:

- Environment dependence of bonding in metals (vacancy and surfaces)
- Elastic constants and plastic deformation
- Phase transformations (melting & solid-solid)
- Alloys

Not very accurate for:

- Cases where bonding is highly directional

Directional bonding in semiconductors

Diamond,
zincblende and
wurtzite structures

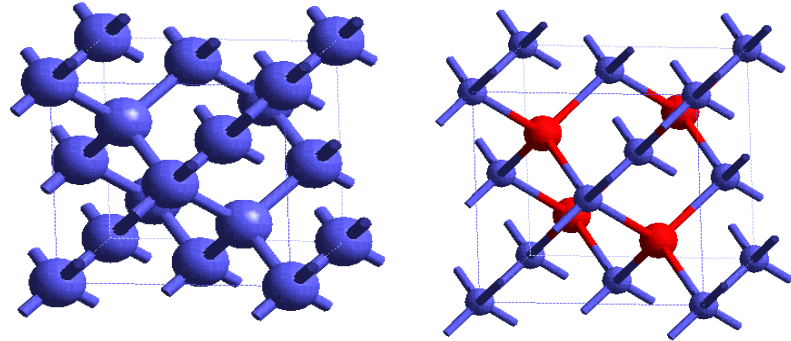
PHYSICAL REVIEW B

VOLUME 31, NUMBER 8

15 APRIL 1985

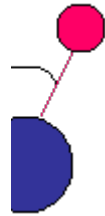
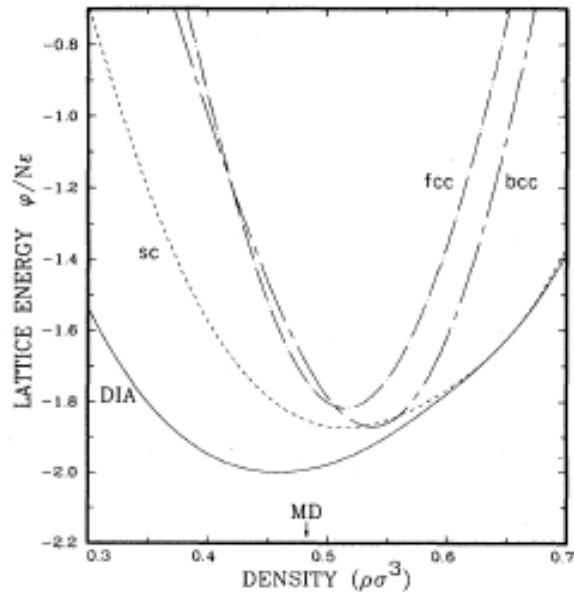
Computer simulation of local order in condensed phases of silicon

Frank H. Stillinger and Thomas A. Weber
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 7 November 1984)



$$V(\{r_i\}) = \sum_{i < j} f_2(r_{ij}) + \sum_{i < j < k} f_3(r_i, r_j, r_k)$$

$$f_2(r) = \begin{cases} A(Br^{-p} - r^{-q})\exp[(r-a)^{-1}], & r < a \\ 0, & r \geq a \end{cases}$$



$$f_3(r_i, r_j, r_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj}),$$

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda \exp[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}] \times (\cos\theta_{jik} + \frac{1}{3})^2;$$

Interatomic potentials for molecular materials

$$V(\{r_i\}) = V_{\text{cov}}(\{r_i\}) + V_{\text{electr}}(\{r_i\}) + V_{\text{vdW}}(\{r_i\})$$

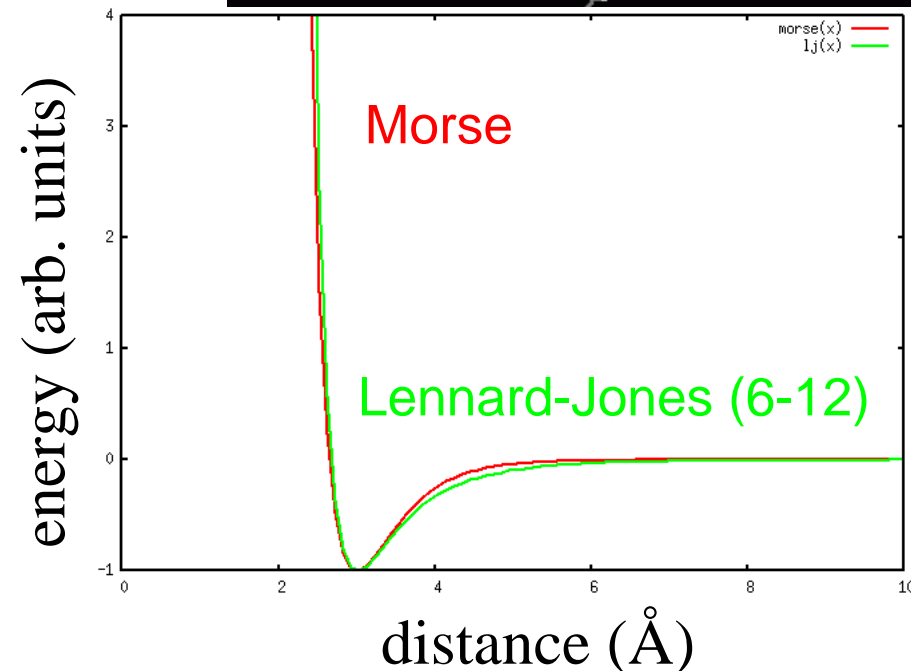
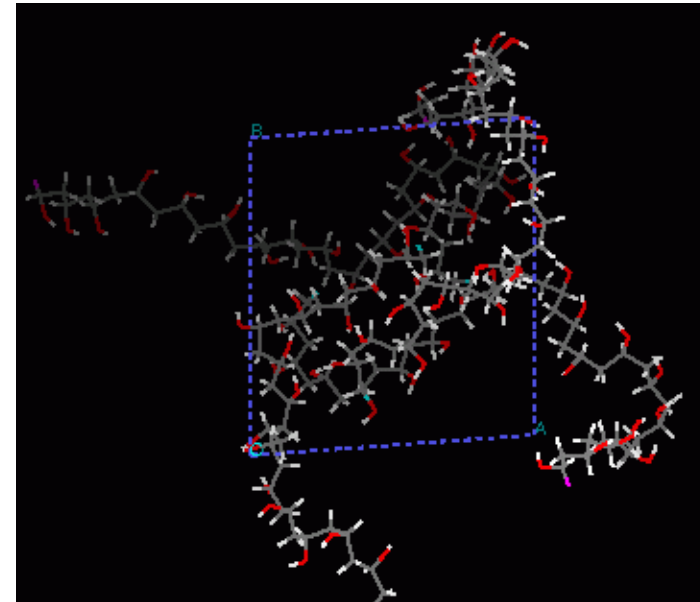


vdW interactions between bonded atoms:

Most molecular potentials use exclusions

No vdW for:

- Bonded atoms
- 1-3 (atoms separated by two covalent bonds)
- 1-4 (atoms separated by three covalent bonds)



More non-bond interactions: electrostatics

Difference in atomic electron affinity and ionization potential leads to charge transfer

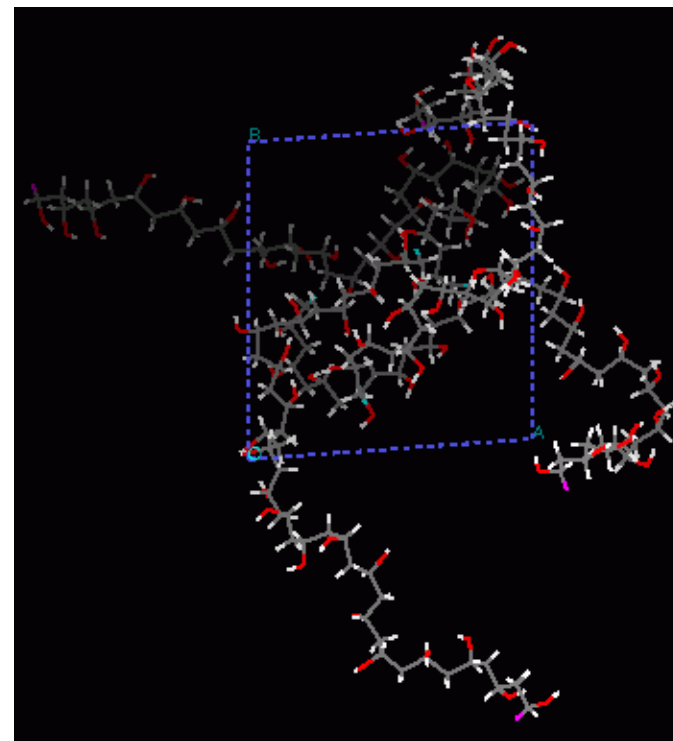
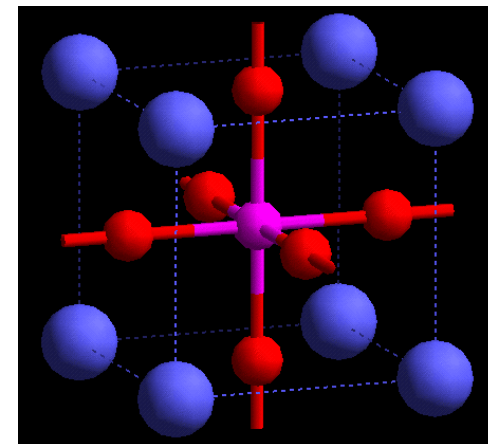
Electrostatic energy:

Assuming point charges:

$$V_{elec} = C_{unit} \sum_{i < j} \frac{q_i q_j}{r_{ij}}$$

How to obtain atomic charges?

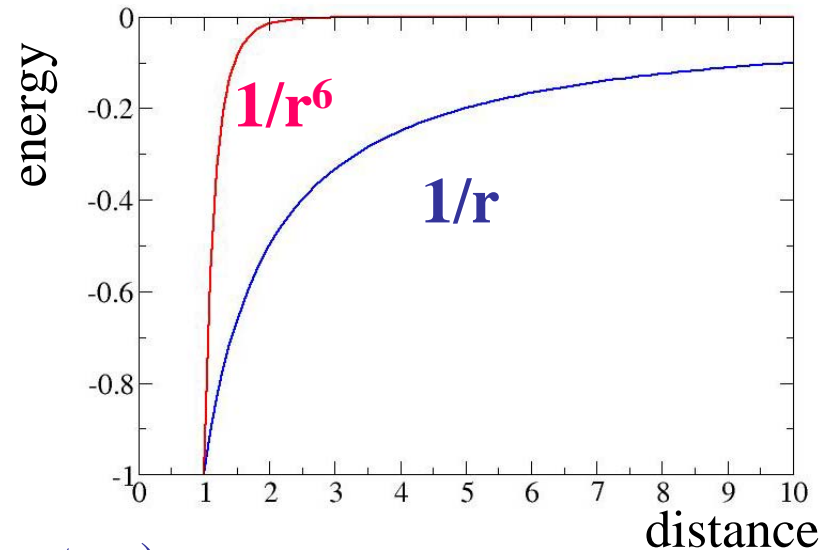
- Formal charge
- Dipole moment or polarization
- From electronic structure calculations
- Self-consistently charge equilibration



Electrostatics & periodic boundary conditions

Coulomb interaction decays
very slowly

$$V_{elec} = C_{unit} \sum_{i < j} \frac{q_i q_j}{r_{ij}}$$



With periodic boundary conditions (infinite system):

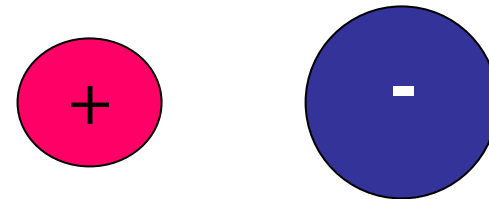
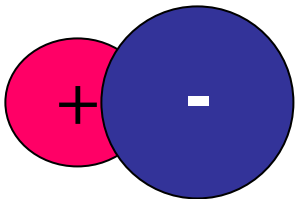
- The Coulomb sum is conditionally convergent:
 - Result depends on the order of the summands
 - Result depends on charge arrangement on the surface
- Need to use special sum techniques and boundary conditions
 - Ewald method [part of the sum in real space and part in reciprocal Fourier space]
 - Particle-mesh Ewald and other techniques

de Leeuw et al. *Proc. Roy. Soc. Lond. A* **373**, 27 (1980)

de Leeuw et al. *Proc. Roy. Soc. Lond. A* **373**, 57 (1980)

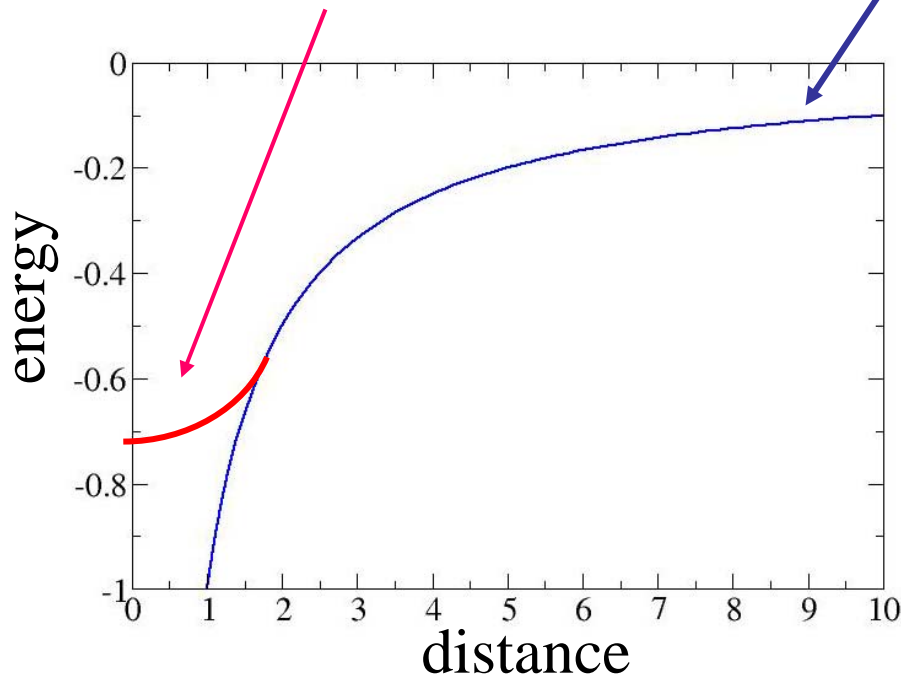
Electrostatics: shielding

• Charge distributions are not point-like



Short distances:
Shielded Coulomb

Long interatomic distances: $1/r$

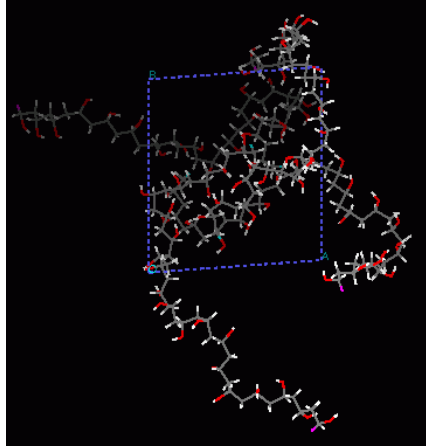


Exclusions again

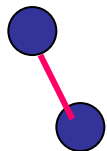
No Coulomb for:

- Bonded atoms
- 1-3 (atoms separated by two covalent bonds)
- 1-4 (atoms separated by three covalent bonds)

Covalent interactions

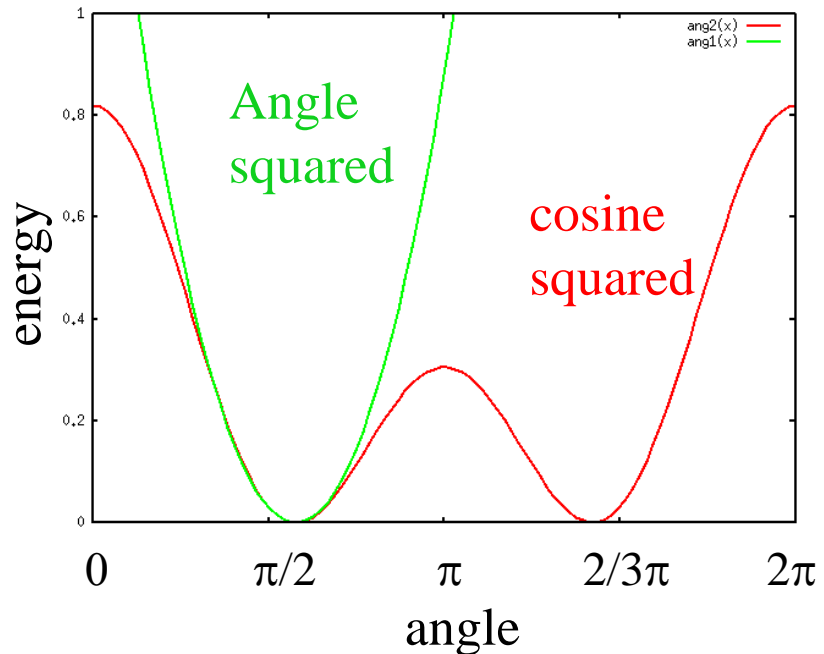


Interaction between atoms separated by chemical bonds

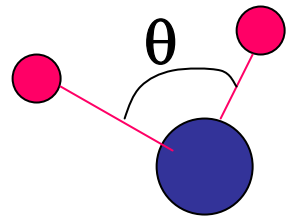


Bond stretch:

$$\phi_{bond}(r) = \begin{cases} \frac{1}{2} k_{ij} (r - r_{ij}^0)^2 \\ \text{Morse, } L - J \end{cases}$$

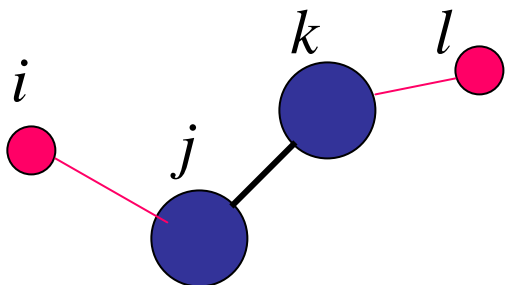


Angle bending:



$$\phi_{angle}(\theta) = \begin{cases} \frac{1}{2} k_{ijk} (\theta - \theta_{ijk}^0)^2 \\ \frac{1}{2} \frac{k_{ijk}}{\sin^2 \theta_{ijk}^0} [\cos \theta - \cos \theta_{ijk}^0]^2 \end{cases}$$

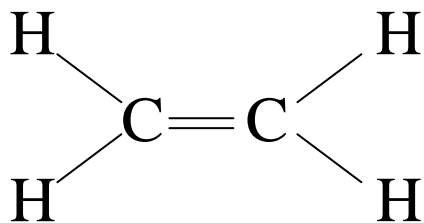
Covalent interactions



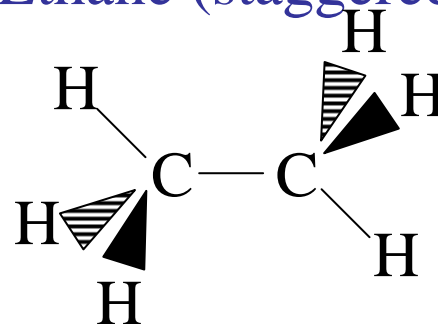
Torsion bending (dihedral angles)

$$\phi_{\text{torsions}}(\varphi) = k_{ijkl} \left[1 - \cos(n_{jk}(\varphi - \varphi_{jk}^0)) \right]$$

Ethylene (planar)



Ethane (staggered)



sp² hybridization

- Equilibrium at 0° & 180°
- Maxima at: 90° & 270°
- High torsional barrier
 - Rotating around C-C bond breaks the PI bond

sp³ hybridization

- Equilibrium at 60°, 180°, & 300°
- Maxima at: 0°, 120°, & 240°
- Low torsional barrier
 - Dominated by vdW between H H

Atom types in molecular force fields

- Element alone is not enough to determine the interactions
 - E.g.: sp^3 carbon and sp^2 carbon behave differently
- In traditional molecular force fields the user specifies *force field types* to establish the character of the atom
 - Force field types & connectivities need to be determined prior to MD simulation
 - FF types and connectivities are kept fixed during run

Widely used force fields for molecular simulations:

AMBER: Cornell, Cieplak, Bayly, Gould, Merz, Ferguson, Spellmeyer, Fox, Caldwell, and Kollman. *J. Am. Chem. Soc.*, **117**, 5179 (1995).

DREIDING: Mayo, Olafson, and Goddard, III, *J. Chem. Phys.* 94, 8897 (1990).

CHARMM: Brooks, Bruccoleri, Olafson, States, Swaminathan, and Karplus. *J. Comput. Chem.*, **4**, 187 (1983).