Purdue MSE597G Lectures on Molecular Dynamics simulations of materials

Lecture 5

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Molecular Dynamics simulations
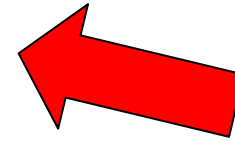
<u>Introduction</u>
- What is molecular dynamics (MD)? Examples of current research
- Why molecular dynamics?

<u>Part 1</u>: the theory behind molecular dynamics
- Basic ideas & algorithms
- Brief introduction to the physics necessary to run & understand MD

<u>Part 2</u>: total energy and force calculations
- Quantum mechanical origin of atomic interactions
- Inter-atomic potentials: "averaging electrons out"

<u>Part 3</u>: 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**

Capturing many-body effects in metals

Embedded atom model (EAM)

Mike Baskes and collaborators 1980's + other groups

$$V = \sum_{i<j} \phi(r_{ij})$$

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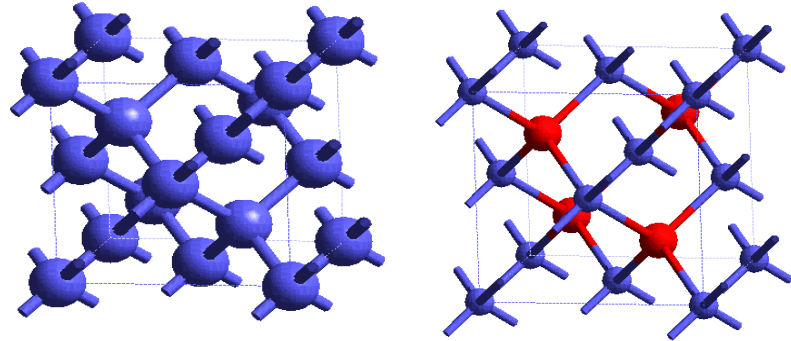
Diamond, zincblende and wurtzite structures
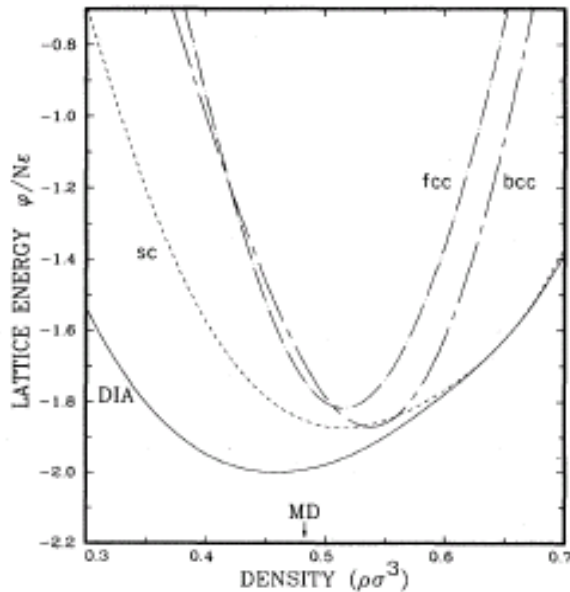
Frank H. Stillinger and Thomas A. Weber
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 7 November 1984)

$$V(\{r_i\}) = \sum_{i<j} f_2(r_{ij})$$

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

$$f_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk})$$
$$+ h(r_{ki}, r_{kj}, \theta_{ikj}) ,$$

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

Interatomic potentials for molecular materials

$$V\left(\{r_i\}\right) = V_{\text{cov}}\left(\{r_i\}\right)$$

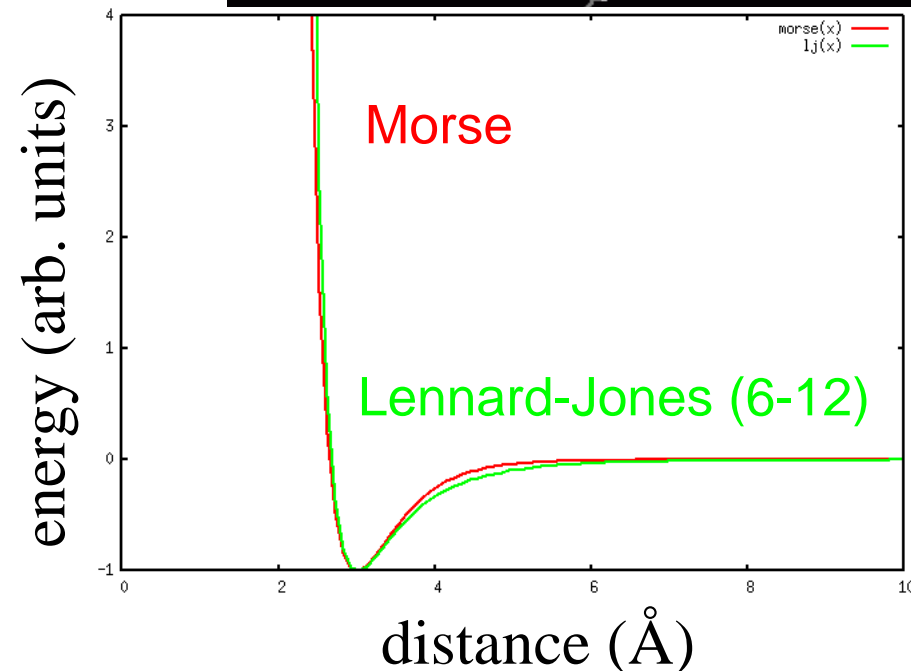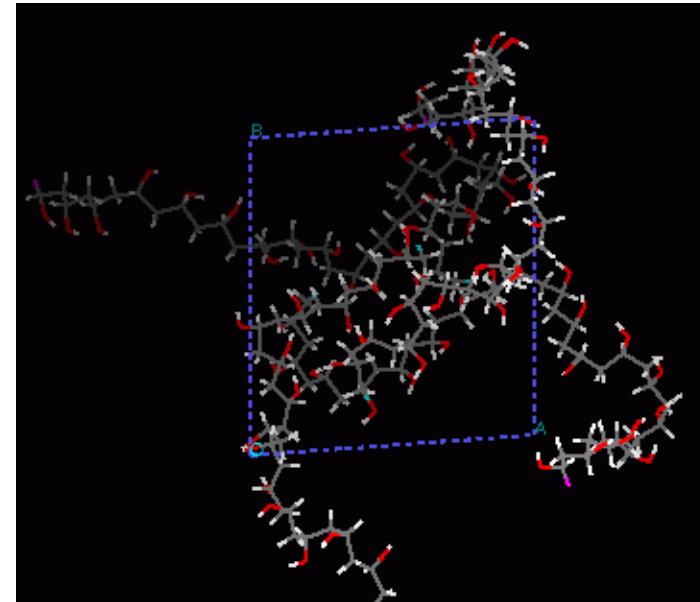$$+ V_{electr}\left(\{r_i\}\right) + V_{vdW}\left(\{r_i\}\right)$$

✓

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)

Morse

Lennard-Jones (6-12)

energy (arb. units)

distance (Å)

More non-bond interactions: electrostatics

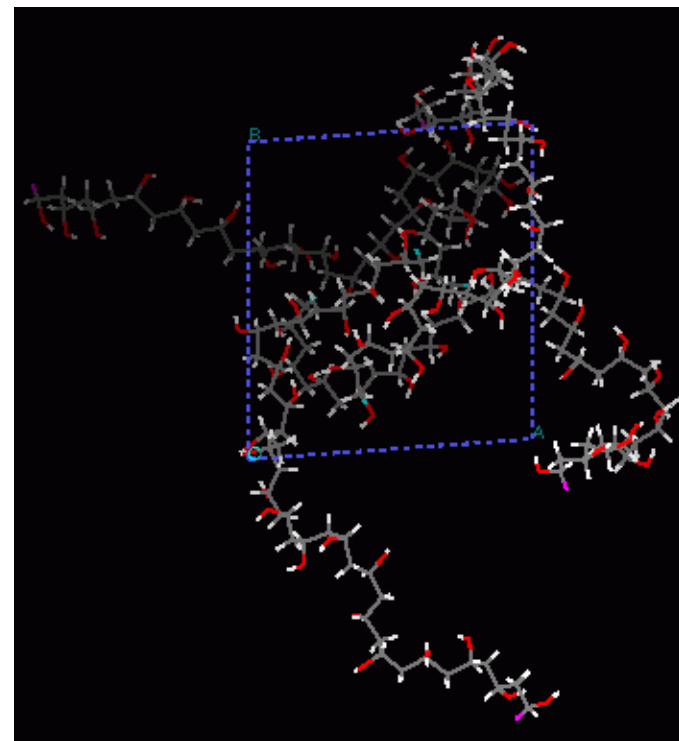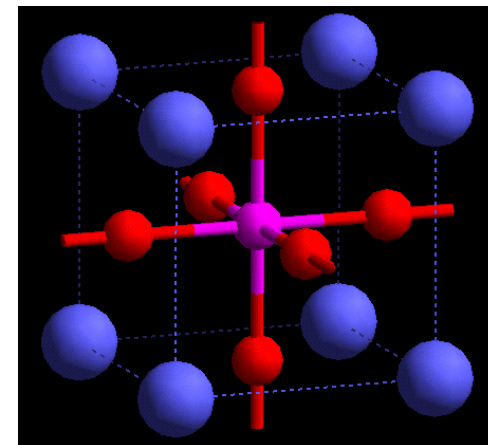Difference in atomic electron affinity and ionization potential leads to charge transfer

Electrostatic energy:

Assuming point charges:

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

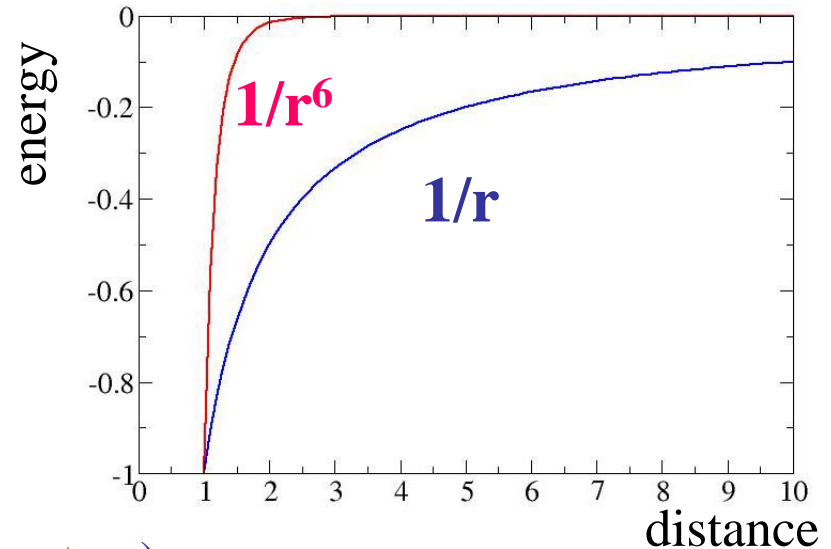How to obtain atomic charges?
- Formal charge
- Dipole moment or polarization
- From electronic structure calculations
- Self-consistently charge equilibration

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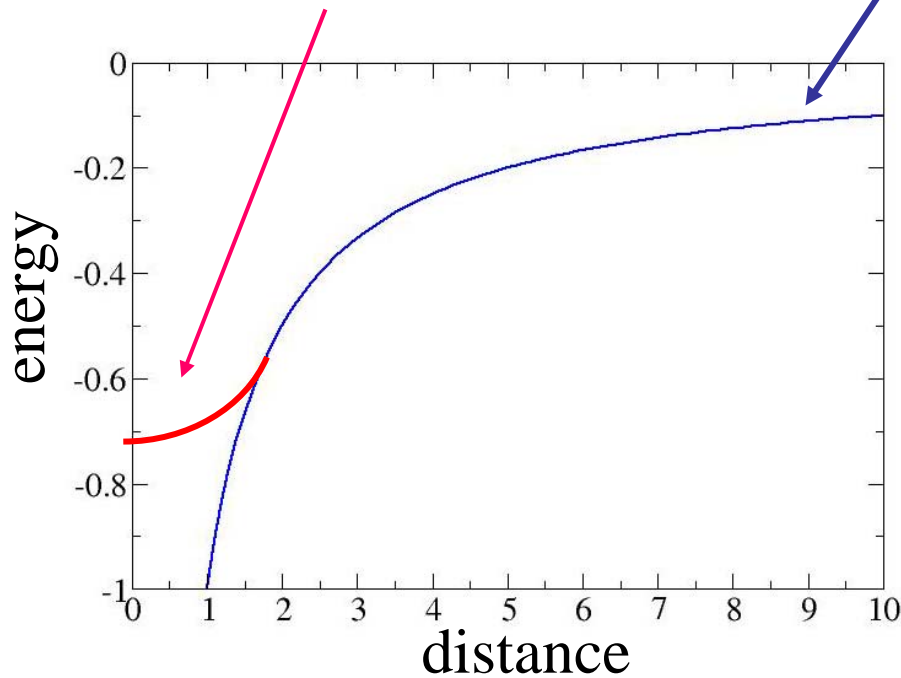de Leeuw et al. *Proc. Roy. Soc. Lond.* A **373**, 57 (1980)

Electrostatics: shielding

• **Charge distributions are not point-like**
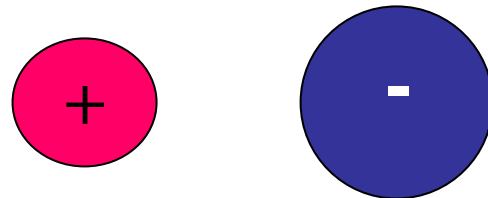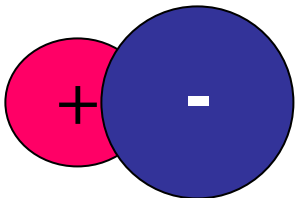
Short distances:
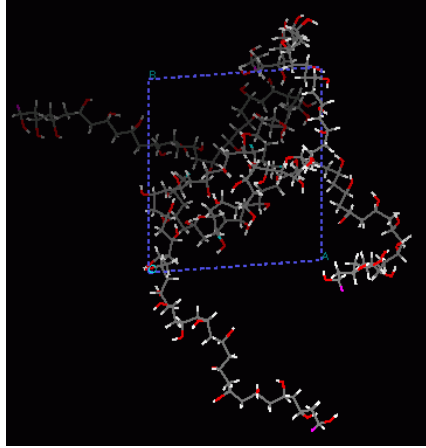Shielded Coulomb

Long interatomic distances: 1/r
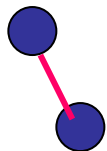
Exclusions again
No Coulomb for:
• Bonded atoms
• 1-3 (atoms separated by two covalent bonds)
• 1-4 (atoms separated by three covalent bonds)
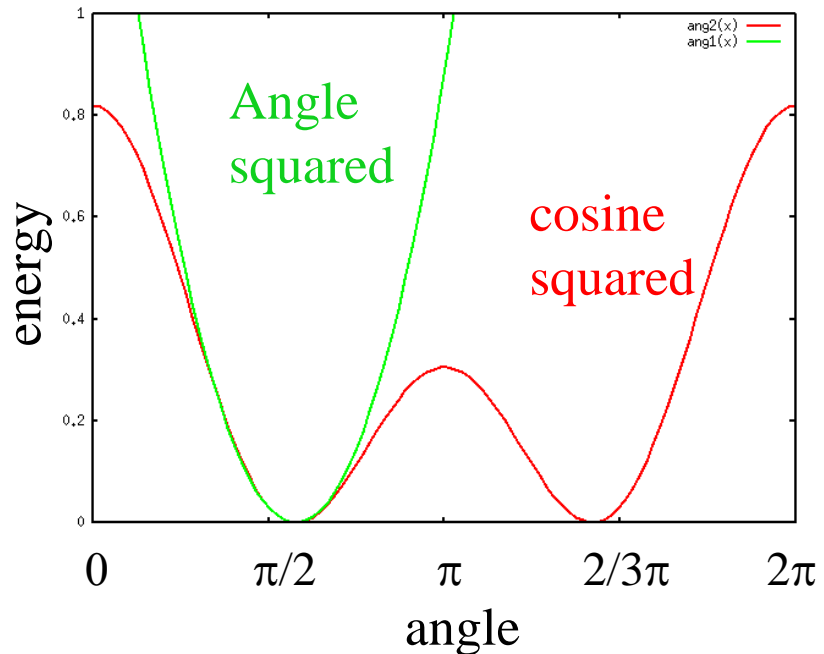
Covalent interactions
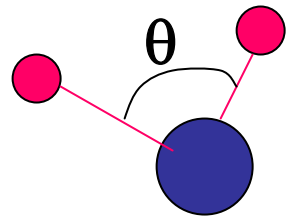

Interaction between atoms separated by chemical bonds

Bond stretch:

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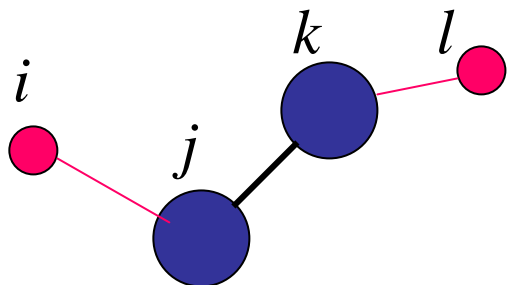

Angle bending:

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

In the plot: energy vs angle, with labels "Angle squared" (green) and "cosine squared" (red). x-axis: 0, $\pi/2$, π, $2/3\pi$, 2π. Legend: ang2(x), ang1(x).
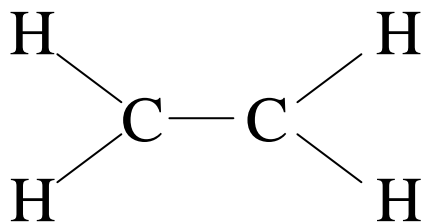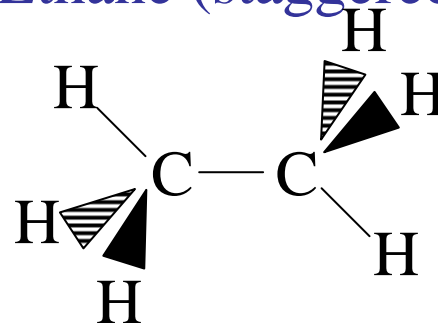
Covalent interactions

Torsion bending (dihedral angles)

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

Ethylene (planar)

Ethane (staggered)

sp^2 hybridization
- Equilibrium at 0° & 180°
- Maxima at: 90° & 270°
- High torsional barrier
  - Rotating around C-C bond breaks the PI bond

sp^3 hybridization
- Equilibrium at 60°, 180°, & 300°
- Maxima at: 0°, 120°, & 240°
- Low torsional barrier
  - Dominated by vdW between H