

Purdue MSE597G Lectures on Molecular Dynamics simulations of materials

Lecture 5

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Molecular Dynamics simulations

Introduction

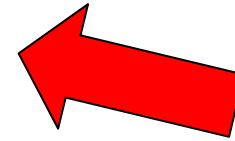
- What is molecular dynamics (MD)? Examples of current research
- Why molecular dynamics?

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

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

PHYSICAL REVIEW B

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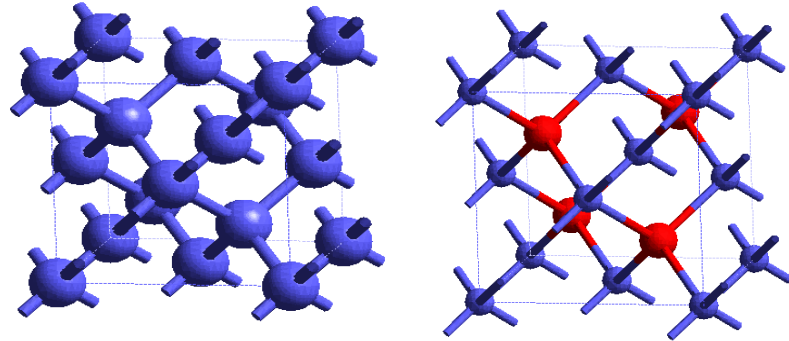
15 APRIL 1985

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)

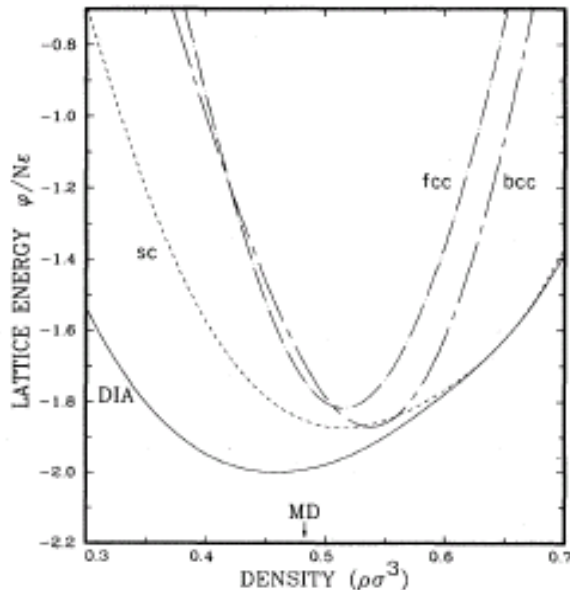


$$V(\{r_i\}) = \sum_{i < j} f_2(r_{ij})$$

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

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

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



Interatomic potentials for molecular materials

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

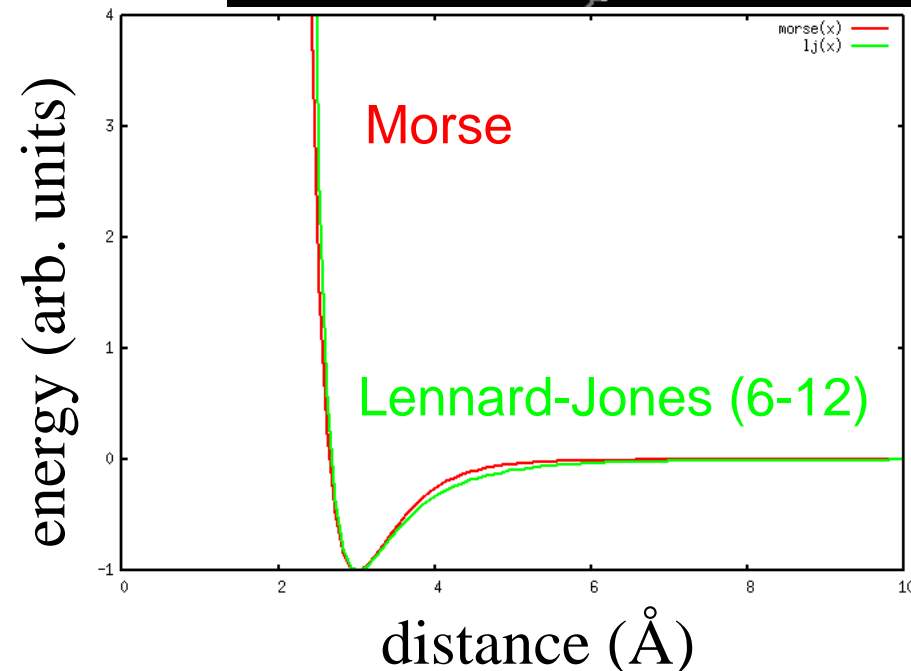
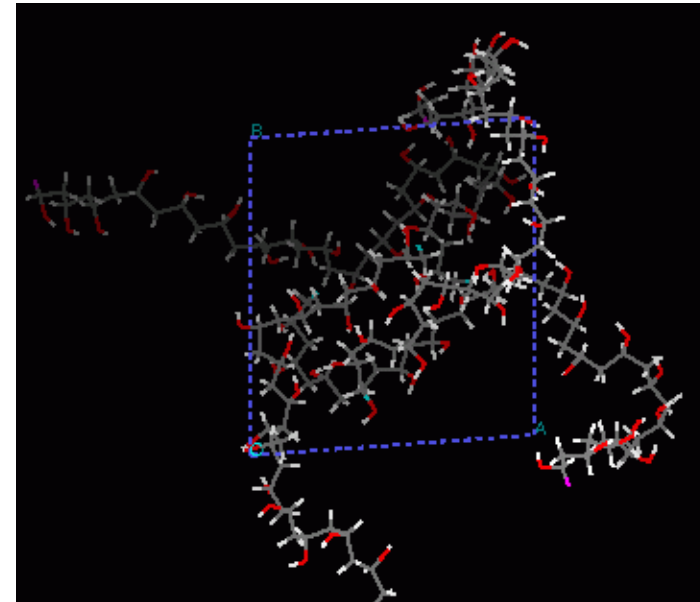


vdW interactions between bonded atoms:

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

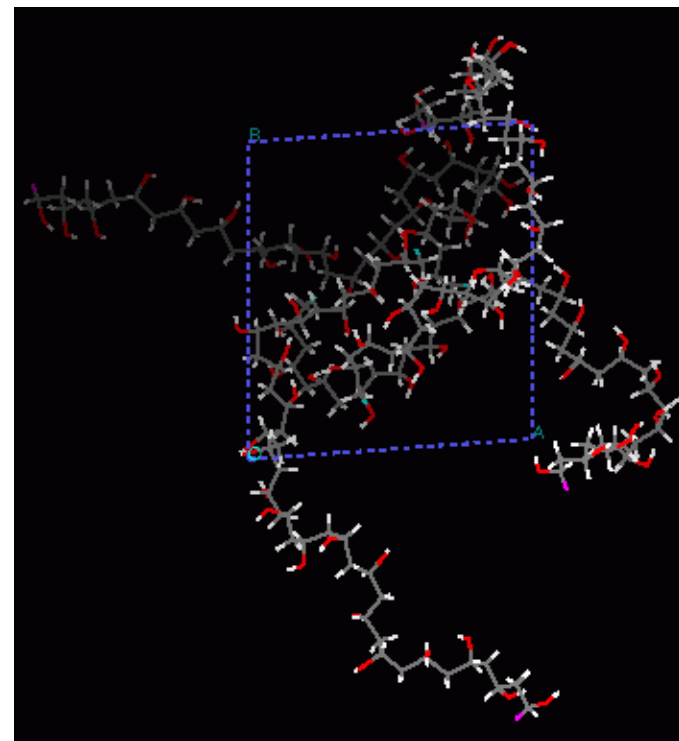
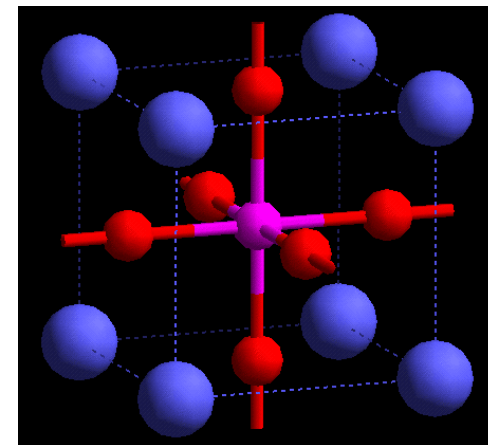
Electrostatic energy:

Assuming point charges:

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

How to obtain atomic charges?

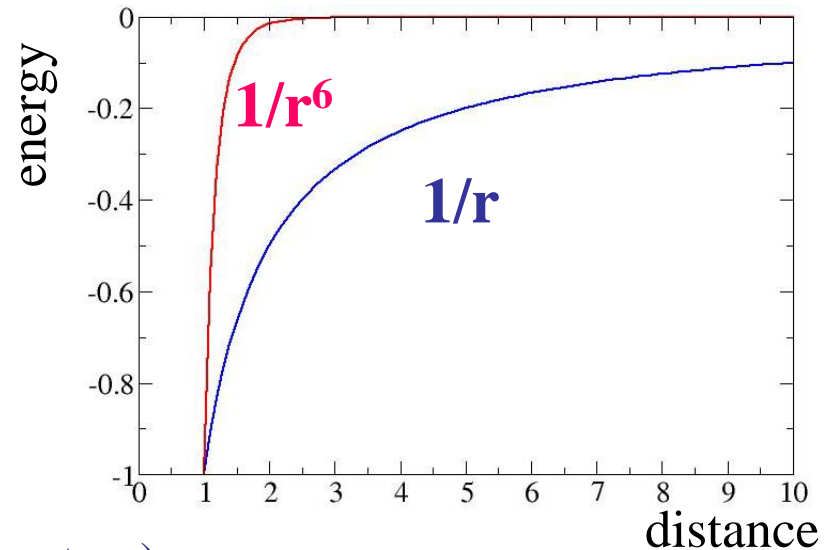
- Formal charge
- Dipole moment or polarization
- From electronic structure calculations
- Self-consistently charge equilibration



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):

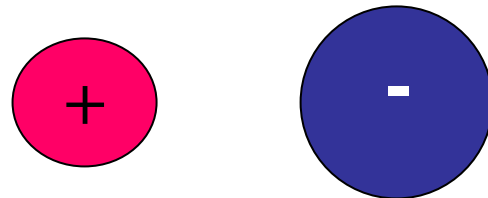
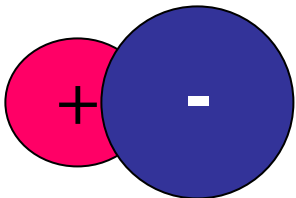
- The Coulomb sum is conditionally convergent:
 - Result depends on the order of the summands
 - Result depends on charge arrangement on the surface
- Need to use special sum techniques and boundary conditions
 - Ewald method [part of the sum in real space and part in reciprocal Fourier space]
 - Particle-mesh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

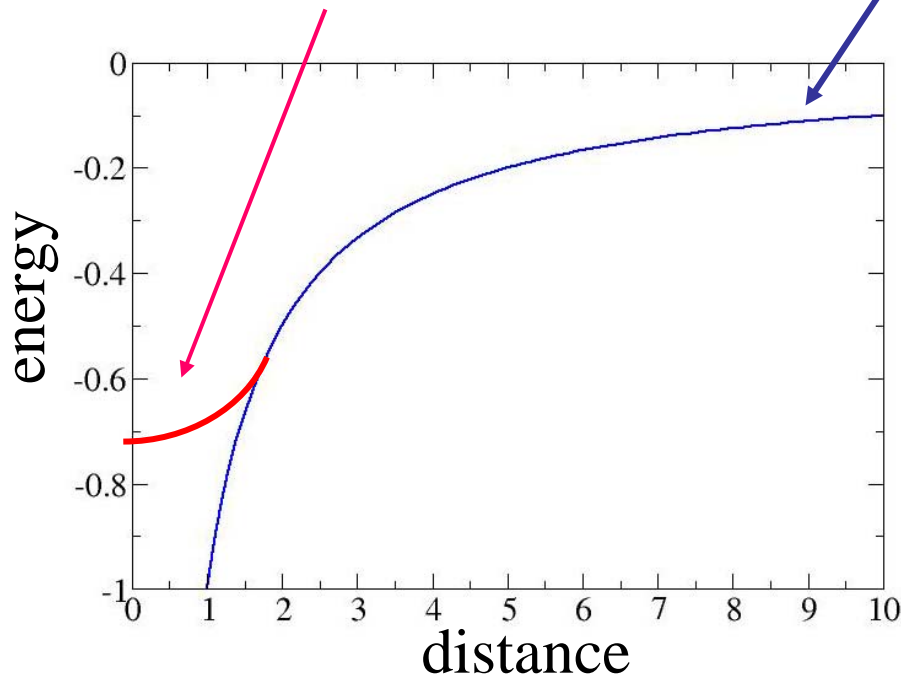
Electrostatics: shielding

• Charge distributions are not point-like



Short distances:
Shielded Coulomb

Long interatomic distances: $1/r$

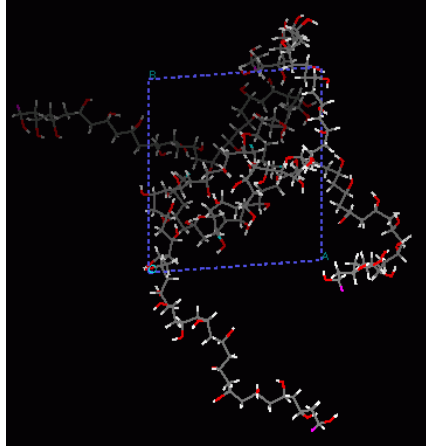


Exclusions again

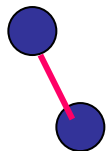
No Coulomb for:

- Bonded atoms
- 1-3 (atoms separated by two covalent bonds)
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Covalent interactions

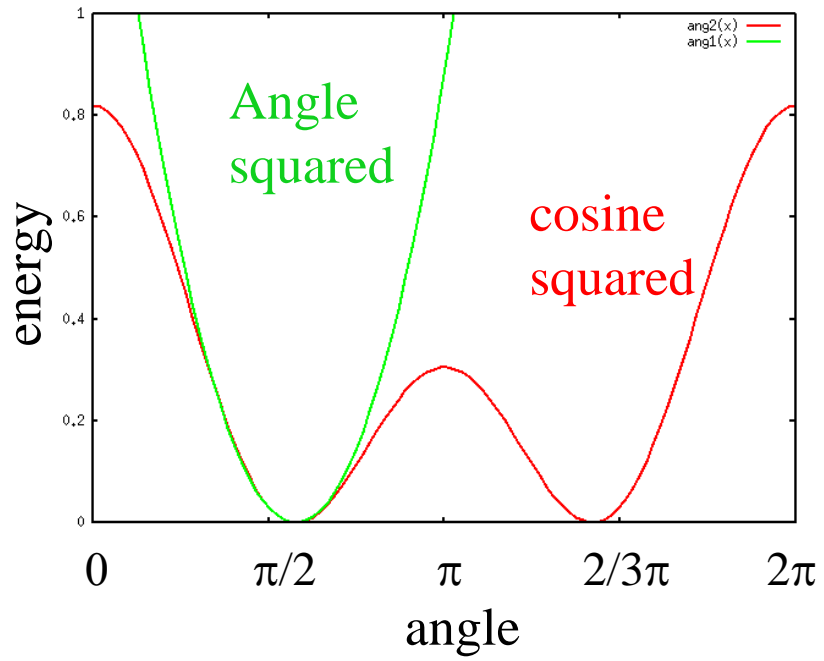


Interaction between atoms separated by chemical bonds

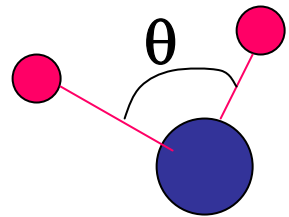


Bond stretch:

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

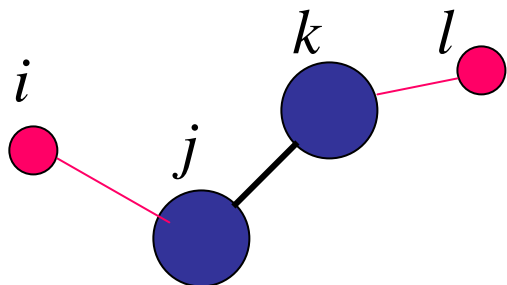


Angle bending:



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

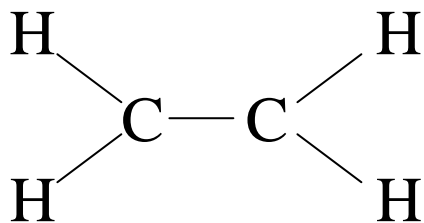
Covalent interactions



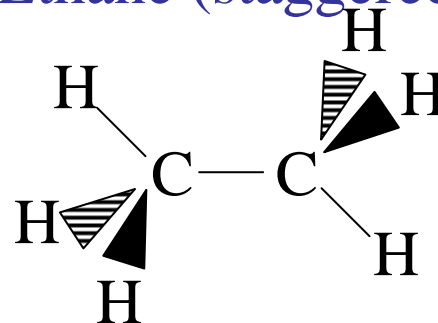
Torsion bending (dihedral angles)

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

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