Modeling & Simulation of Glass Structure

VCG Lecture 21

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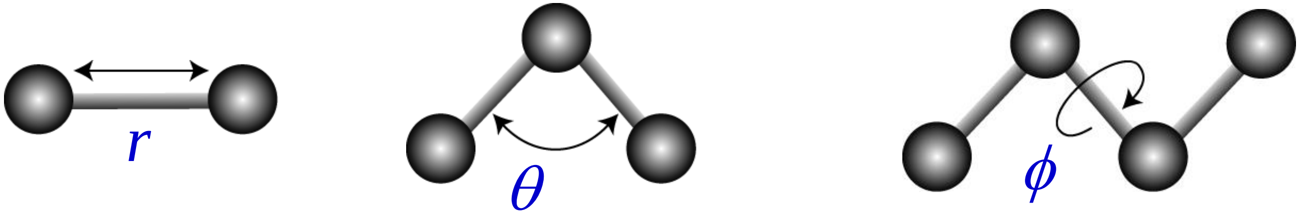
Overview …

- Historical perspective
- Simulation methodologies
  - Theoretical background
  - Monte Carlo simulation
  - Molecular dynamics simulation
  - Reverse Monte Carlo
- Force fields
- Information retrieval
  - Statistical mechanical formalisms
  - Structural analyses
  - Dynamics
- Application examples

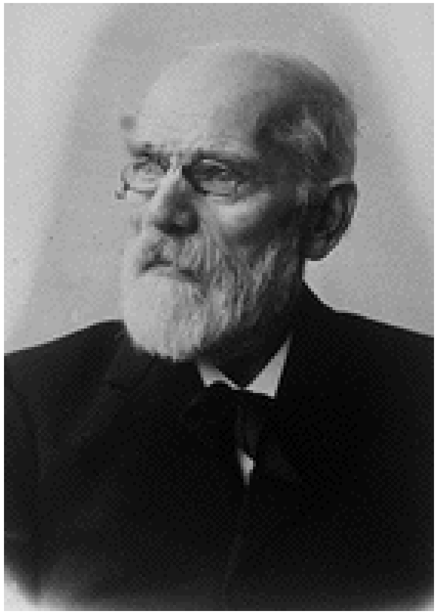
Force Fields

- Types of interactions between two molecules
  - Electrostatic interactions
    - Between charges (if ions) and between permanent dipoles, quadrupoles and higher multipole moments
      - May be represented through partial charges
    - Embedding terms (metals)
  - Induction interactions
    - Between, for example, a permanent dipole and an induced dipole
  - Dispersion interactions
    - Long-range attraction that has its origin in fluctuations of the charge distribution
  - Valence (overlap) interactions
    - Covalent bonds
    - Repulsive interaction at short range which arises from exclusion principle
  - Residual valence interactions
    - Specific chemical forces giving rise to association and complex formation - e.g., hydrogen bonding
- Types of interactions within a molecule
  - Bond stretch, bond-angle bending, torsional potential

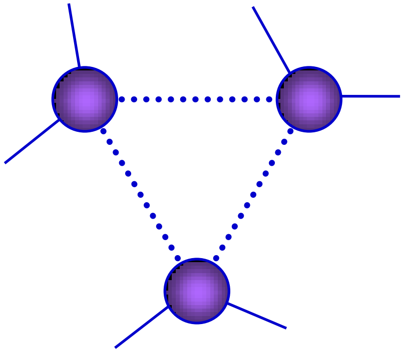


Force Fields

- Non-bonded interactions are typically long-range and involve a large number of particles. Yet, contributions to the total energy and forces are considered as pair-wise additive

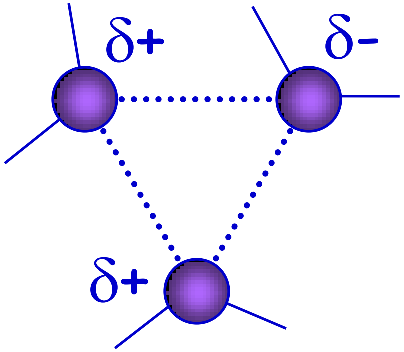


Johannes Diderik
Van der Waals
1837-1923



Non-bonded
(van der Waals)

Non-bonded
(electrostatic)

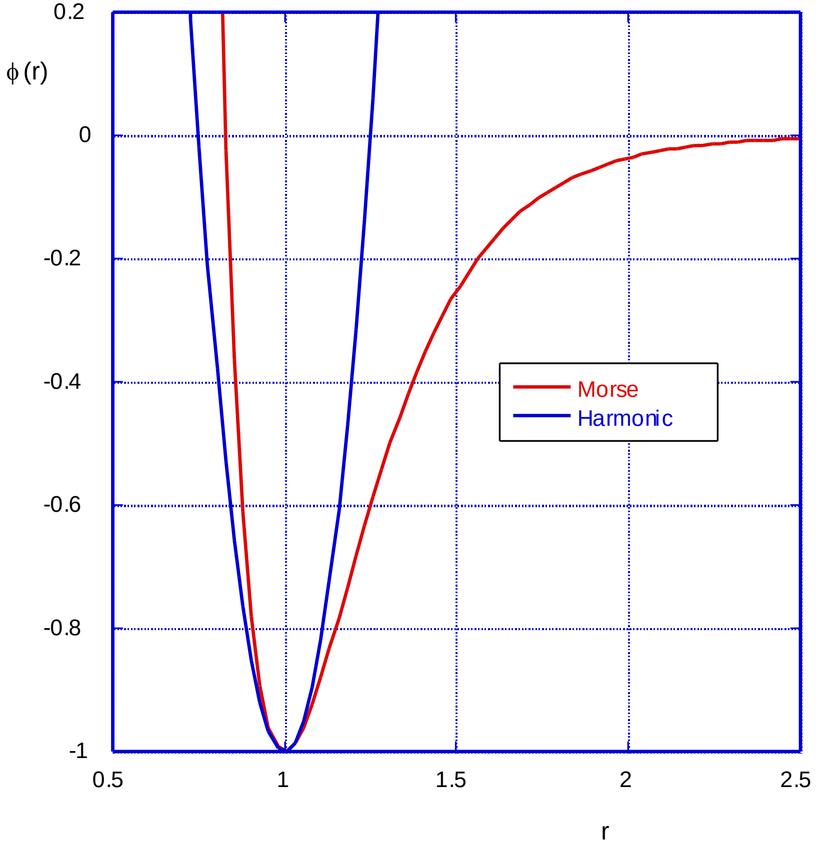


Metals

- Example: Morse force field
  - Approximate physical behavior
  - Computationally efficient

$$\phi(r) = D_0 \left\{ e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \right\}$$

$$= D_0 e^{-a(r-r_0)} \left\{ e^{-a(r-r_0)} - 2 \right\}$$



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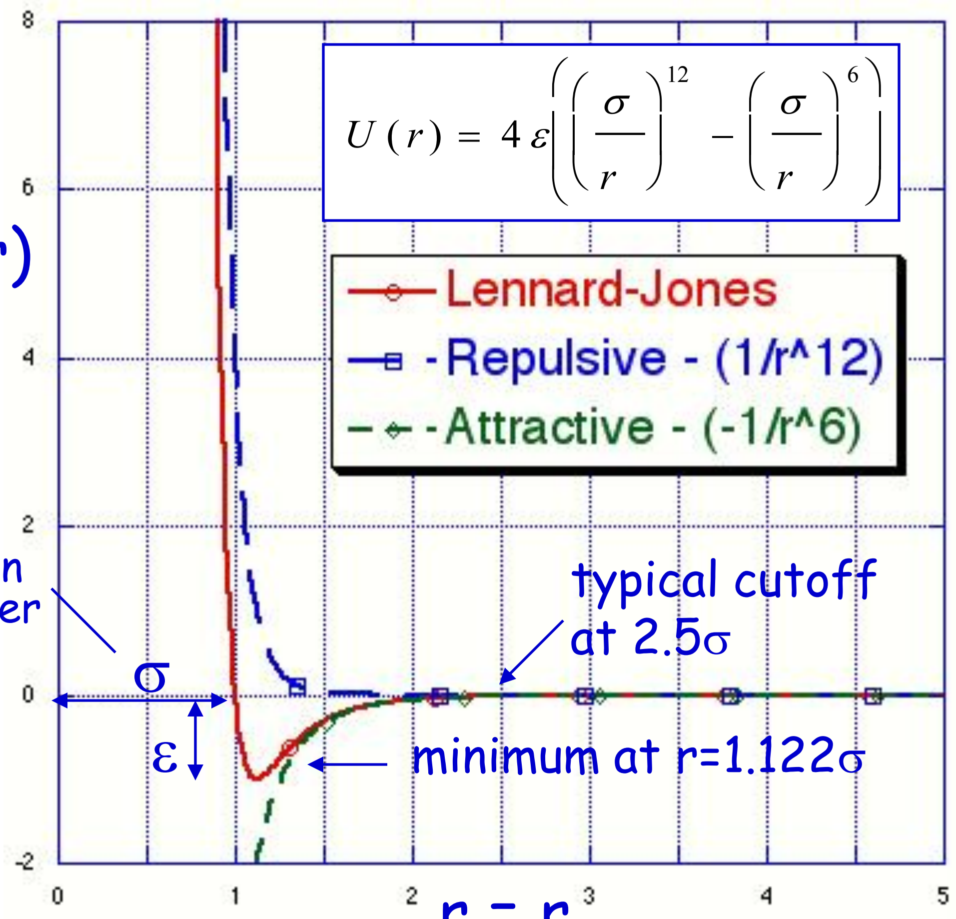
Van der Waals interactions

- The most popular model of the van der Waals non-bonded interactions between atoms is the Lennard-Jones potential.



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

U(r)

Collision diameter

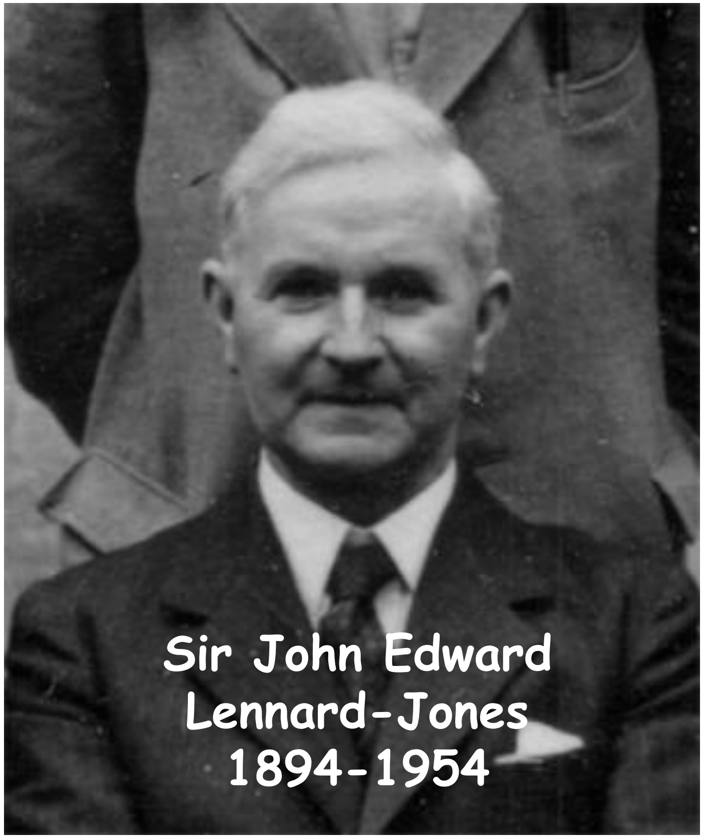
σ

ε

typical cutoff at 2.5σ

minimum at r=1.122σ

$r = r_{ij}$



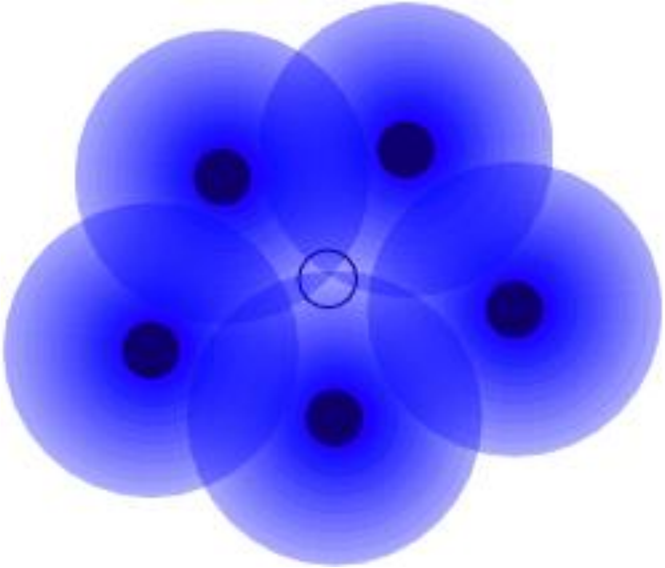
Sir John Edward Lennard-Jones 1894-1954

Metals

- Embedded atom method

$$E_t = \sum_i F(\rho_i) + \frac{1}{2}\sum_i \sum_{j \neq i} \phi\left(r_{ij}\right)$$

$$\rho_i = \sum_{j \neq j} f\left(r_{ij}\right)$$

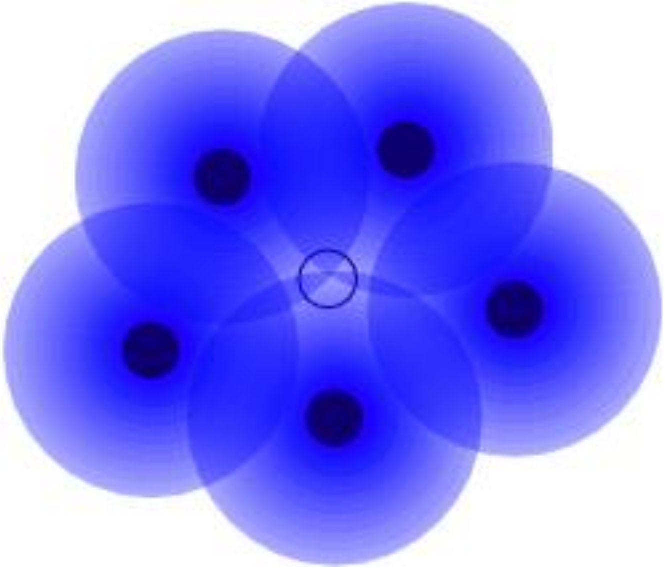


Metals

- Embedded atom method

$$f(r) = f_e e^{-\beta\left(r/r_e - 1\right)}$$

$$\phi(r) = \phi_e e^{-\gamma\left(r/r_e - 1\right)}$$



$$F(\rho) = -E_c\left(1 - \ln\left(\rho/\rho_e\right)^{\alpha/\beta}\right)\left(\rho/\rho_e\right)^{\alpha/\beta} - 6\phi_e\left(\rho/\rho_e\right)^{\gamma/\beta}$$

Embedded atom method

$$F(\rho) = -E_c\left(1 - \ln(\rho/\rho_e)^{\alpha/\beta}\right)(\rho/\rho_e)^{\alpha/\beta} - 6\phi_e(\rho/\rho_e)^{\gamma/\beta}$$

$$\alpha = \left(\frac{\Omega B}{E_c}\right)^{1/2}$$

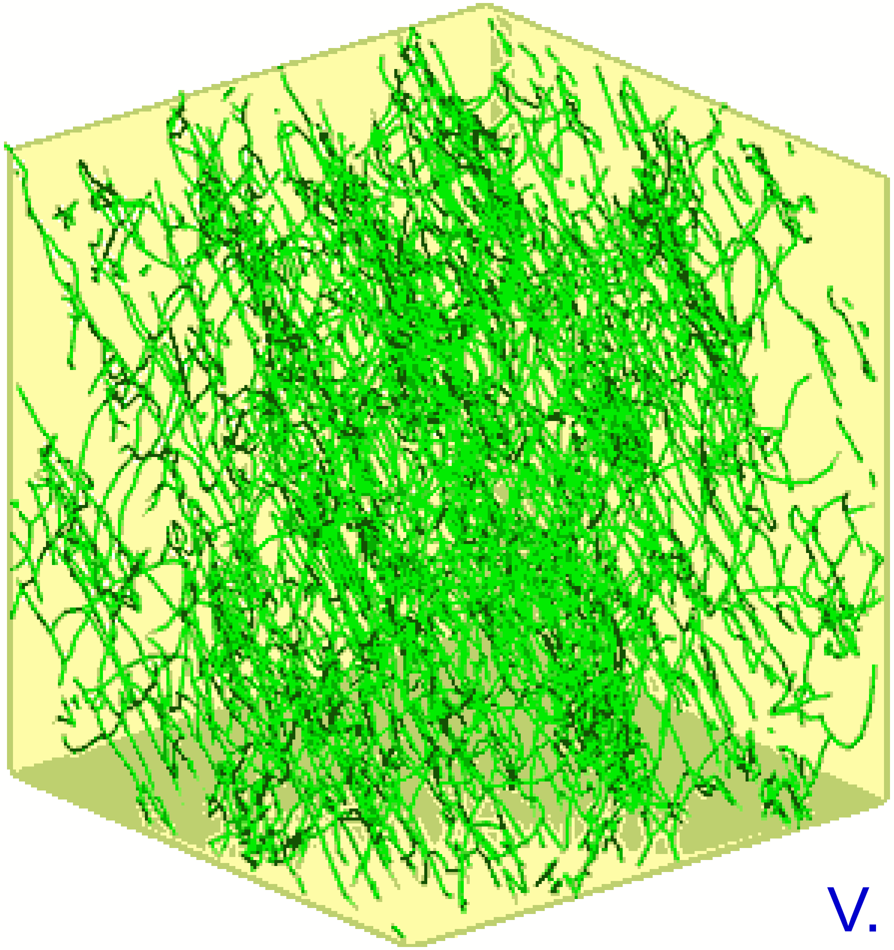
E_c = cohesive energy

B = bulk modulus

Ω = atomic volume

Other factors are model parameters that are determined based on lattice parameter, bulk modulus, shear modulus, cohesive energy, vacancy formation energy, and average electron density

Formation of dislocations in metals



V. Bulatov, LLNL

Simulation of Laser Ablation on Metal Surface

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

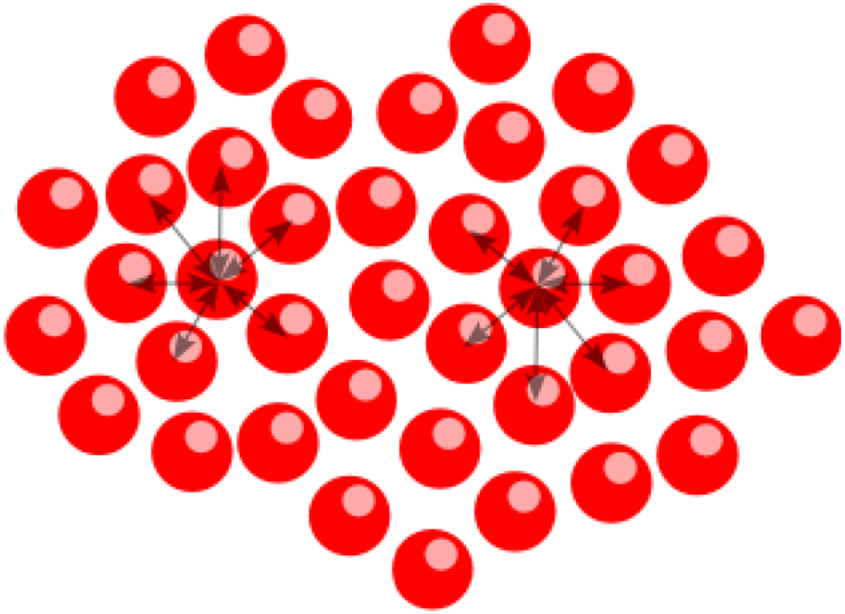
G.H. Gilmer, LLNL
$3 \cdot 10^6$ atoms x 140 ps

Embedded atom method

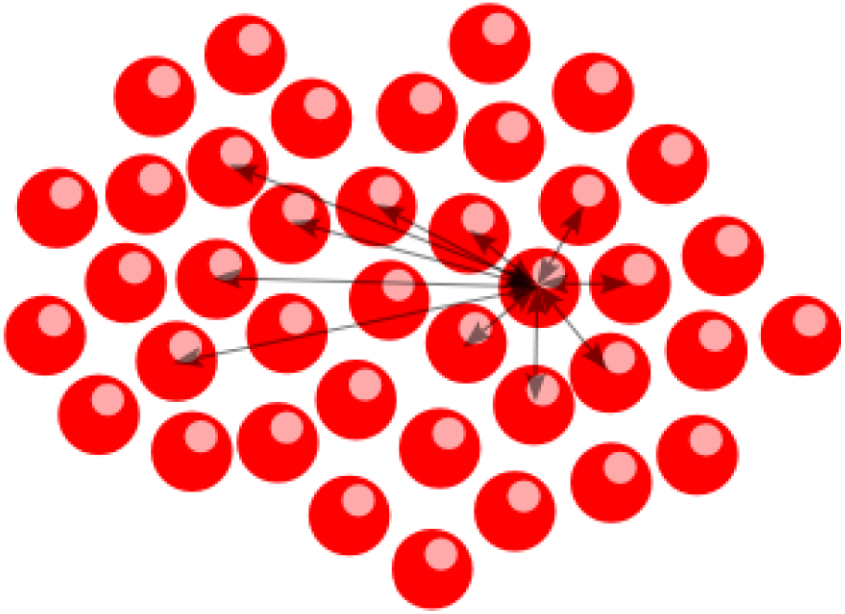
- Simple closed form
- Computationally efficient
- Based on density functional theory concept
- Accurate for highly symmetric structures (FCC, BCC)
- Accurate for spherical electron orbitals

- Increasingly inaccurate for complex atomic electron configurations and low-symmetry structures

Range of interactions



Short-range interactions:
1/2·N·N_C force calculations



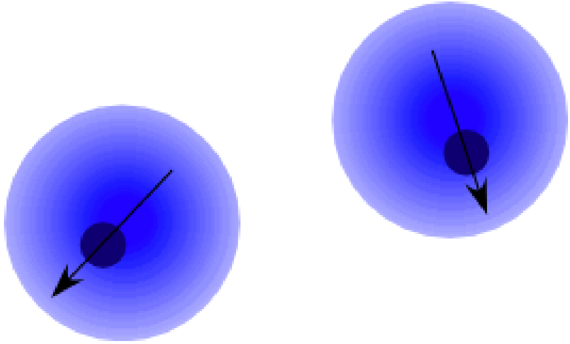
Long-range interactions:
1/2·N·(N-1) force calculations

Ionic Materials

- Coulomb interactions are fundamental to atomistic systems
- Coulomb interactions have long-range effects

$$\phi^{CC} = \frac{1}{4\pi\varepsilon_0}\sum_{i}^{N}\sum_{j>i}^{N}\frac{q_i q_j}{r_{ij}}$$

Ionic Materials



- Degree of charge localization can vary
- Charge polarization effects can be accounted for analytically

$$\phi^{CD} = \frac{1}{4\pi\varepsilon_0}\sum_{i}^{N}\sum_{j>i}^{N}\frac{q_i}{r_{ij}^3}\vec{\mu}_j\cdot\vec{r}_{ij} \qquad \phi^{DC} = \frac{1}{4\pi\varepsilon_0}\sum_{i}^{N}\sum_{j>i}^{N}\frac{q_j}{r_{ij}^3}\vec{\mu}_i\cdot\vec{r}_{ij}$$

$$\phi^{DD} = \frac{1}{4\pi\varepsilon_0}\sum_{i}^{N}\sum_{j>i}^{N}\left[\frac{3}{r_{ij}^5}\left(\vec{\mu}_i\cdot\vec{r}_{ij}\right)\left(\vec{\mu}_j\cdot\vec{r}_{ij}\right)-\frac{\vec{\mu}_i\cdot\vec{\mu}_j}{r_{ij}^3}\right]$$

Ionic Materials

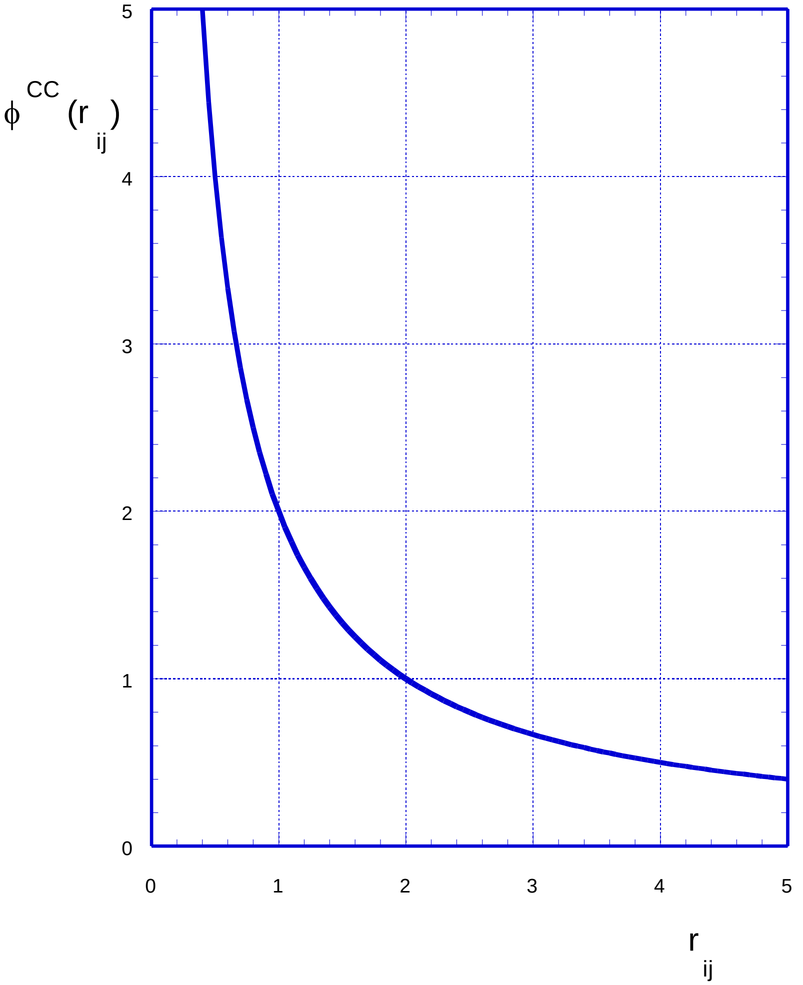
- Repulsion due to electron orbital overlap
- Repulsion due to interactions between nuclei

… handled by empirical function

$$\phi^{BM} = \sum_{i}^{N} \sum_{j=1}^{NC} A_{ij} \left(1 + \frac{z_i}{n_i} + \frac{z_j}{n_j} \right) e^{(\sigma_i + \sigma_j - r_{ij})\rho_{ij}}$$

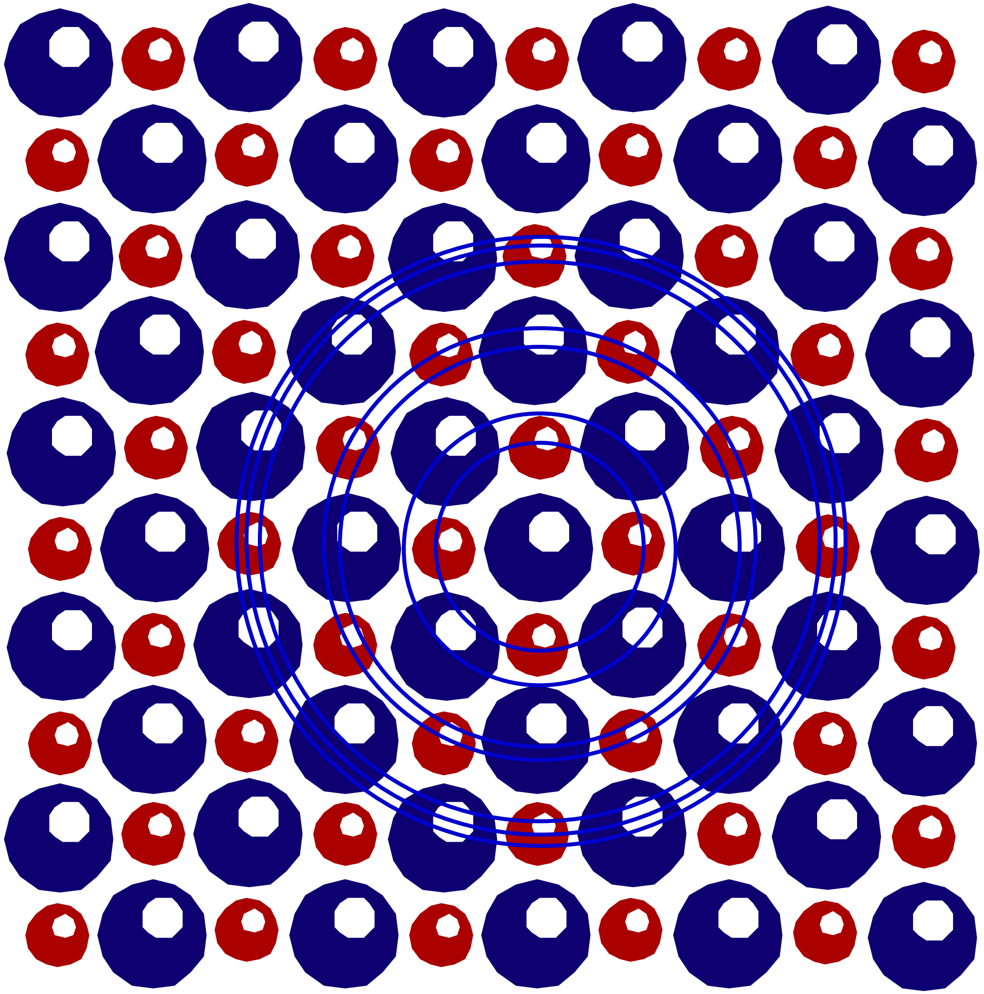
The trouble with Coulomb interactions

$$\phi^{CC} = \frac{1}{4\pi\varepsilon_0}\sum_{i}^{N}\sum_{j>i}^{N}\frac{q_i q_j}{r_{ij}}$$



The trouble with Coulomb interactions

Conditionally convergent …
I.e., depends on how one adds it up …



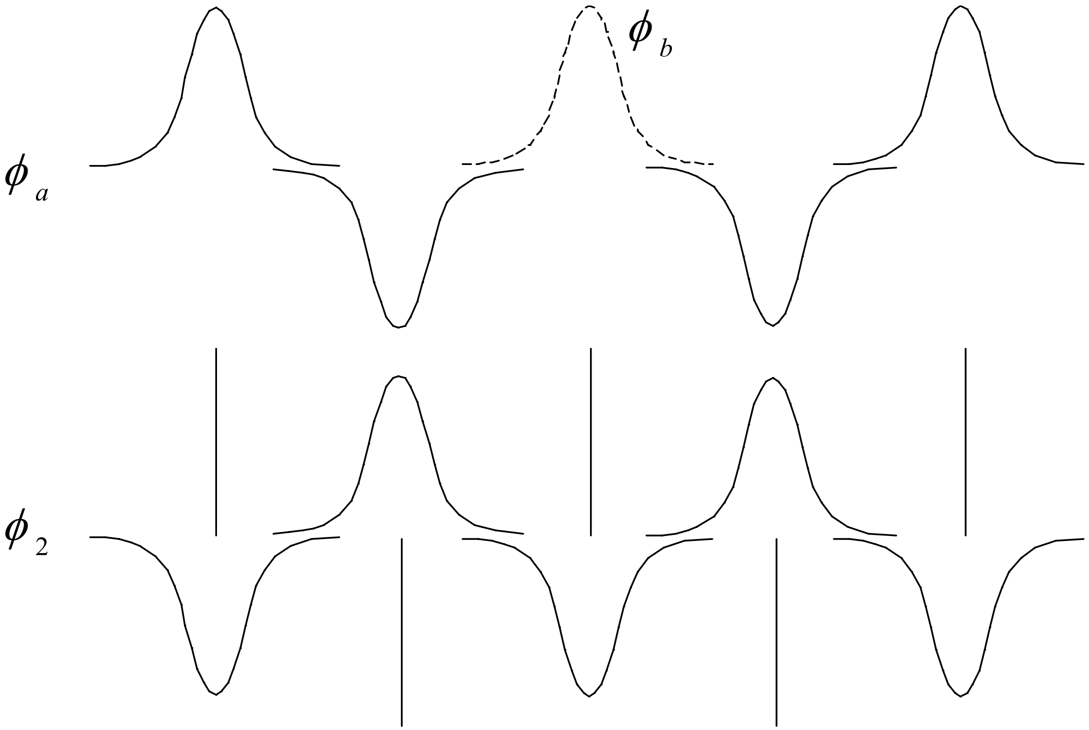
Long-range interactions: Ewald summation method

Total potential energy of one ion at the reference point. Summation decomposed into two parts, one to be evaluated in real space, the other in reciprocal space. …

$$\phi = \phi_1 + \phi_2$$

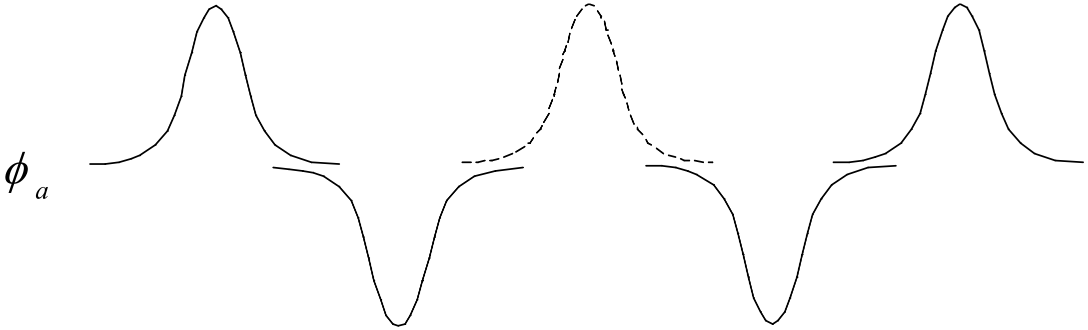
$$\phi_1 = \phi_a - \phi_b$$

$$\rho\left(\mathbf{r} - \mathbf{r}_l\right) = q_l \left(\frac{\eta}{\pi}\right)^{3/2} e^{-\eta\left(r - r_l\right)^2}$$



Reciprocal space

$$\nabla^2 \phi_a = -4\pi\rho$$

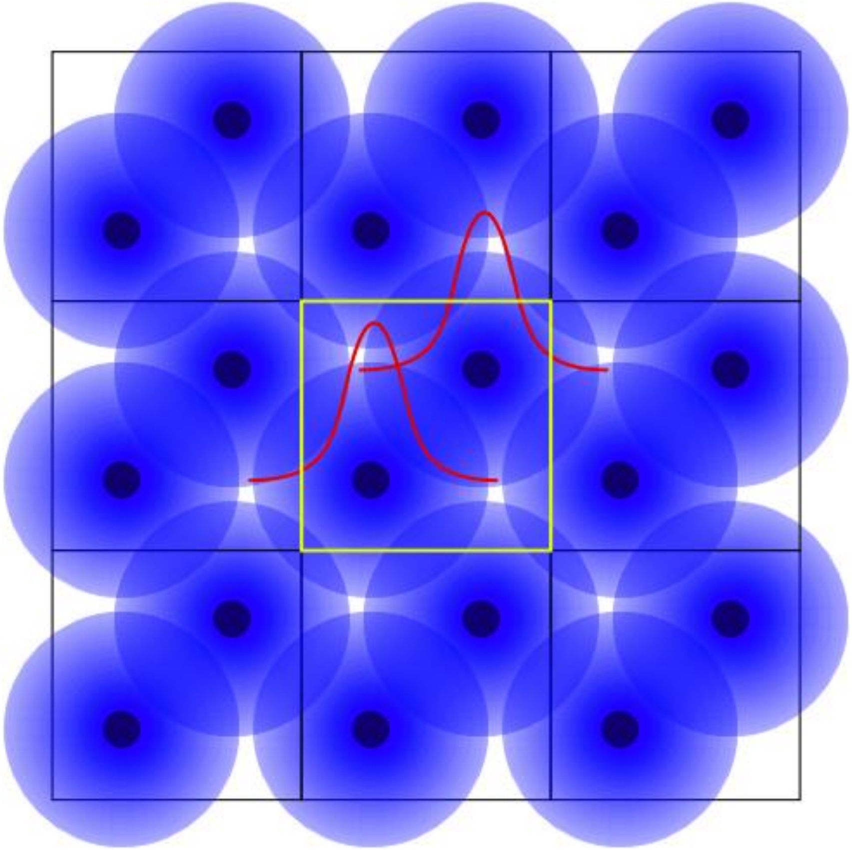


$$\phi_a = \sum_{\mathbf{G}} c_G e^{i\mathbf{G}\mathbf{r}}$$

$$\rho = \sum_{\mathbf{G}} \rho_G e^{i\mathbf{G}\mathbf{r}}$$

$$\sum_{\mathbf{G}} G^2 c_G e^{i\mathbf{G}\mathbf{r}} = 4\pi \sum_{\mathbf{G}} \rho_G e^{i\mathbf{G}\mathbf{r}} \quad \Rightarrow c_G = 4\pi\rho_G / G^2$$

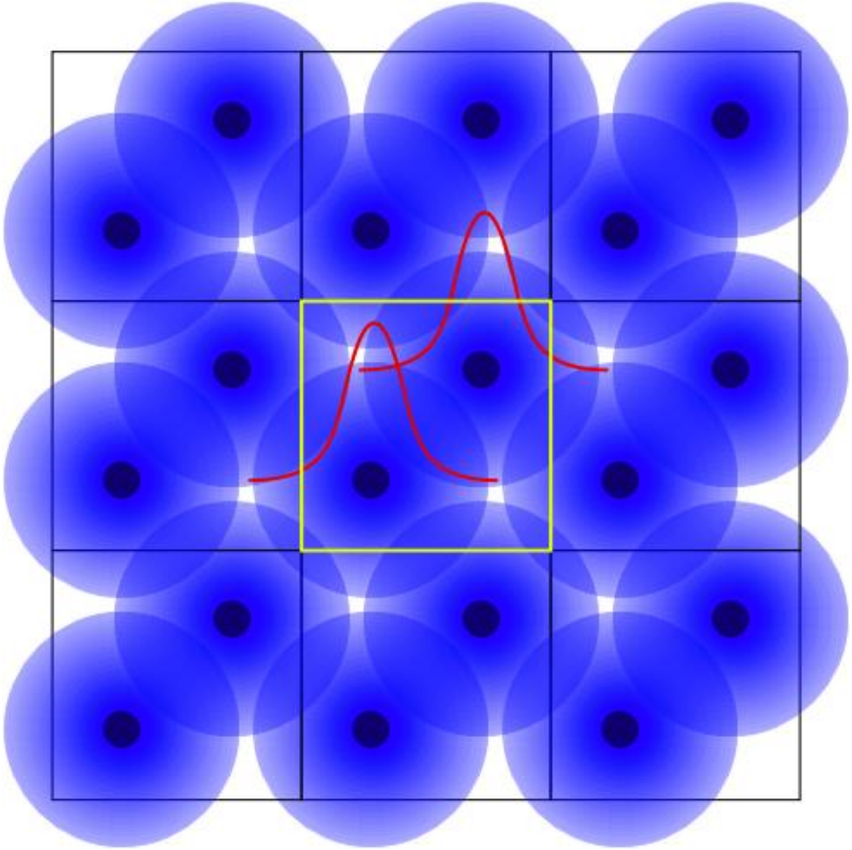
Reciprocal space



$$\rho = \sum_{\mathbf{G}} \rho_G e^{i\mathbf{G}\mathbf{r}}$$

$$\rho = \sum_{l} \rho(\mathbf{r} - \mathbf{r}_l) = \sum_{l} q_l (\eta/\pi)^{3/2} e^{-\eta (r - r_l)^2}$$

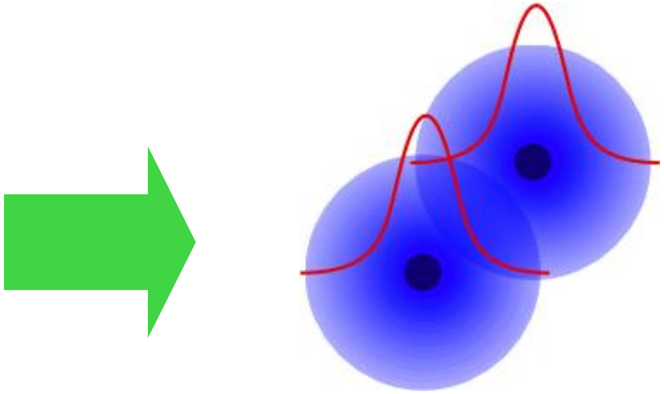
Reciprocal space



$$\rho_G \int_{cell} e^{i\mathbf{Gr}} e^{-i\mathbf{Gr}} \, d\mathbf{r} = \rho_G \Delta$$

$$\int_{cell} \rho e^{-i\mathbf{Gr}} \, d\mathbf{r} = \int_{cell} \left(\sum_l q_l (\eta/\pi)^{3/2} e^{-\eta (r-r_l)^2} \right) e^{-i\mathbf{Gr}} \, d\mathbf{r}$$

Reciprocal space



$$\rho_G \int_{cell} e^{i\mathbf{Gr}} e^{-i\mathbf{Gr}} \, d\mathbf{r} = \rho_G \Delta$$

$$\int_{cell} \rho e^{-i\mathbf{Gr}} \, d\mathbf{r} = \int_{space} \left(\sum_t q_t (\eta/\pi)^{3/2} e^{-\eta(r-r_t)^2} e^{-i\mathbf{Gr}} \right) d\mathbf{r}$$

Reciprocal space

$$\rho_G \int_{cell} e^{i\mathbf{Gr}} e^{-i\mathbf{Gr}} \, d\mathbf{r} = \rho_G \Delta = \int_{space} \left(\sum_t q_t (\eta/\pi)^{3/2} e^{-\eta (r - r_t)^2} e^{-i\mathbf{Gr}} \right) d\mathbf{r}$$

$$\rho_G \Delta = \sum_t q_t (\eta/\pi)^{3/2} e^{-i\mathbf{Gr}_t} \int_{space} e^{-\left(i\mathbf{G}\cdot\xi + \eta \xi^2\right)} d\mathbf{r}$$

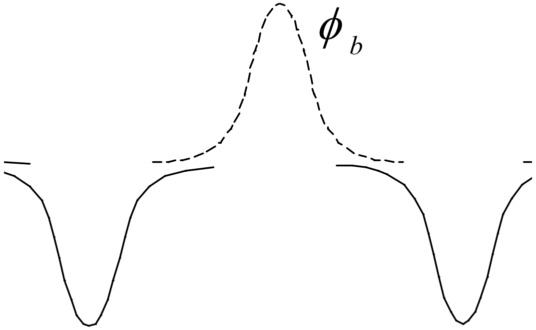
$$\rho_G \Delta = \left(\sum_t q_t e^{-i\mathbf{Gr}_t} \right) e^{-G^2/4\eta} = S(G) e^{-G^2/4\eta}$$

Reciprocal space

$$\phi_a = \frac{4\pi}{\Delta} \sum S(\mathbf{G}) G^{-2} e^{\left(i\mathbf{G}\cdot\mathbf{r} - G^2/4\eta\right)}$$

At r = 0: $$\phi_a = \frac{4\pi}{\Delta} \sum S(\mathbf{G}) G^{-2} e^{-G^2/4\eta}$$

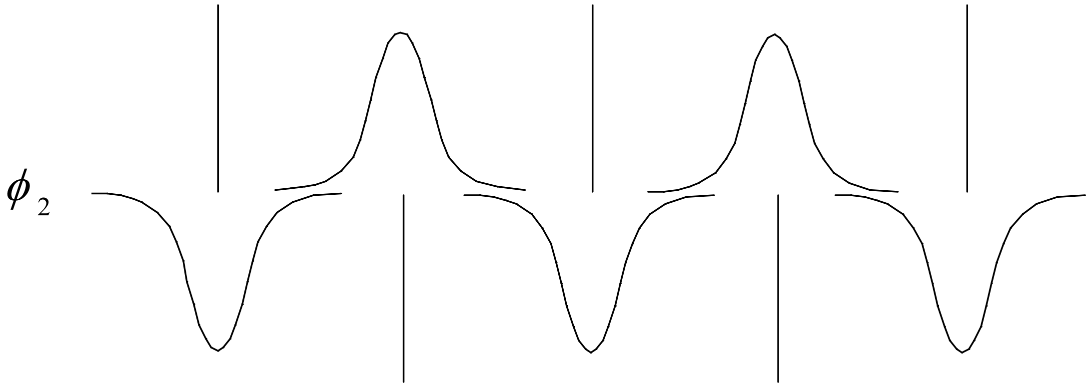
Self-energy correction



$$\phi_b = \int_0^{\infty} 4\pi r^2 (\rho/r)\,dr = 2q_t(\eta/\pi)^{1/2}$$

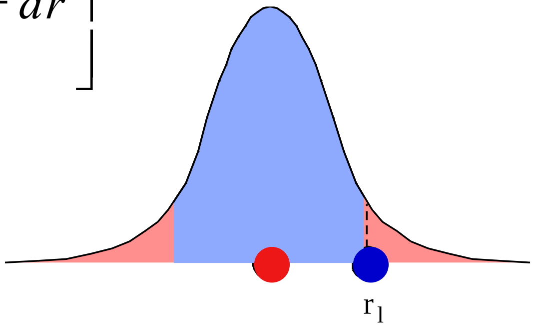
$$\phi_1 = \frac{4\pi}{\Delta} \sum S(\mathbf{G}) G^{-2} e^{-G^2/4\eta} - 2q_t(\eta/\pi)^{1/2}$$

Real space



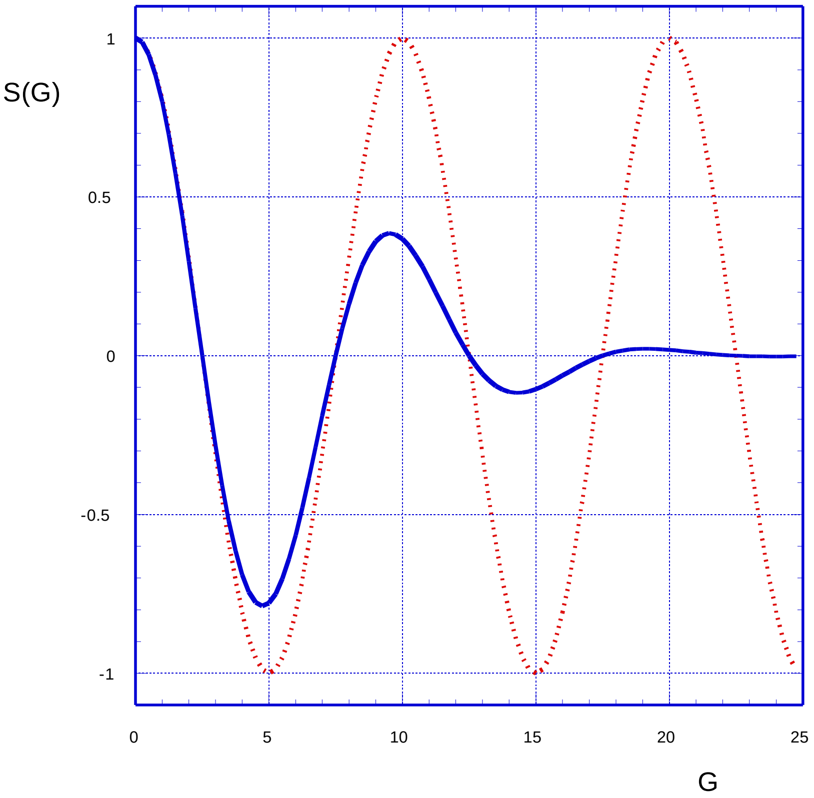
$$\phi_2 = \sum_l q_l \left[\frac{1}{r_l} - \frac{1}{r_l}\int_0^{r_l} \rho(r)\,dr - \int_{r_l}^{\infty} \frac{\rho(r)}{r}\,dr \right]$$

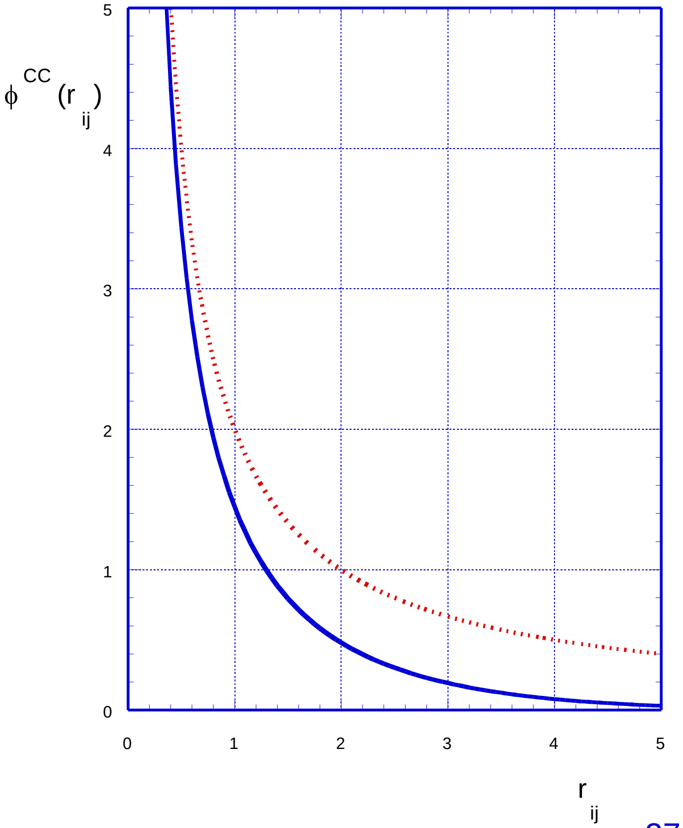
$$\phi_2 = \sum_l \frac{q_l}{r_l}\,\mathrm{erfc}\left(\sqrt{\eta r_l}\right)$$



Convergence in real and reciprocal space

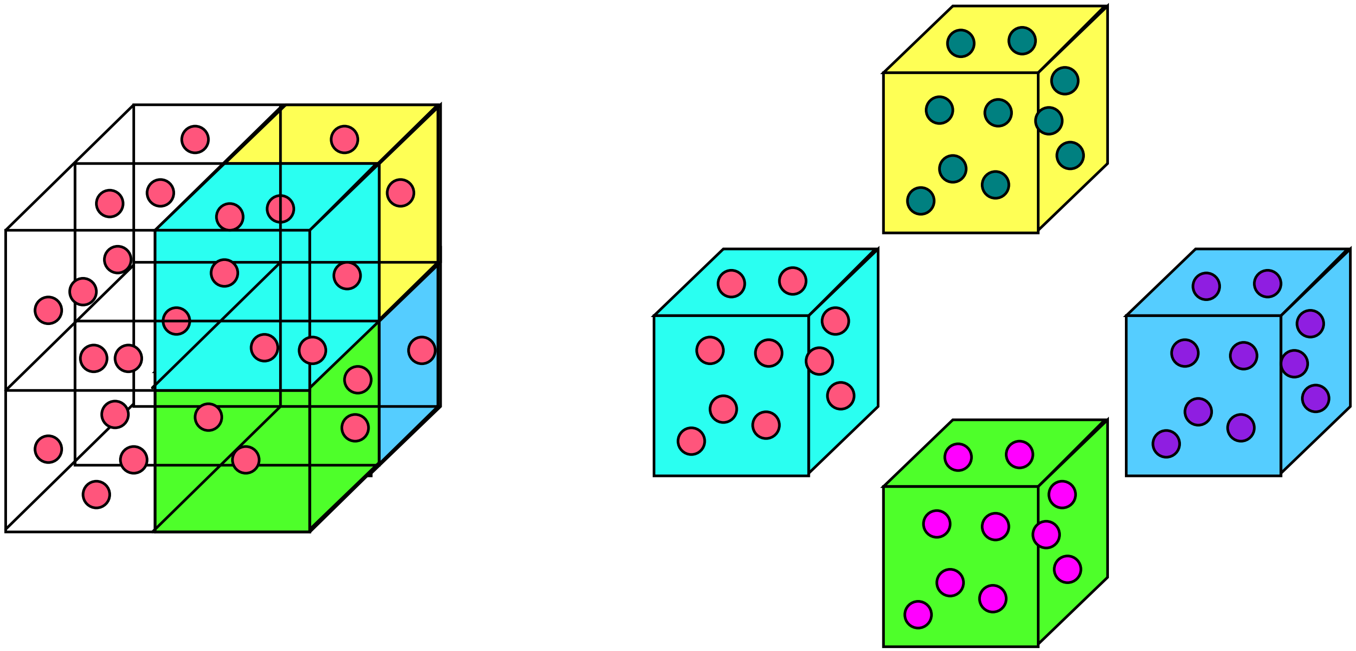
$$\phi_i = \frac{4\pi}{\Delta}\sum S(\mathbf{G})G^{-2}e^{-G^2/4\eta} - 2q_i(\eta/\pi)^{1/2} + \sum_l \frac{q_l}{r_l}\operatorname{erfc}\left(\sqrt{\eta}\, r_l\right)$$



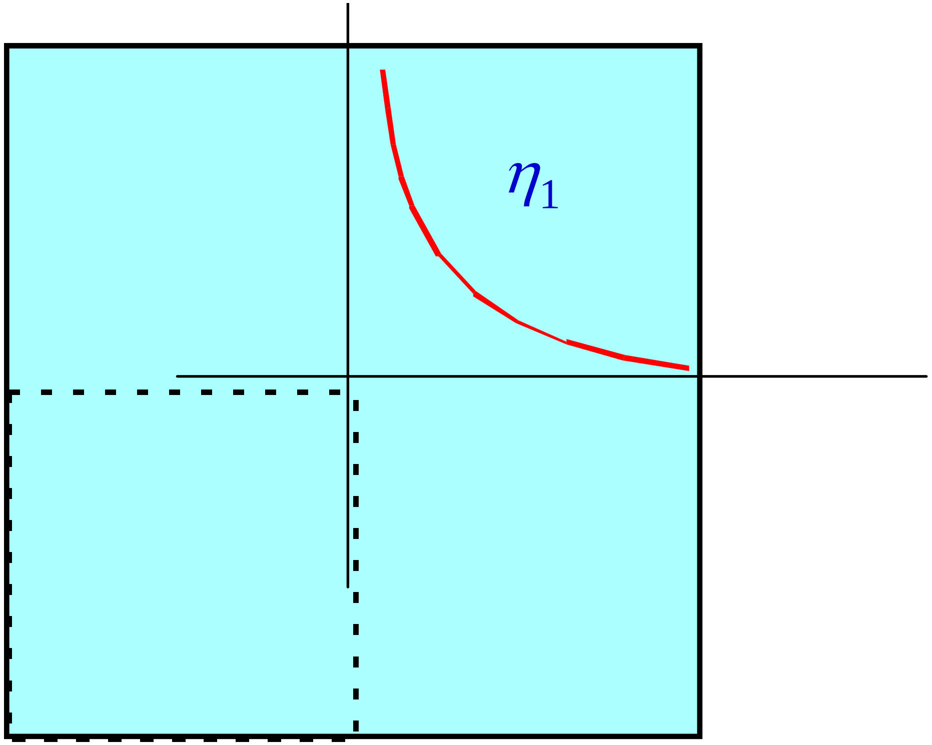


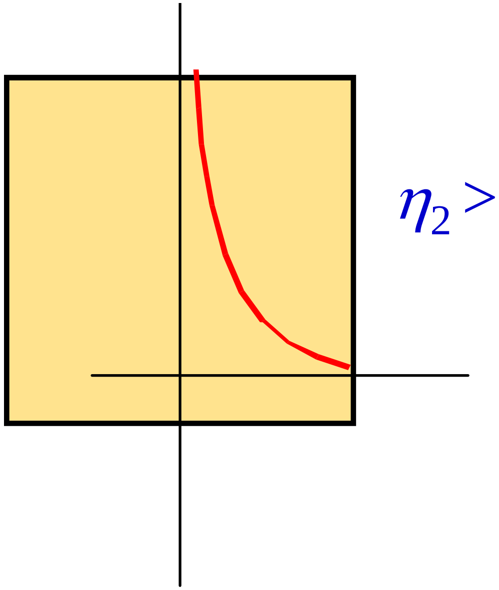
Molecular Simulation

- Massively parallel molecular dynamics
  - Spatial domain decomposition - large systems
  - Replicated data - long simulation times



Spatial Decomposition and Ewald Sum



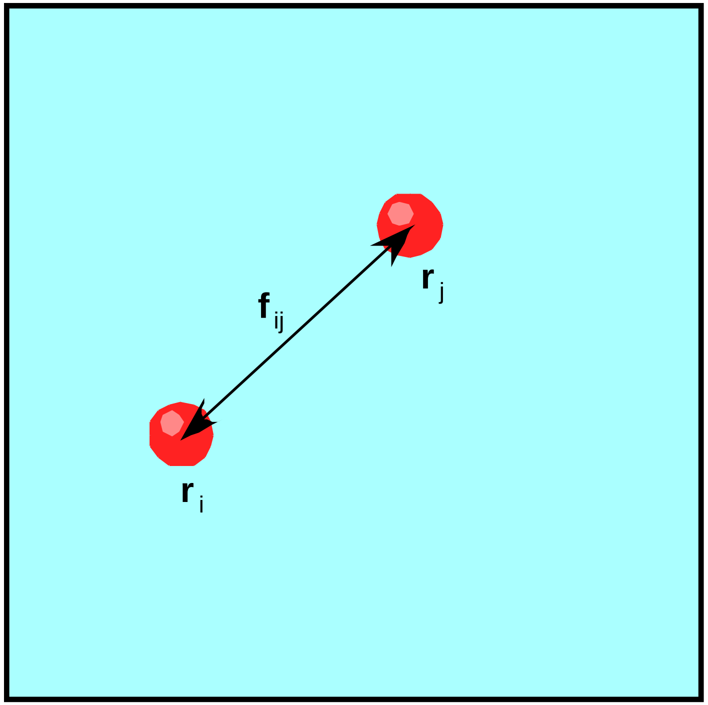


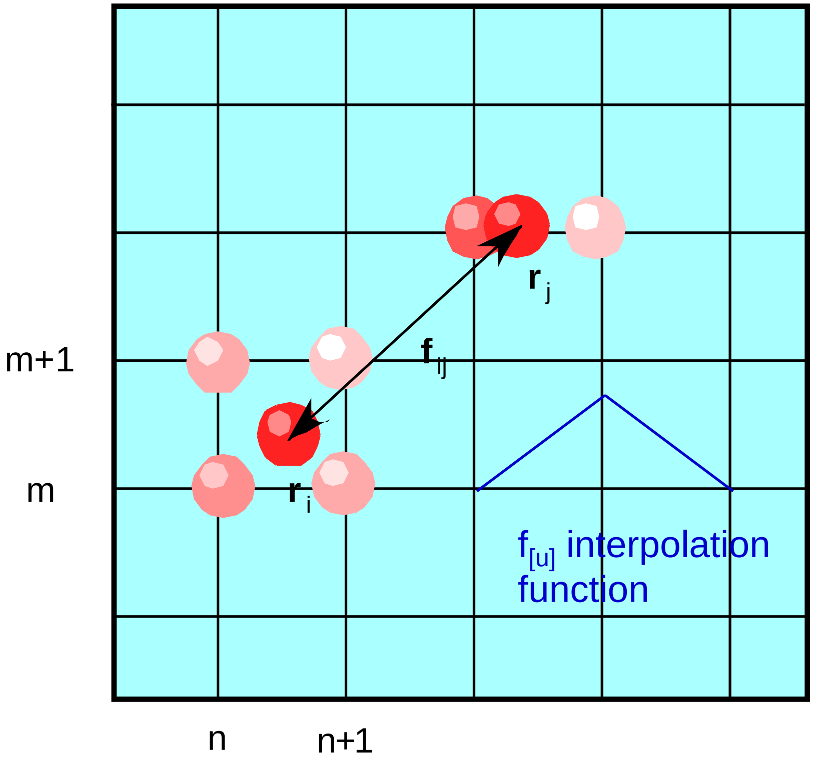
Requires larger **G**

$$\phi_i = \frac{4\pi}{\Delta}\sum_{\mathbf{G}} S(\mathbf{G})\,G^{-2}e^{-G^2/4\eta} - 2q_i(\eta/\pi)^{1/2} + \sum_l \frac{q_l}{r_l}\,\mathrm{erfc}\left(\sqrt{\eta}\,r_l\right)$$

Particle-Mesh Ewald Method

$$S(G)=\sum_t q_t e^{-i\mathbf{G}\mathbf{r}_t}=\sum_t q_t e^{-i(hx_t+ky_t+lz_t)}$$





$$S(G)=\sum_t f_{[u]}(q)e^{-i\mathbf{G}[\mathbf{u}]}=\sum_t q_t e^{-i(hu+kv+lw)}$$

Example: fracture in brittle materials

QuickTime™ and a
GIF decompressor
are needed to see this picture.

Overview …

- Historical perspective
- Simulation methodologies
  - Theoretical background
  - Monte Carlo simulation
  - Molecular dynamics simulation
  - Reverse Monte Carlo
- Force fields
- Information retrieval
  - Statistical mechanical formalisms
  - Structural analyses
  - Dynamics
- Application examples

Ionic materials

- Fundamentally correct
- Accurate for strongly ionic compounds, including many ceramics and salts …
- Long-range interactions cause computational expense

- Increasingly inaccurate when partially covalent interactions and charge transfer occurs

Questions?

“Universal” force fields

- Goal is to develop force field that can be to describe intra- and inter-molecular interactions for arbitrary molecules
  - ❖ UFF (Universal force field)
    - A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard and W. M. Skiff, "UFF, a Full Periodic-Table Force-Field for Molecular Mechanics and Molecular-Dynamics Simulations," J. Am. Chem. Soc, 114, 10024-10035 (1992)
    - Used for many nanoscale carbon structures (buckyballs, nanotubes)
  - ❖ COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies)
    - Sun, H; Rigby, D. "Polysiloxanes: Ab Initio Force Field And Structural, Conformational And Thermophysical Properties", *Spectrochimica Acta (A)* ,**1997** ,*53* , 130, and subsequent references
    - http://www.accelrys.com/cerius2/compass.html
  - ❖ AMBER (Assisted Model Building with Energy Refinement)
    - Both a force field and a simulation package for biomolecular simulations
    - http://amber.scripps.edu

$$E_{total} = \sum_{bonds} K_r (r - r_{eq})^2 + \sum_{angles} K_\theta (r - r_\theta)^2 + \sum_{dihedrals} \frac{V_n}{2} [1 + \cos(n\phi - \gamma)]$$

$$+ \sum_{i<j} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^{6}} + \frac{q_i q_j}{\varepsilon R_{ij}} \right] + \sum_{H-bonds} \left[\frac{C_{ij}}{R_{ij}^{12}} - \frac{D_{ij}}{R_{ij}^{10}} \right]$$

“Universal” force fields

- CHARMM (Chemistry at HARvard Macromolecular Mechanics)
  - Both a force field and a simulation package for biomolecular simulations
  - B. R. Brooks, R. E. Bruccoleri, B. D. Olafson, D. J. States, S. Swaminathan, and M. Karplus, “A Program for Macromolecular Energy, Minimization, and Dynamics Calculations, J. Comp. Chem. 4 (1983) 187-217 (1983)
  - http://www.charmm.org/
- Others
  - GROMOS (http://www.igc.ethz.ch/gromos)
  - Jorgensen’s Optimized Potential for Liquid Simulation (OPLS) (http://zarbi.chem.yale.edu)
  - DREIDING (Mayo, S. L., Olafson, B. D. & Goddard, W. A. Dreiding - a Generic Force-Field for Molecular Simulations. Journal of Physical Chemistry 94 (1990) 8897-8909)
- Specific systems
  - Alkanes and related systems
    - SKS: B. Smit, S. Karaborni, and J.I. Siepmann, `Computer simulation of vapor-liquid phase equilibria of n-alkanes', J. Chem. Phys. 102 , 2126-2140 (1995); `Erratum', 109 , 352 (1998)
    - TraPPE: Siepmann group (http://siepmann6.chem.umn.edu)

Latest trends: Charge transfer

- Charge localization depends on environment
  - Chemical nature of surrounding atoms
  - Local structure

Electronegativity $$\chi_i^0 = \left(\frac{\partial E}{\partial q_i}\right)_{i0} = 1/2\,(IP + EA)$$

Atomic hardness $$J_{ii}^0 = \left(\frac{\partial^2 E}{\partial q_i^2}\right)_{i0} = IP - EA$$

IP = first ionization potential; EA = electron affinity

Charge transfer

Energy of an isolated atom: $E_i(q) = E_i(0) + \chi_i^0 q_i + 1/2\, J_{ii}^0 q_i^2 + \ldots$

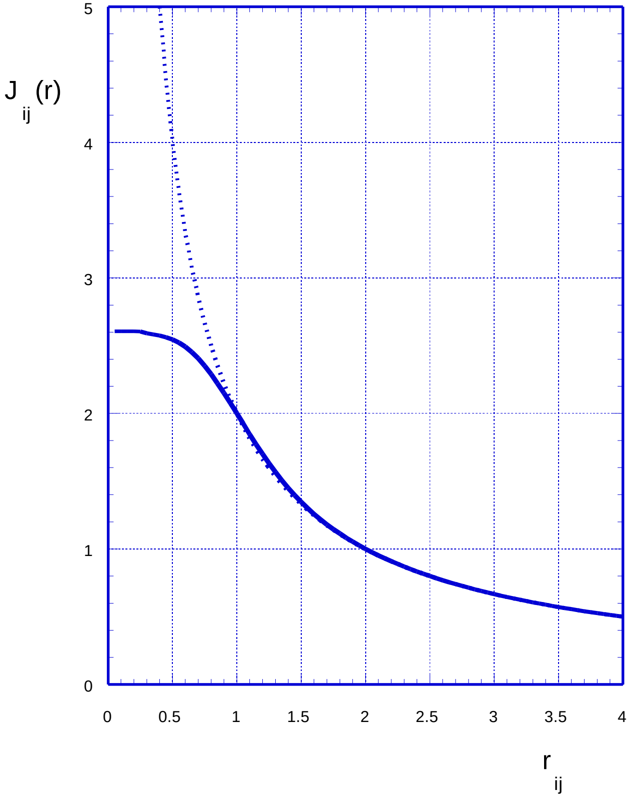
Energy of an N atoms:

$$E(q_1,\ldots,q_N) = \sum_i^N E_i(0) + \chi_i^0 q_i + 1/2\, J_{ii}^0 q_i^2 + \sum_i^N q_i \sum_{j>i}^N q_j J_{ij}$$

$$= \sum_i^N E_i(0) + \chi_i^0 q_i + \frac{1}{2}\sum_{i=1}^N \sum_{j=1}^N q_i q_j J_{ij}$$

Charge transfer

$$J_{ij}(r) = \int \rho_i(r_i) \frac{1}{\mathbf{r}_i - \mathbf{r}_j - \mathbf{r}} \rho_j\left(r_j\right) d\mathbf{r}_i d\mathbf{r}_j$$



Spherically symmetric Slater-type orbitals are assumed for $\rho(r)$

Charge transfer

Chemical potential of electrons associated with atom *i*:

$$\frac{\partial E}{\partial q_i} = \chi_i = \chi_i^0 + \sum_{j=1}^{N} q_j J_{ij}$$

Equilibrium requires $\chi_1 = \chi_2 = \chi_3 = \ldots = \chi_N$, which yields N–1 equations. In addition, charge neutrality requires that

$$\sum_{j=1}^{N} q_j = 0$$

Charge transfer

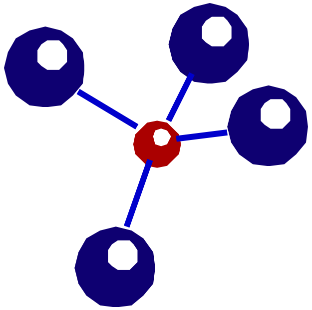
Solving the system of equations yields the equilibrium charges

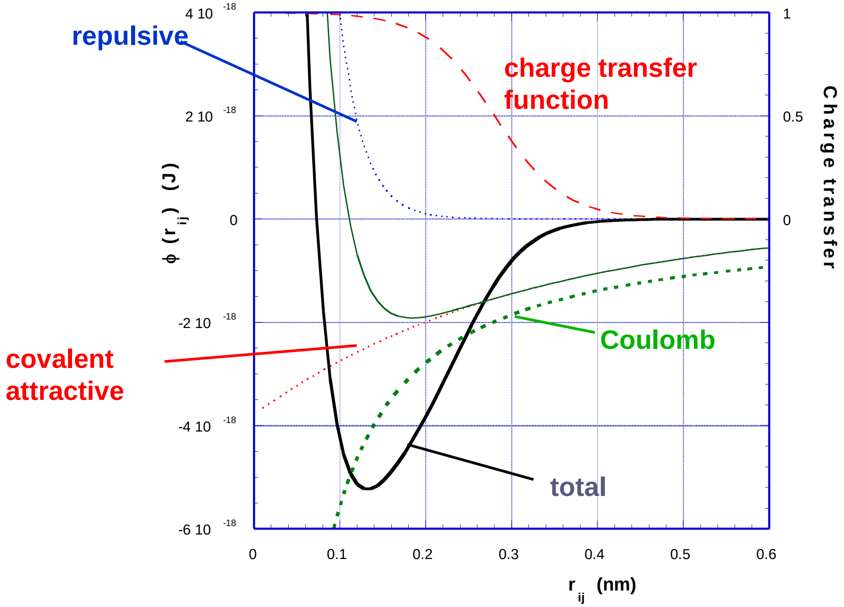
$$\begin{pmatrix} 1 & \cdots & 1 \\ J_{21} - J_{11} & & J_{2N} - J_{1N} \\ & \ddots & \\ J_{N1} - J_{11} & & J_{NN} - J_{1N} \end{pmatrix} \begin{pmatrix} q_1 \\ q_2 \\ \vdots \\ q_N \end{pmatrix} = \begin{pmatrix} 0 \\ \chi_1^0 - \chi_2^0 \\ \vdots \\ \chi_1^0 - \chi_N^0 \end{pmatrix}$$

Equilibrium charges depend on the chemical nature of species and on the geometry of the configuration, by virtue of the fact that

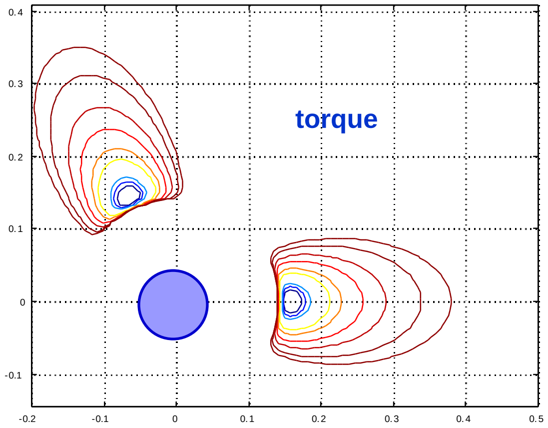
$$J_{ij}(r) = \int \rho_i(r_i) \frac{1}{\mathbf{r}_i - \mathbf{r}_j - \mathbf{r}} \rho_j(r_j) d\mathbf{r}_i d\mathbf{r}_j$$

Covalently bonded materials





$$\phi^{3B} = \sum_{i=1}^{N}\sum_{j=1}^{NC-1}\sum_{k=j-1}^{NC}\left(\varphi_{ij}+\varphi_{ik}\right)\Lambda\left(\theta_{ijk}\right)$$



- Directional character of bonds

$$\Lambda\left(\theta_{ijk}\right)$$

- Covalent bonding term (empirical), e.g.,

$$\varphi_{ij} = A_{ij}\left[e^{(\sigma_i+\sigma_j-r_{ij})\rho_{ij}} - \kappa_{ij}e^{-(\zeta_{ij}-r_{ij})\eta_{ij}}\left(1+e^{(r_{ij}-b_{ij})a_{ij}}\right)^{-1}\right]$$

Reactive force fields …

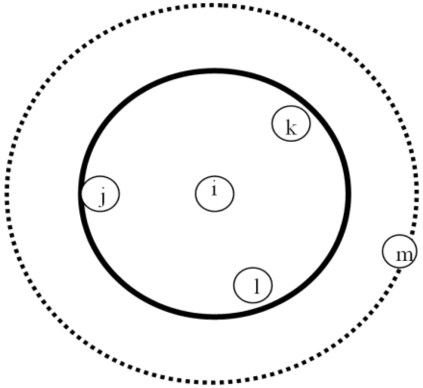
$$\phi^{3B} = \sum_{i=1}^{N}\sum_{j=1}^{NC-1}\sum_{k=j-1}^{NC}\left(\varphi_{ij}+\varphi_{ik}\right)\Lambda\left(\theta_{ijk}\right)$$

- Charge redistribution

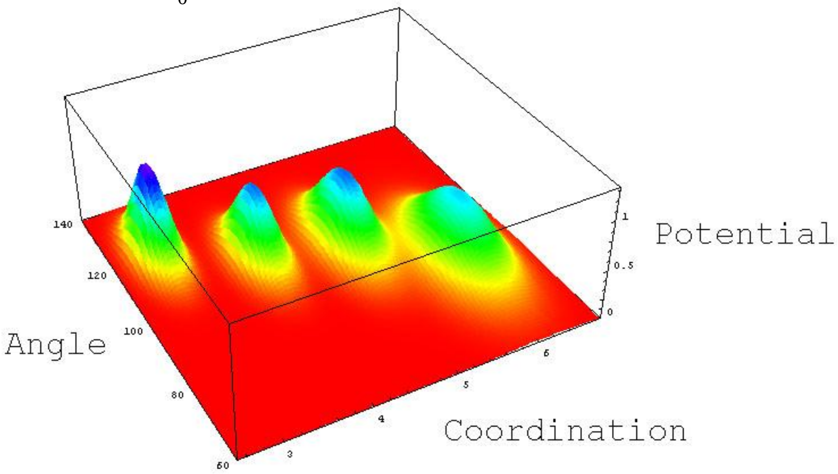
$$q_i = q_i^{o} + e\sum_{j=1}^{NC}\delta_{ij}\left(1+e^{b_{ij}\left(r_{ij}-a_{ij}\right)}\right)^{-1}$$

- Flexible coordination

$$\Lambda\left(\theta_{ijk}\right) = \sum_{Z_0=3}^{6} C_{Z_0}\, e^{-A_{Z_0}(Z_0-Z_i)^2}\, e^{-\gamma_{Z_0}(\bar{\theta}_{Z_0}-\theta_{ijk})^2}$$



$$Z_i = \sum_{j\neq i}^{N}\left(e^{(|r_{ij}|-a_Z)b_Z}+1\right)^{-1}$$



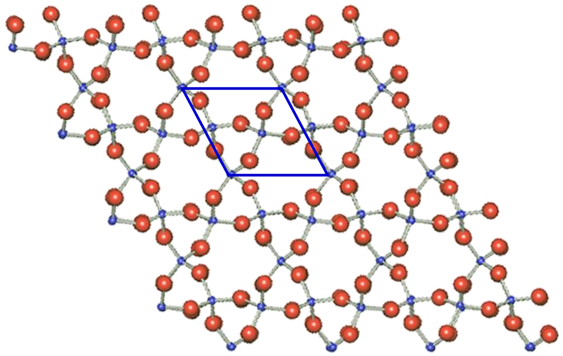
L. P. Huang and J. Kieffer,
J. Chem. Phys. **118**, 1487 (2003)

Force field parameterization

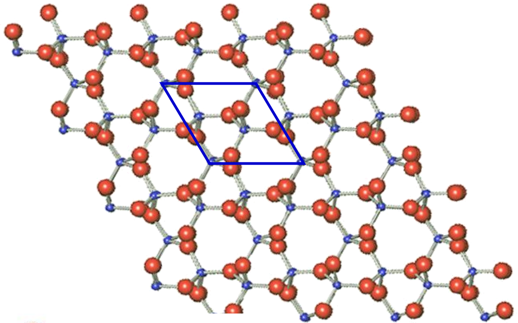
- Reproduce known structures (static properties)
  - density at ambient pressure
  - equation of state (density vs. pressure)
  - mechanical properties (elastic moduli, strength, etc.)
- Reproduce dynamic properties
  - melting temperatures
  - vibrational spectra
- Compare with results from *ab initio* calculations
  - bonding energies
  - Interatomic forces

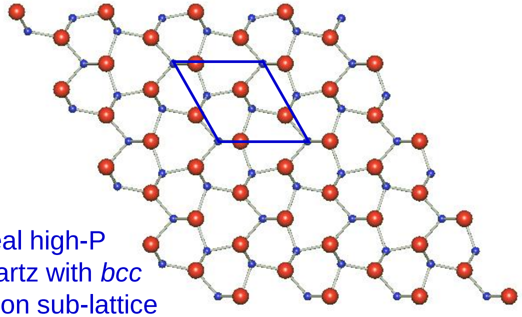
Crystalline silica polymorphs – one parameterization

α-quartz at **0 GPa**



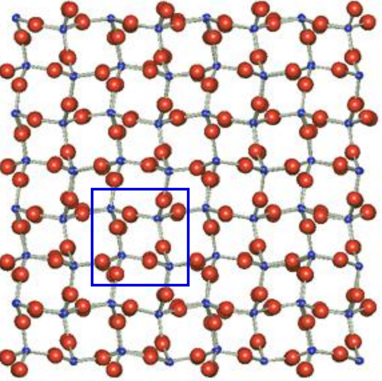
High-P quartz at **25 GPa**



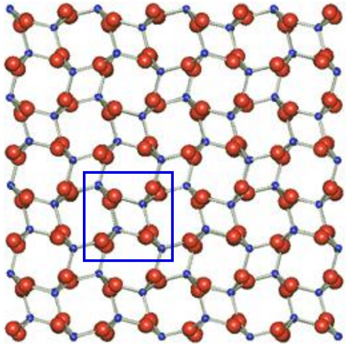


Ideal high-P quartz with *bcc* anion sub-lattice

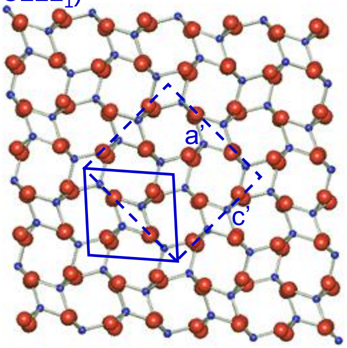
0 GPa (P$4_1 2_1 2$) α-cristobalite
a = 4.9 Å
b = 4.9 Å
c = 5.4 Å



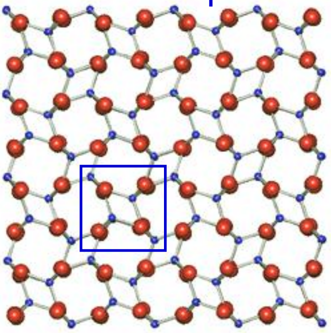
14 GPa (P$4_1 2_1 2$)



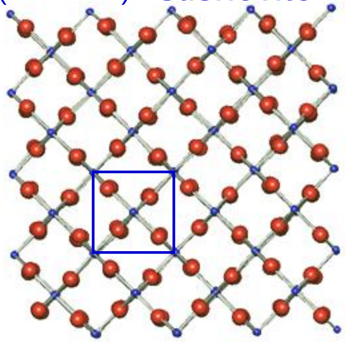
16 GPa (C222_1)
a' = 6.7 Å
b' = 5.7 Å
c' = 6.1 Å



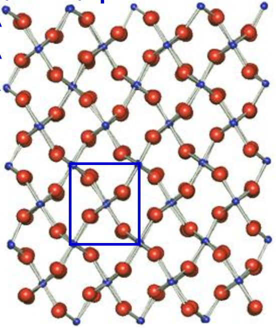
20 GPa (P$4_1 2_1 2$) X-I phase
a = 4.2 Å
b = 4.2 Å
c = 6.0 Å



25 GPa (P42/mnm) stishovite
a = 4.2 Å
b = 4.2 Å
c = 2.8 Å



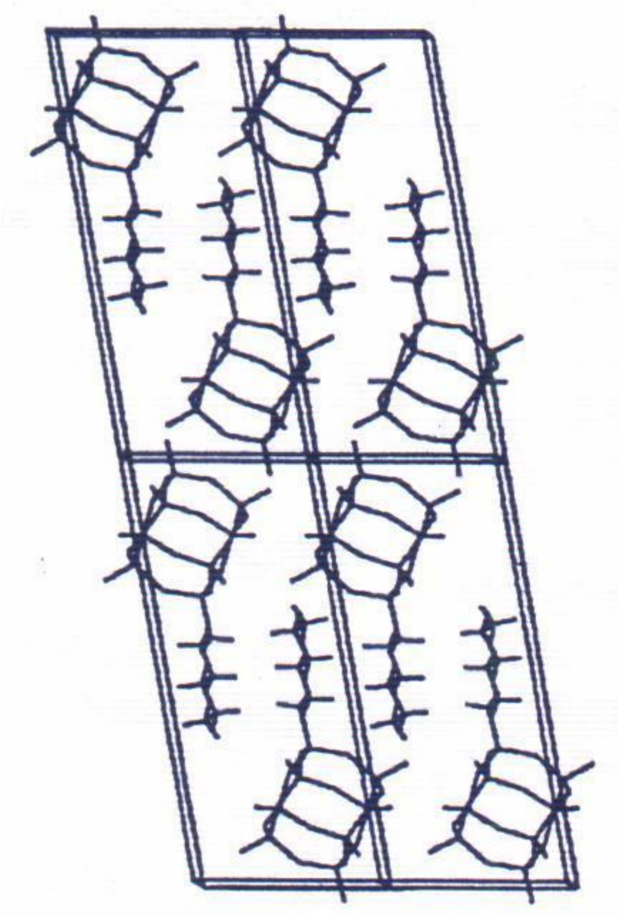
40 GPa (Pnnm) post-stishovite
a = 3.7 Å
b = 4.5 Å
c = 2.8 Å

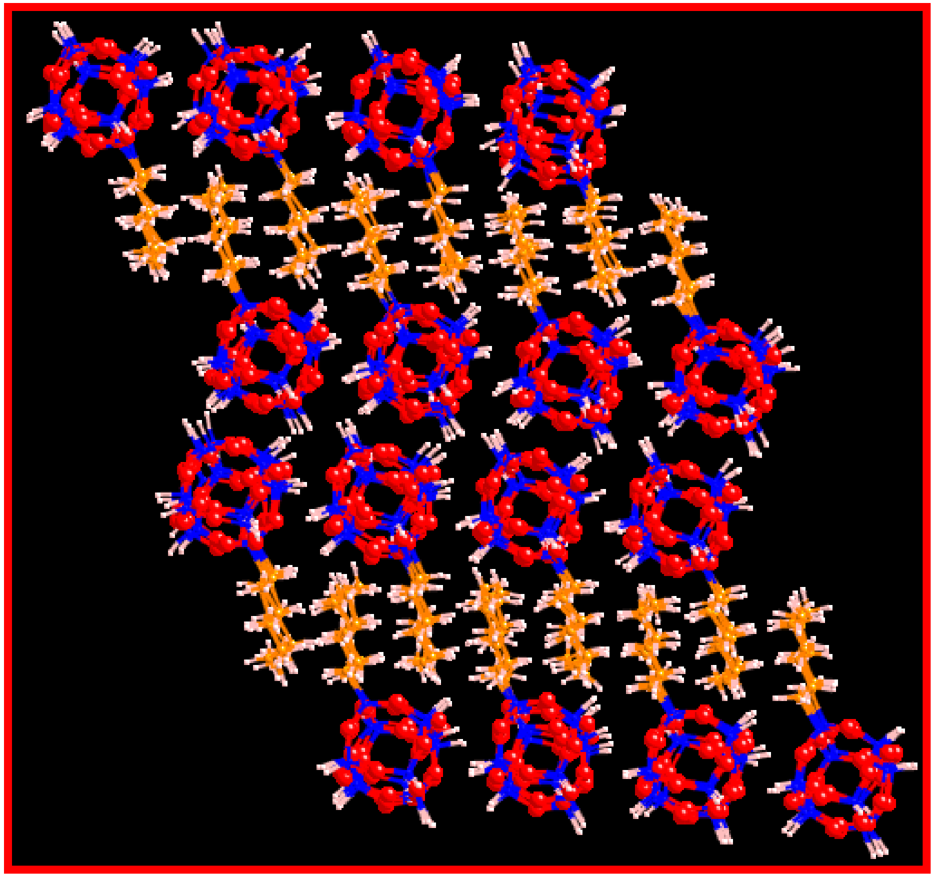


Huang, Durandurdu and Kieffer, Nature Materials (in press)

Parameter Optimization: Crystal Structures

(Hexyl-POSS)

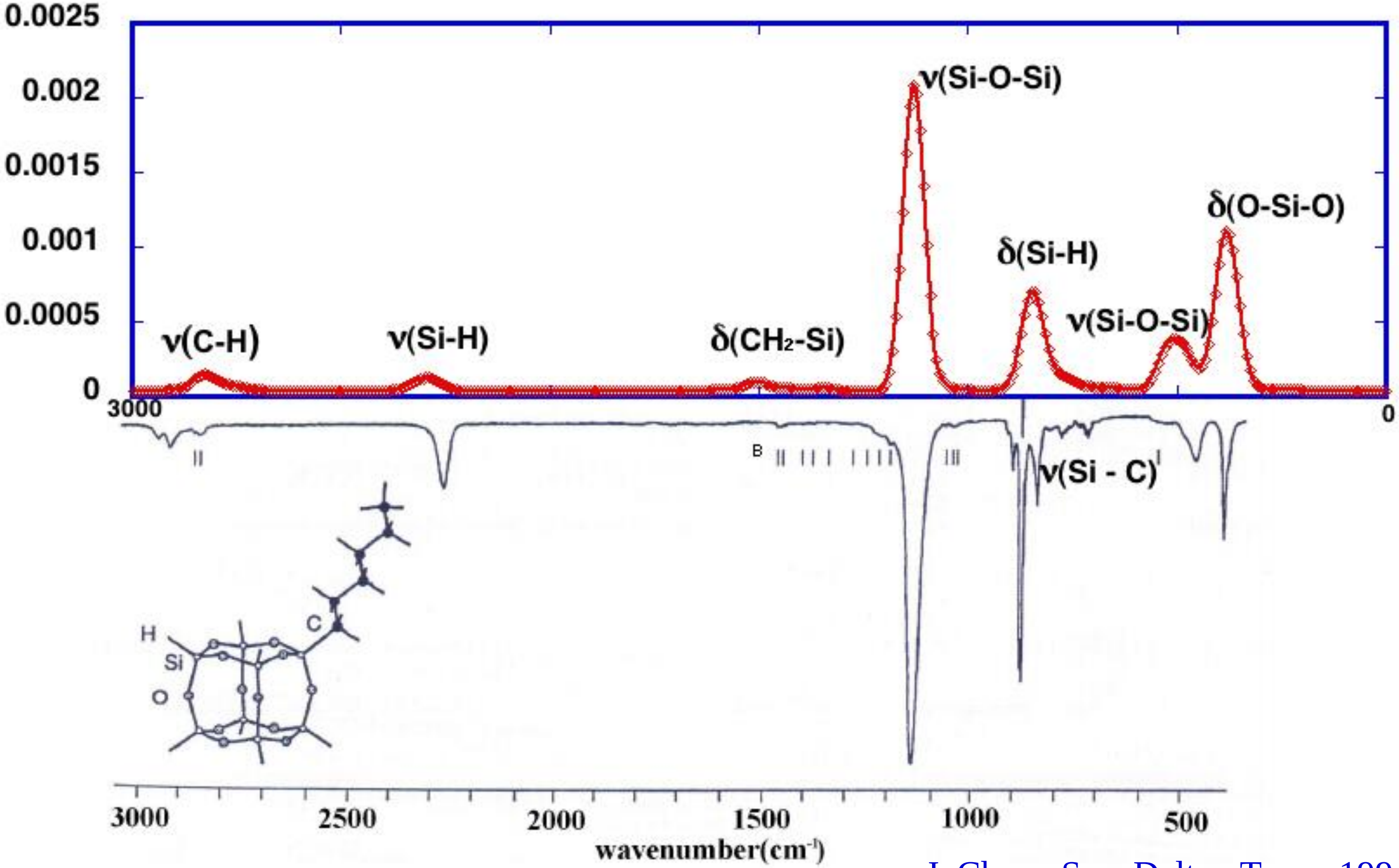




J. Chem. Soc. Dalton Trans. 1994, 3123-3128

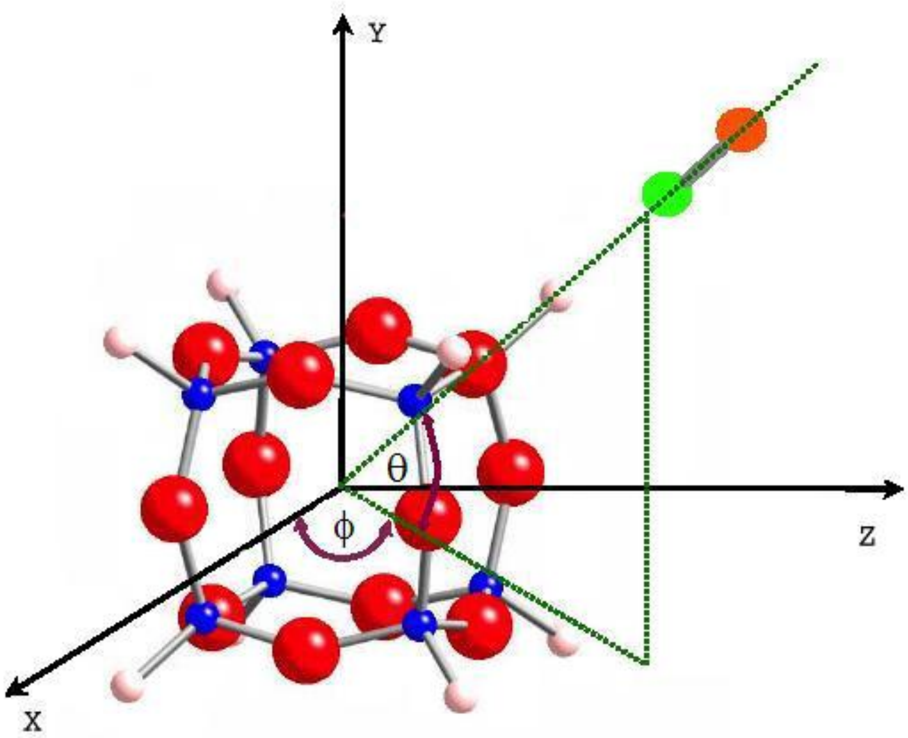
291K, NVT, 64 molecules

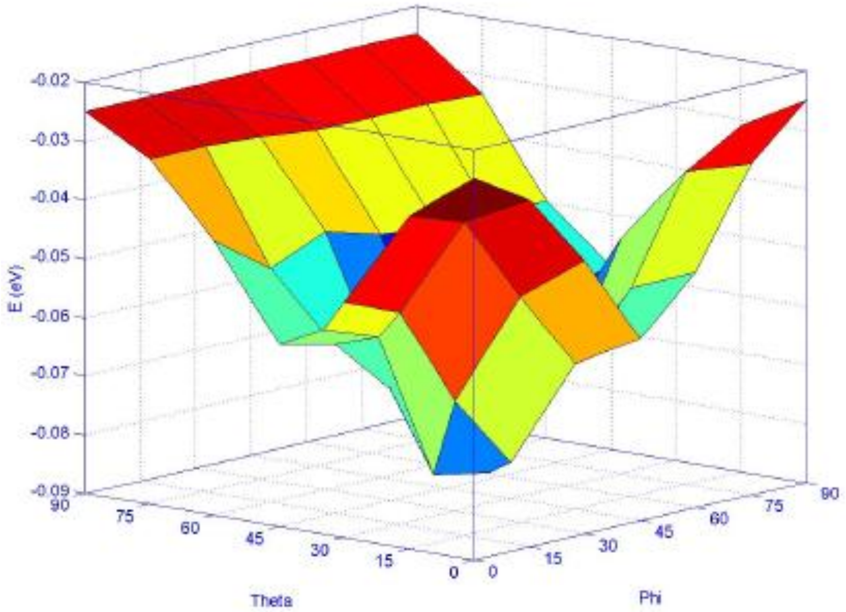
Parameter Optimization: IR Spectrum



J. Chem. Soc. Dalton Trans. 1994, 3123-3128

Parameter Optimization: Fitting to Electronic Structure Calculations





POSS-NaCl Potential Surface

🟥 High

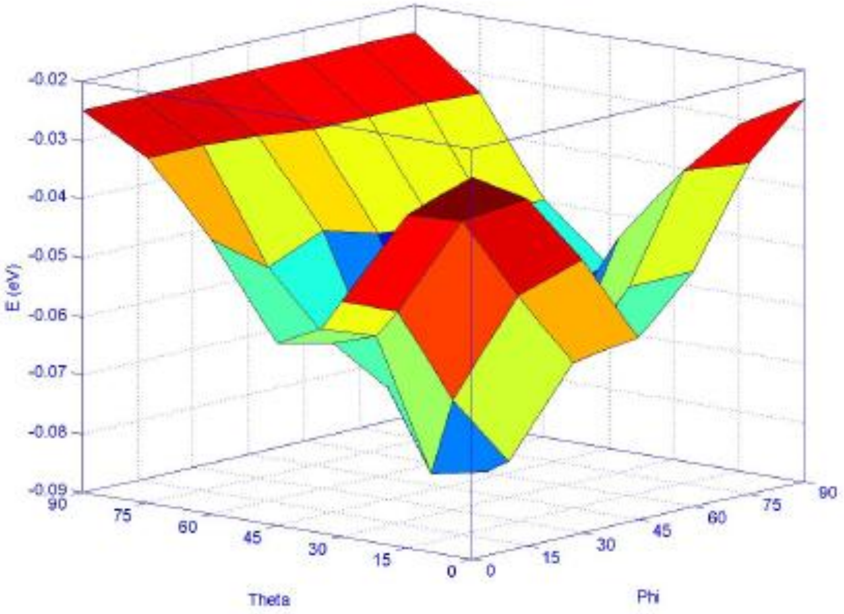
🟨 Intermediate

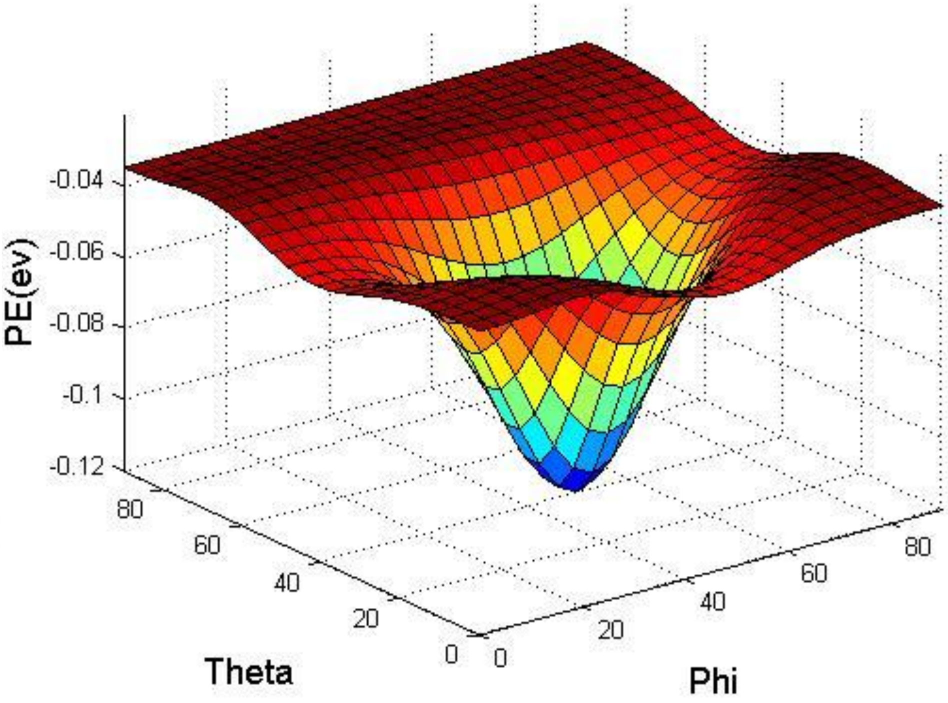
🟦 Low

Fitting Results

	Mulliken	point	shell	EEM
Si	1.094	3.417	2.685	0.7
O	-0.65	-2	-1.545	-0.46
H	-0.119	-0.417	-0.3675	-0.01~0.01
$\Sigma(\Delta E)^2$	0.107583	0.104569	0.0541699	0.00427882

Charge Equilibration Method





Questions?

QM Methods

- Doing a QM simulation or calculation means including the electrons explicitly.
- With QM methods, we can calculate *properties that depend upon the electronic distribution*, and to study processes like chemical reactions in which bonds are formed and broken.
- The explicit consideration of electrons distinguishes QM models and methods from classical force field models and methods.

Different QM Methods

- Several approaches exist. The two main ones are:
  - Molecular orbital theory
    - Came from chemistry, since primarily developed for individual molecules, gases and now liquids.
    - Two “flavors”
      - Ab initio: all electrons included (considered exact)
      - Semi-empirical: only valence electrons included
  - Density functional theory
    - Came from physics and materials science community, since originally conceived for solids.
    - All electrons included via electronic density (considered exact).

Fundamentals

- The operator that returns the system energy is called the Hamiltonian operator H.

Eigenvalue equation
for system energy

$$\mathbf{H}\Psi = \mathrm{E}\Psi$$

Time-independent
Schrodinger Equation

$$H = -\sum_{i} \frac{\hbar^{2}}{2m_{e}} \nabla_{i}^{2} - \sum_{k} \frac{\hbar^{2}}{2m_{k}} \nabla_{k}^{2} - \sum_{i} \sum_{k} \frac{e^{2} Z_{k}}{r_{ik}} + \sum_{i<j} \frac{e^{2}}{r_{ij}} + \sum_{k<l} \frac{e^{2} Z_{k} Z_{l}}{r_{kl}}$$

Kinetic energy of electrons	Kinetic energy of nuclei	Potential energy of electrons & nuclei	Potential energy of electrons	Potential energy of nuclei

Born-Oppenheimer Approximation

Need to simplify!

- Neutrons & protons are >1800 times more massive than electrons, and therefore move much more slowly.
- Thus, electronic “relaxation” is for all practical purposes instantaneous with respect to nuclear motion.
- We can decouple the motion, and consider the electron-electron interactions independently of the nuclear interactions. *This is the Born-Oppenheimer approximation.*
- For nearly all situations relevant to soft matter, this assumption is entirely justified.

$$(\mathbf{H}_{el}+V_{n})\Psi_{el}(q_{i};q_{k}) = E_{el}\Psi_{el}(q_{i};q_{k})$$

The Electronic Schrodinger Equation

QM Methods

- Goal of all QM methods in use today:

  Solve the *electronic* Schrodinger equation for the ground state energy of a system and the wavefunction that describes the positions of all the electrons.

  - The energy is calculated for a given trial wavefunction, and the “best” wavefunction is found as that wavefunction that minimizes the energy.

QM Methods

- Solving SE is not so easy! Anything containing more than two elementary particles (i.e. one e- and one nucleon) can't be solved exactly: the "many-body problem".

- Even after invoking Born-Oppenheimer, still can't solve exactly for anything containing more than two electrons.

- So -- all QM methods used today are APPROXIMATE after all, even if considered "exact"! That is, they provide *approximate solutions to the Schrodinger equation*.
  - Some are more approximate than others.

Molecular Orbital Theory

- MOT is expressed in terms of molecular wave functions called molecular orbitals.
- Most popular implementation: write molecular orbital as a linear combination of atomic orbitals ϕ (LCAO):

Eq. 2.68 in Leach

$$\psi_i = \sum_{\mu=1}^{K} a_{\mu i} \phi_\mu$$

K = # atomic orbitals

- Many different ways of writing "basis set", which leads to many different methods and implementations of MOT.

Molecular Orbital Theory

- Dozens of approaches for writing basis sets (e.g. in terms of Gaussian wavefunctions, or as linear combos of Gaussians).
- Different implementations retain different numbers of terms.
- Semi-empirical MOT methods consider only valence electrons.
- Some methods include electron exchange.
- Some methods include electron correlation.

Density Functional Theory

- A different approach for solving Schrodinger’s equation for the ground state energies of matter.
- Based on theory of Hohenberg and Kohn (1964) which states that it is not necessary to consider the motion of each individual electron in the system. Instead, it suffices to know the average number of electrons at any one point in space.
- The HK theorem enables us to write E_{el} as a functional of the electron density ρ.

$$\left\{ -\frac{\nabla_1^2}{2} - \left(\sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + V_{XC}\left[\mathbf{r}_1\right] \right\} \psi_i(\mathbf{r}_i) = \varepsilon_i \psi_i(\mathbf{r}_i)$$

- To perform a DFT calculation, one optimizes the energy with respect to the electron probability density, rather than with respect to the electronic wave function.

For a given density, the lowest energy is the best one.

Density Functional Theory

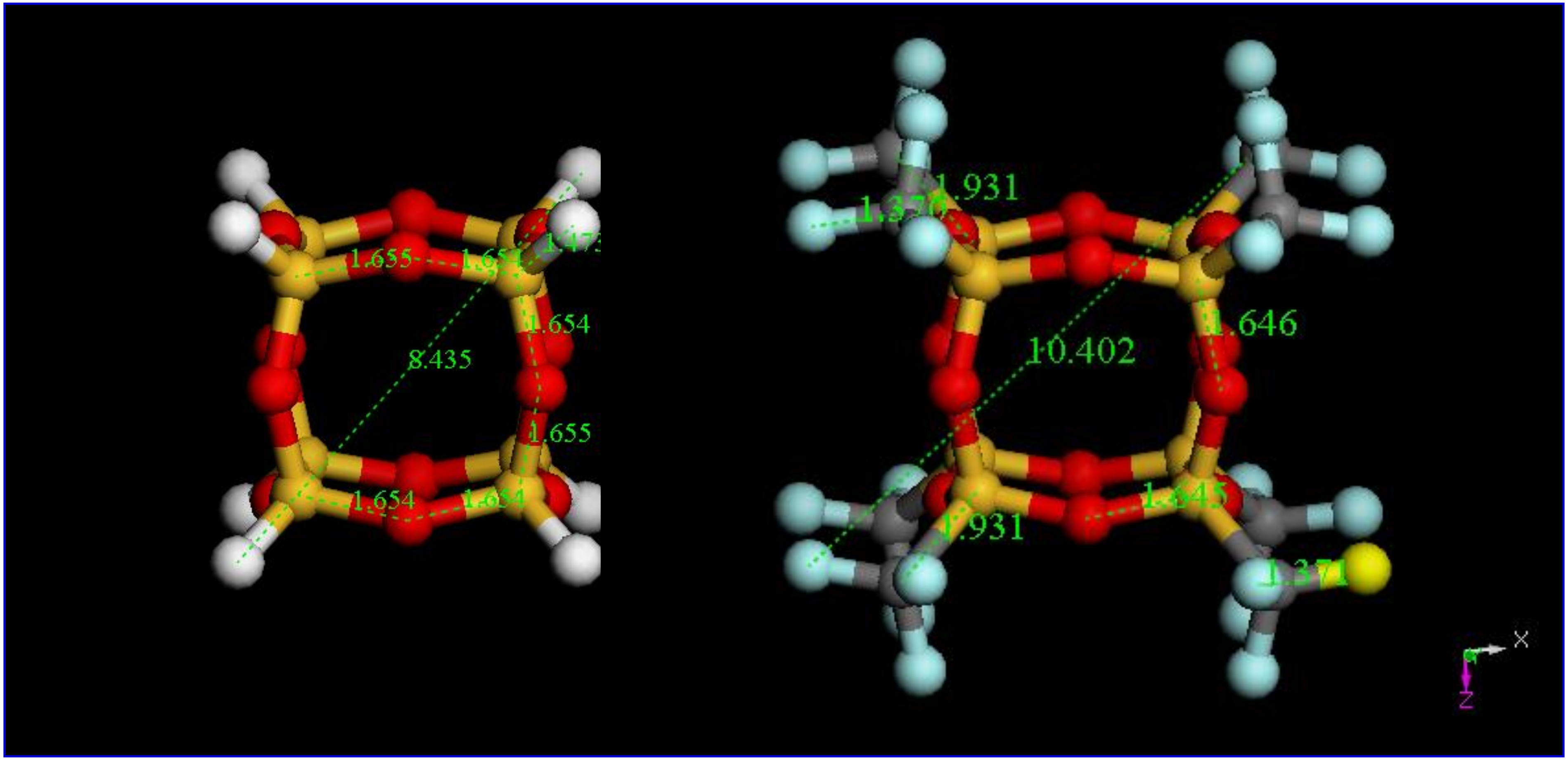
- In the commonly used Kohn-Sham implementation, the density is written in terms of one-electron molecular orbitals called “Kohn-Sham orbitals”.

- This allows the energy to be optimized by solving a set of one-electron Schrodinger equations (the KS equations), but with electron correlation included. This is a key advantage of the DFT method - it’s easier to include electron correlation.

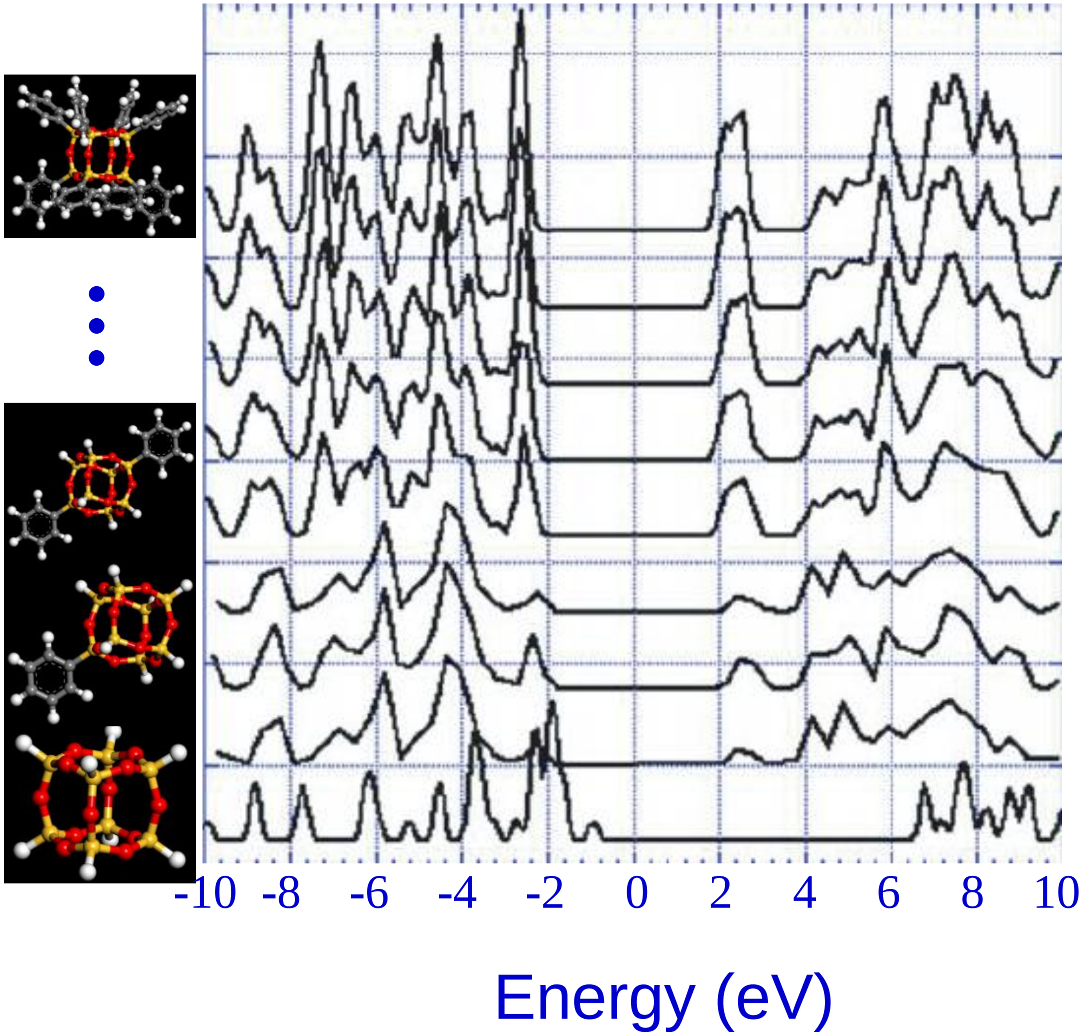
- Different choices of basis sets, how many terms to use, of what type, contribute to difficulty of calculation. More than a few hundred light atoms is still too time-consuming, even on big computers.

- For molecules or systems with large numbers of electrons, pseudopotentials are used to represent the wavefunctions of valence electrons, and the core is treated in a simplified way.

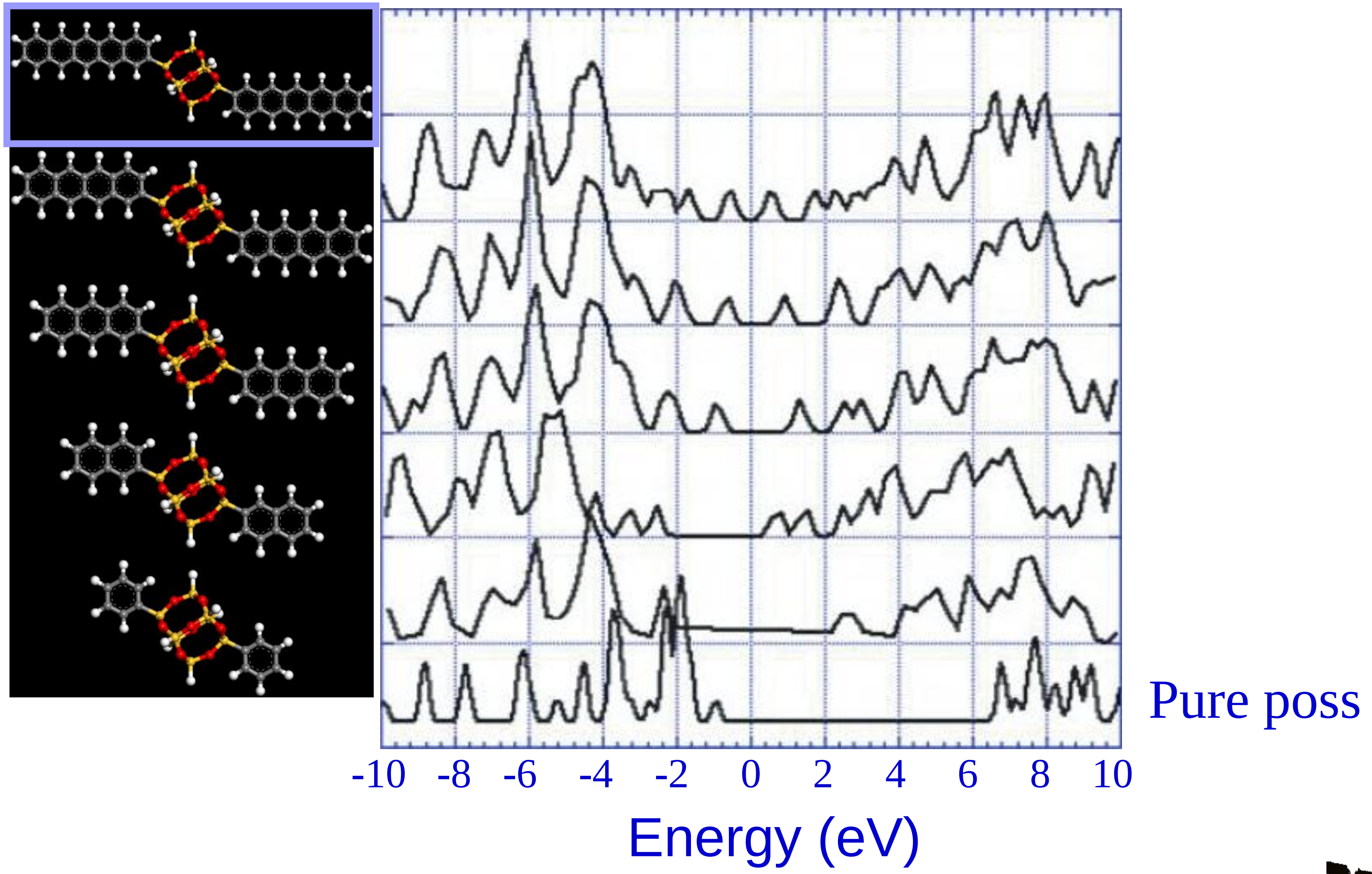
Applications of ab initio computations using DMol^3



Electronic band structure of POSS cubes functionalized with *n* benzene molecules (*n* = 0-8)

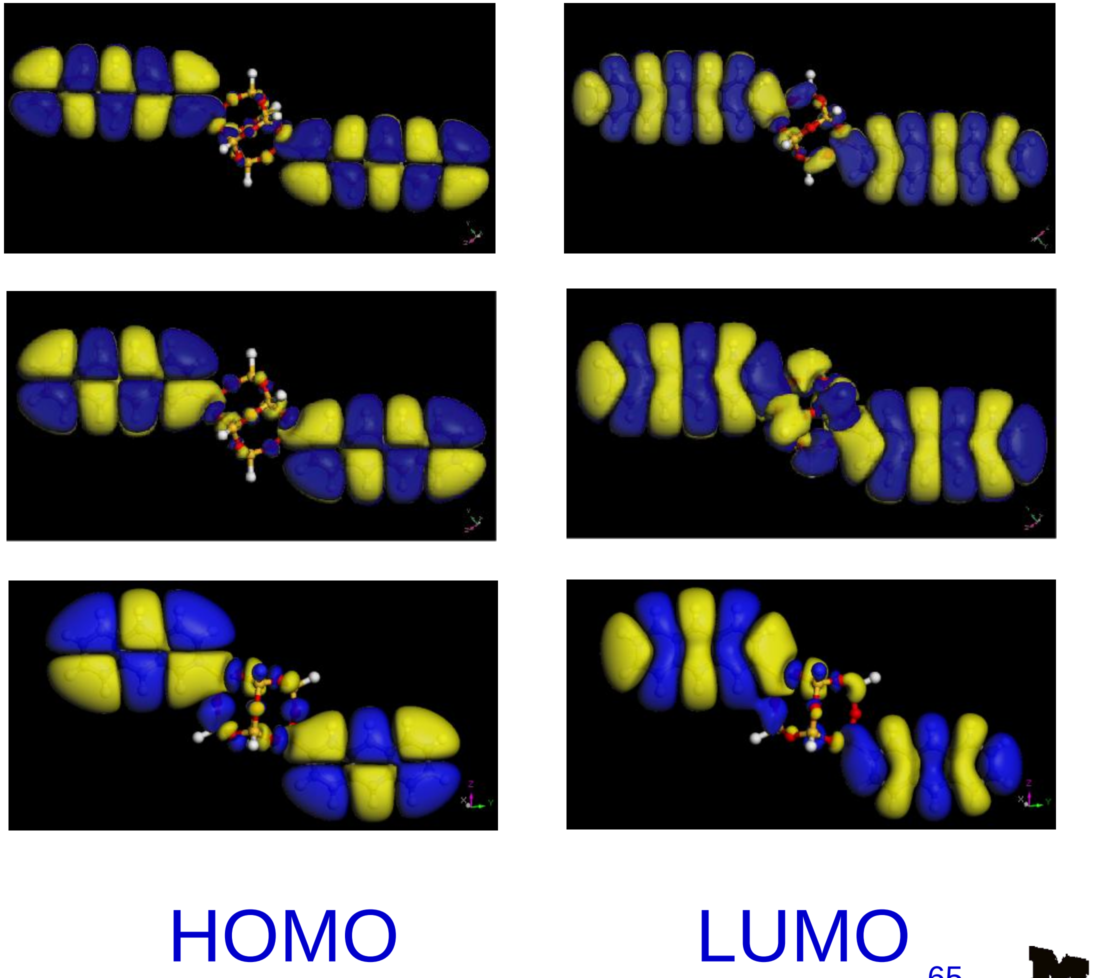


Electronic band structure of POSS cubes functionalized with acene molecules (benzene, naphtalene, anthracene, tetracene, and pentacene)

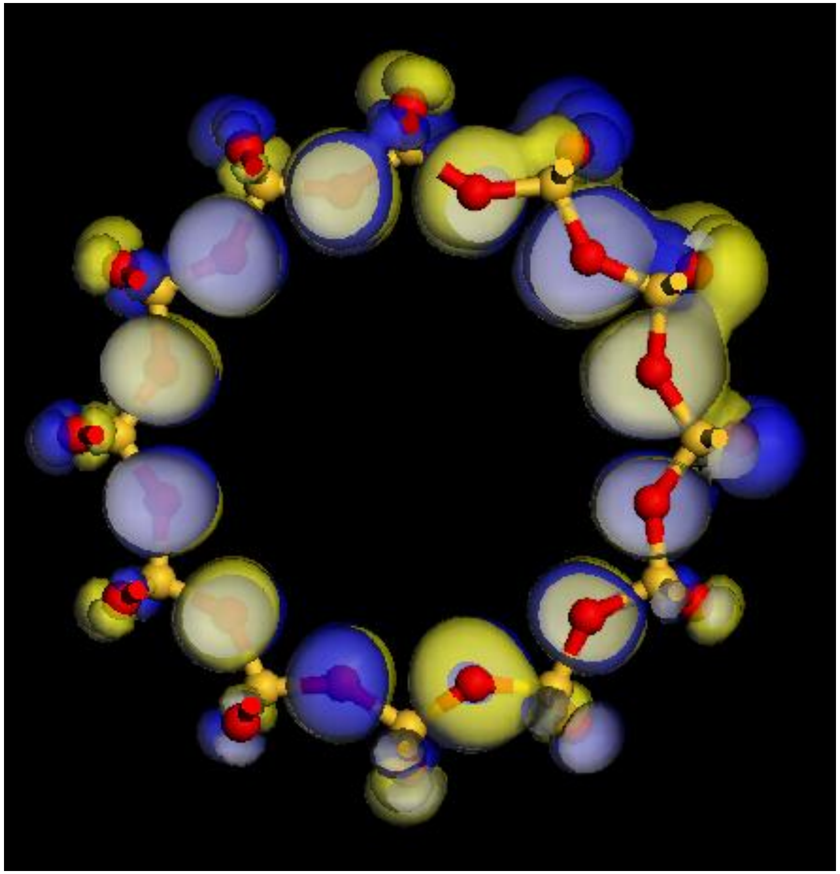


Electron densities of acene-functionalized POSS

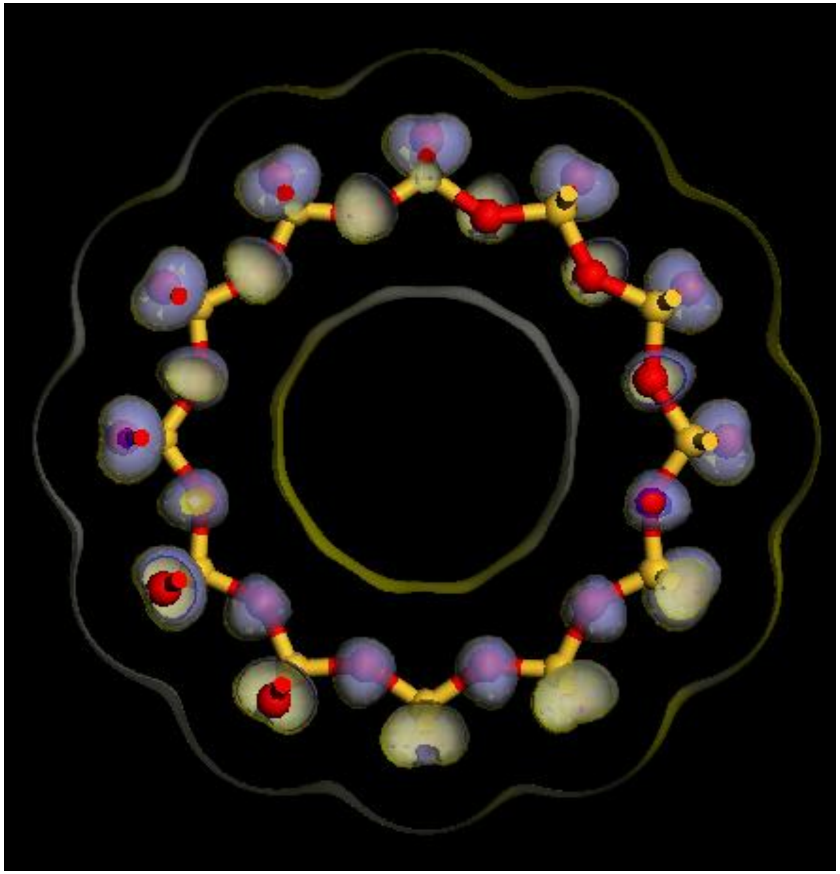
Molecule	Band Gap (eV)	Pure Acene (eV)
P-POSS	0.999	1.335
T-POSS	1.486	1.597
A-POSS	2.295	3.268
N-POSS	3.325	3.348
B-POSS	4.842	13.776
POSS	8.4	-



Electron densities of silica nanotubes



HOMO



LUMO

Classical vs. ab initio methods

Classical

- No electronic properties
- Phenomenological potential energy surface (typically 2-body contributions)
- Difficult to describe bond breaking/formation
- Can do up to a billion particles

ab initio

- Electronic details included
- Potential energy surface calculated directly from Schrodinger equation (many body terms included automatically)
- Describes bond breaking/formation
- Limited to several hundred atoms with significant dynamics

Editor's Note:
Lecture 21 ended here – 4/2/07

Questions?

Overview …

- Historical perspective
- Simulation methodologies
  - Theoretical background
  - Monte Carlo simulation
  - Molecular dynamics simulation
  - Reverse Monte Carlo
- Force fields
- Information retrieval
  - Statistical mechanical formalisms
  - Structural analyses
  - Dynamics
- Application examples

Simulation Observables: Thermodynamics

In a classical, many body system, the temperature is defined from the equipartition theorem in terms of the average kinetic energy per degree of freedom:

$$\frac{1}{2} m \left\langle v_x^2 \right\rangle = \frac{1}{2} k_B T$$

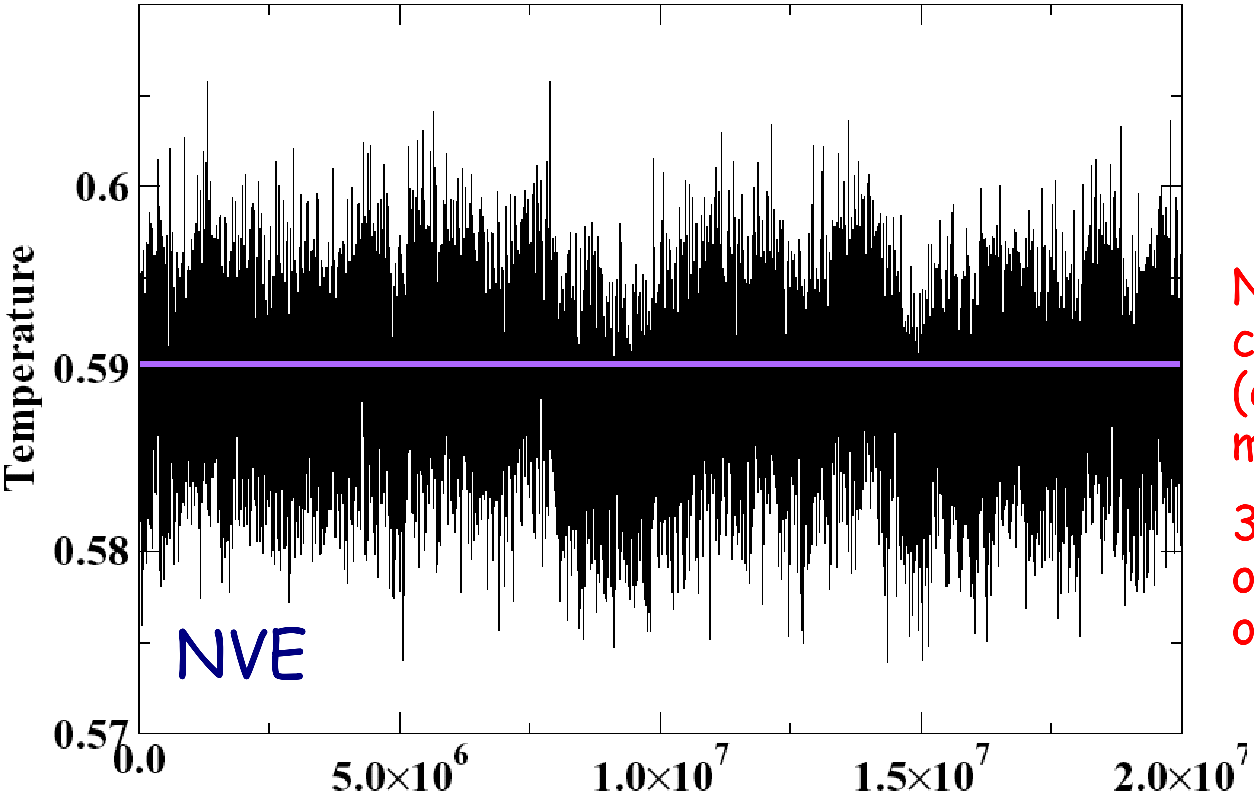
In a simulation, we use this equation as an operational definition of T.

Thus the lower the temperature, the lower the kinetic energy, and the slower the average velocity.

Simulation Observables: Thermodynamics

$$T(t) = \sum_{i=1}^{N} \frac{m_i v_i^2(t)}{k_B(3N - N_c)}$$

- Thermodynamic quantities
  - ❖ Calculate T, ρ, p, E etc. depending on ensemble



time steps

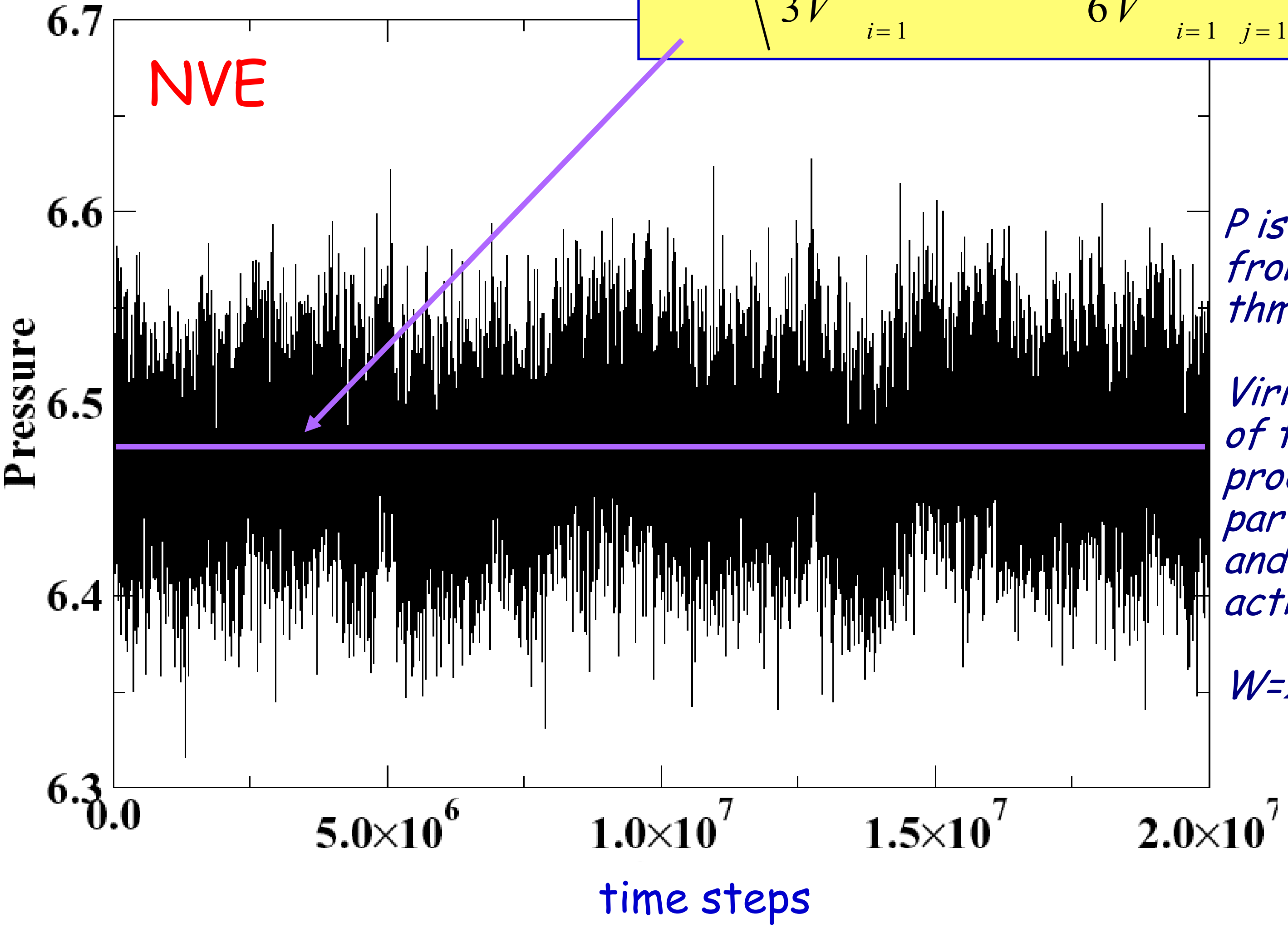
N_c = # of constraints (e.g. linear momentum)

$3N - N_c$ = # of degrees of freedom

Simulation Observables: Thermodynamics

Pressure

$$P = \left\langle \frac{1}{3V}\sum_{i=1}^{N} m_i v_i^2 - \frac{1}{6V}\sum_{i=1}^{N}\sum_{j=1}^{N} f_{ij} r_{ij} \right\rangle$$



P is obtained from the virial thm of Clausius.

Virial = exp. value of the sum of the products of the particle coords and the forces acting on them.

$W = \Sigma x_i f_{xi} = -3Nk_BT$

Measuring quantities in molecular simulations

•Suppose we wish to measure in an experiment the value of a property, A, of a system such as pressure or density or heat capacity.

•The property A will depend on the positions and momenta of the N atoms or molecules that comprise the system. The instantaneous value of A is:

$$A(\mathbf{p}^N(t),\mathbf{r}^N(t)) = A(p_{1x},p_{1y},p_{1z}, \ldots, x_1,y_1,z_1,\ldots t).$$

•Over time, A fluctuates due to interactions between the atoms.

Measuring quantities in molecular simulations

- In any experiment, the value that we measure is an average of A over the time of the measurement (*a time average*).

- As the time, t, of the measurement increases to infinity, the “true” average value of A is attained:

$$\overline{A} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t=0}^{\tau} A\left(\mathbf{p}^N(t), \mathbf{r}^N(t)\right) dt$$

Note that strictly speaking this is true only for ergodic systems in equilibrium.

Measuring quantities in molecular simulations

- To calculate properties in a molecular simulation, we average a property A over successive configurations in the trajectory generated by the equations of motion.

$$\overline{A} = \lim_{n_{steps} \to \infty} \frac{1}{n_{steps}} \sum_{t=0}^{n_{steps}} A\left(\mathbf{p}^N(t), \mathbf{r}^N(t)\right)$$

- The larger n_{steps} is, the more accurate the estimate of the true time-averaged value of A.

Ensemble averages

- In statistical mechanics we learn that experiments and simulations may be performed in different *ensembles*.

- An *ensemble* is a collection of individual systems that can be studied *en masse* to yield macroscopic properties of the entire collection.

- Every equilibrium configuration we generate via MD represents a unique *microstate* of the ensemble.

Ensemble averages

- There are many different thermodynamic ensembles, each of which is characterized by thermodynamic variables that are fixed in the simulation.
  - NVE - microcanonical
  - NVT - canonical
  - NPT - isobaric-isothermal
  - μVT - Gibbs

N = number of particles, V = volume, E = total energy, T = temperature, P = pressure, μ = chemical potential

- The simplest MD simulation has constant N, V and E. The NVE ensemble is the microcanonical ensemble; all states are equally likely.

- In NVE MD, solve F=ma for an *isolated system*, one for which no exchange of energy or particles with the outside.

Molecular Dynamics Simulation: NVT

Velocity Rescaling

- Recall KE = $mv^2/2 = 3Nk_BT/2$ in an unconstrained system.
- Simple way to alter T: *rescale velocities every time step by a factor $\lambda(t)$:*
  - If temperature at time t is T(t) and v is multiplied by λ, then the temperature change is

$$\Delta T = \frac{1}{2}\sum_{i=1}^{N}\frac{2}{3}\frac{m_i(\lambda v_i)^2}{Nk_B} - \frac{1}{2}\sum_{i=1}^{N}\frac{2}{3}\frac{m_i v_i^2}{Nk_B}$$

$$\Delta T \equiv T_{\text{target}} - T(t) = (\lambda^2 - 1)T(t)$$

$$\lambda = \sqrt{T_{\text{target}} / T(t)}$$

Molecular Dynamics Simulation: NVT

Velocity Rescaling

- This method does not generate configurations in the canonical ensemble.

- Why? Because system is not coupled to an external reservoir, or heat bath.

- Thus *not a good method for controlling temperature*, since it’s unknown how rescaling affects properties of the system.

- Instead, use a “proper” thermostat.
  - Using a weakly coupled thermostat can help eliminate drift in total energy due to algorithm inaccuracies and round-off error.

  - *Several types of thermostats; choose wisely depending on your problem!*

Molecular Dynamics Simulation: NVT

Stochastic collision method: *Andersen thermostat*

- Occasionally replace a randomly chosen particle’s velocity with a velocity chosen randomly from a Maxwell-Boltzmann distribution at the desired T.

$$p(v_{ix}) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{1}{2k_B T} m v_{ix}^{2}\right)$$

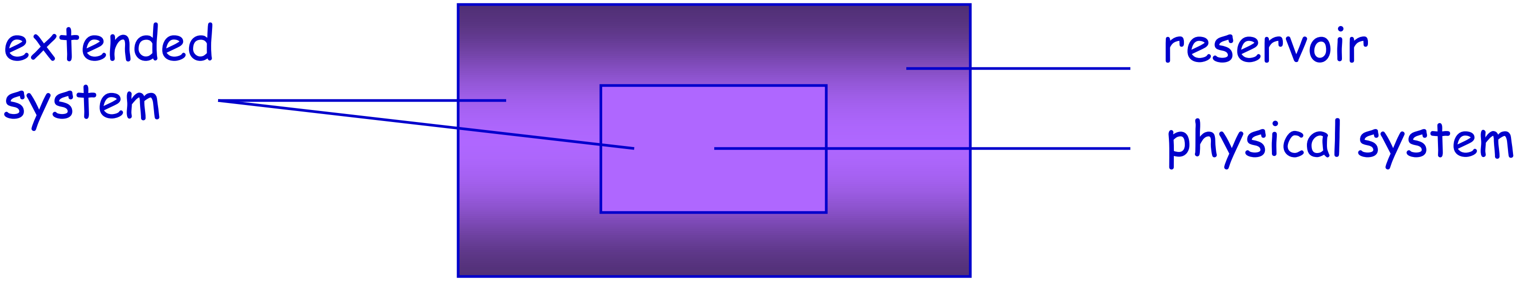
- This replacement represents stochastic collisions with the heat bath.

- Equivalent to the system being in contact with a heat bath that randomly emits thermal particles that collide with the atoms in the system and change their velocity.

Molecular Dynamics Simulation: NVT

Extended system method: *Nose'-Hoover thermostat*

- Introduced by Nose' and developed by Hoover in 1985.
- Considers the thermostat to be part of the system (hence 'extended system').
- Based on extended Lagrangian approach in which an additional dynamical variable or degree of freedom *s*, representing the reservoir, imposes constraint of constant T.



Molecular Dynamics Simulation: NVT

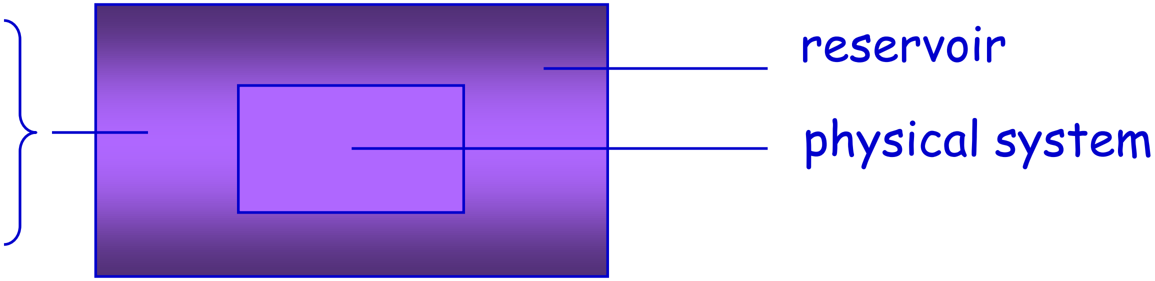
Extended system method: *Nose'-Hoover thermostat*

- Reservoir has potential energy U_{res} and kinetic energy K_{res}.

$U_{res} = (f+1)k_BT \, ln \, s$

$K_{res} = (Q/2)(ds/dt)^2$

$\xi(t) = sp_s / Q$



- f = # of dof in physical system, and T is the desired temperature. Q has dimensions energy x $(\text{time})^2$, and is considered the fictitious "mass" of the additional degree of freedom.

- The magnitude of Q controls the coupling between the physical system and the reservoir, and thus influences the temperature fluctuations.

Molecular Dynamics Simulation: NVT

Extended system method: *Nose'-Hoover thermostat*

- Q controls the energy flow between system and reservoir.
- If Q is large, the energy flow is slow; the limit of infinite Q corresponds to NVE MD since there is then no exchange of energy between system and reservoir.
- If Q is small, then the energy oscillates unphysically, causing equilibration problems.
- Nose' suggested $Q = Cfk_BT$, where C can be obtained by performing trial simulations for a series of test systems and observing how well the system maintains that desired T.
- Upshot: equations of motion are modified and δt is multiplied by Q.

Read in Frenkel and Smit for details if interested.

Molecular Dynamics Simulation: NVT

Extended system method: *Nose'-Hoover thermostat*

- Best and most used thermostat today for NVT simulations.
- Ensures that average total KE per particle is that of the equilibrium isothermal ensemble.
- Reproduces canonical ensemble in every respect (provided only the total energy of the extended system is conserved.)
  - If momentum also conserved, NH still works only if COM fixed.
  - Otherwise, must use the method of "NH chains".
- More complicated than other methods, but can be used with velocity Verlet and predictor-corrector methods.
- Dynamics NOT independent of Q, but better than Andersen.

Molecular Dynamics Simulation: NPT

- Just as one might like to specify T in an MD simulation, one might also like to maintain the system at a fixed pressure P.
- Simulations in the isobaric-isothermal NPT ensemble are the most similar to experimental conditions.
- Certain phenomena may be more easily achieved under conditions of constant pressure, like certain phase transformations.

Molecular Dynamics Simulation: NPT

Two types:

- Andersen Barostat
  - Allows box size to fluctuate but not change shape.
  - Appropriate for liquids, which do not support shear stress.
  - Change volume by rescaling positions: $r = r + \alpha r$

- Rahman-Parinello Barostat
  - Allows box size *and* shape to change.
  - Use only for solids.
  - Necessary for simulating phase transformations.

Read in Frenkel and Smit for details if interested.

Revisit the equations of motion …

Recall Lagrangian

$$L = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\mathbf{r}}_i^T \dot{\mathbf{r}}_i - \sum_{i=1}^{N}\sum_{j>i}^{N} \phi\left(r_{ij}\right)$$

$$\frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{\mathbf{r}}_i}\right) = \frac{\partial L}{\partial \mathbf{r}_i}$$

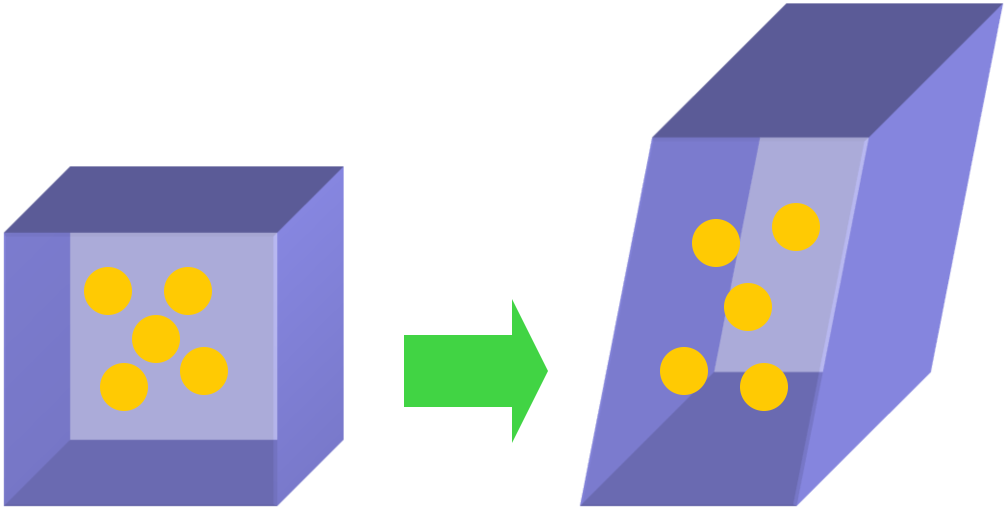
$$\frac{\partial L}{\partial \dot{\mathbf{r}}_i} = m_i \dot{\mathbf{r}}_i \qquad \frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{\mathbf{r}}_i}\right) = m_i \ddot{\mathbf{r}}_i$$

$$\frac{\partial L}{\partial \mathbf{r}_i} = -\sum_{j \neq i} \frac{\partial \phi}{\partial r_{ij}} \frac{\mathbf{r}_{ij}}{\left|\mathbf{r}_{ij}\right|} = \mathbf{f}_i$$

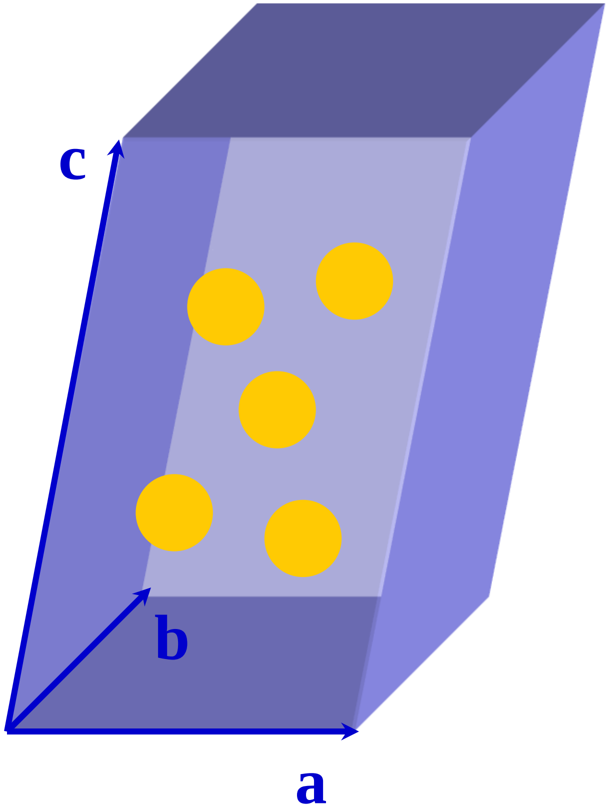
$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i$$

Flexible simulation boxes

- Mechanical deformation
- Structural transitions



Raman-Parinello algorithm



Basis vectors are dynamical variables:

$$\underline{h} = (\mathbf{a} \quad \mathbf{b} \quad \mathbf{c})$$

Raman-Parinello algorithm

$$L = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\mathbf{s}}_i^{T}\,\underline{G}\,\dot{\mathbf{s}}_i + \frac{1}{2} W\,\mathrm{Tr}\left(\dot{\underline{h}}^{T}\,\dot{\underline{h}}\right) - \sum_{i=1}^{N}\sum_{j>i}^{N}\phi\left(r_{ij}\right) - \underline{p}\,\Omega - \frac{1}{2}\mathrm{Tr}\left(\underline{\Sigma}\,\underline{G}\right)$$

$$\frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{\mathbf{s}}_i}\right) = \frac{\partial L}{\partial \mathbf{s}_i} \qquad\qquad \frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{\underline{h}}}\right) = \frac{\partial L}{\partial \underline{h}}$$

Raman-Parinello Nosé-Hoover algorithm

$$L = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\mathbf{s}}_i^{T}\,\underline{G}\,\dot{\mathbf{s}}_i f^{2} + \frac{1}{2} W\,\mathrm{Tr}\left(\dot{\underline{h}}^{T}\,\dot{\underline{h}}\right) + \frac{Q}{2}\dot{f}^{2}$$

$$-\sum_{i=1}^{N}\sum_{j>i}^{N}\phi\left(r_{ij}\right) - \underline{p}\,\Omega - \frac{1}{2}Tr\left(\underline{\Sigma}\,\underline{G}\right) - \left(g+1\right)k_B T\,\ln f$$

Simulation Observables: Thermodynamics

Thermodynamic Response Functions: Heat Capacity

At the end
(less error?)

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{1}{k_B T^2}\underbrace{\left\langle \left(E - \langle E \rangle\right)^2 \right\rangle}_{\langle E^2 \rangle - \langle E \rangle^2}$$

On the fly

- NVE: *Perform simulations at many different E for the same N & V, and measure T. Calculate C_v from derivative of E(T) (numerically or fitting polynomial and then differentiating).*
- NVT: *(1) Fix N and V, perform simulations at different T and measure E. Then calculate C_v from derivative of E(T).*

  (2) Calculate C_v from fluctuations in energy.

Simulation Observables: Thermodynamics

Thermodynamic Response Functions: Adiabatic Compressibility

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \propto \left\langle \left(P - \langle P \rangle\right)^2 \right\rangle$$

- NVE: *(1) Fix N and E, perform simulations at different V and measure P. Calculate κ_S from derivative of V(P).*

  (2) Calculate κ_S from fluctuations in pressure.

- NVT: *Calculate κ_S from fluctuations in pressure.*

Simulation Observables: Thermodynamics

Thermodynamic Response Functions: Isothermal Compressibility

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{k_B T}\frac{\left\langle \left(V - \langle V \rangle\right)^2 \right\rangle}{\left\langle V^2 \right\rangle}$$

- NVT: *Fix N and T, perform simulations at different V and measure P. Calculate* κ_T *from derivative of V(P).*
- NPT: *Fix N and T, perform simulations at different P and measure V. Calculate* κ_T *from derivative of V(P).*
- NPT: *Calculate* κ_T *from fluctuations in volume.*
- μVT: *Calculate* κ_T *from fluctuations in N.*

Questions?