

Welcome to CHE 384T: Computational Methods in Materials Science

Simulating Finite Systems

LeSar Ch. 3



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McKetta Department
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Announcements

HW2 released, due Sept 26, 11:59pm

PS1 peer review reflection, due Sept 16, 11:59pm

Lecture Outline

Sums for pair-wise interactions

Cutoffs

Periodic Boundary Conditions

Long-ranged potentials

Ewald summation

Fast Multipole Method

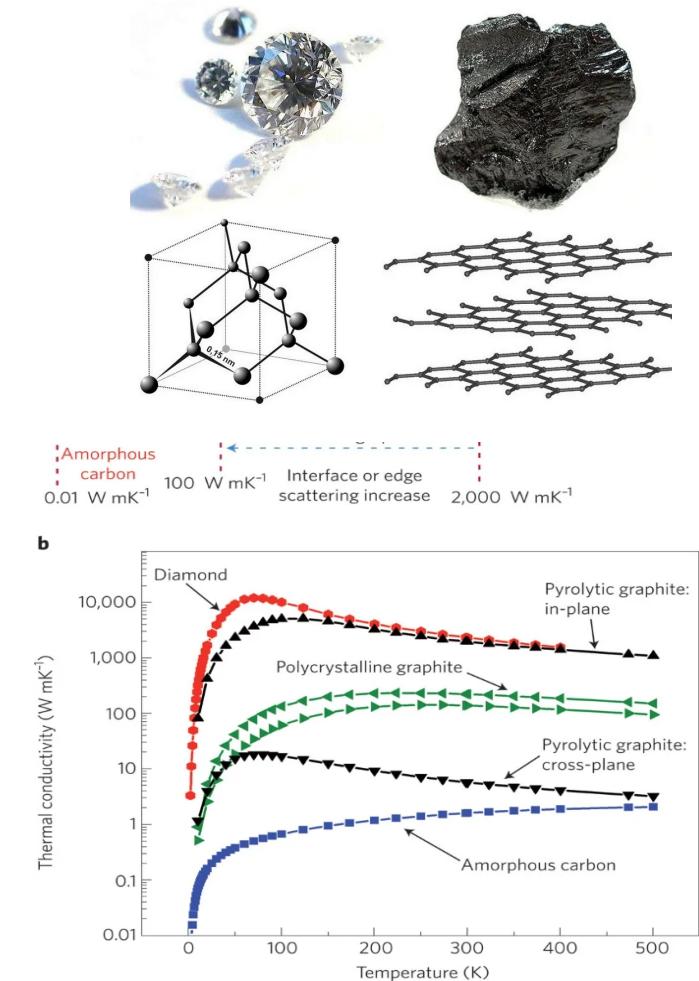
Why is understanding crystallography important?

Material anisotropy- material properties have directionality

Table 3.4
**Modulus of Elasticity
Values for Several
Metals at Various
Crystallographic
Orientations**

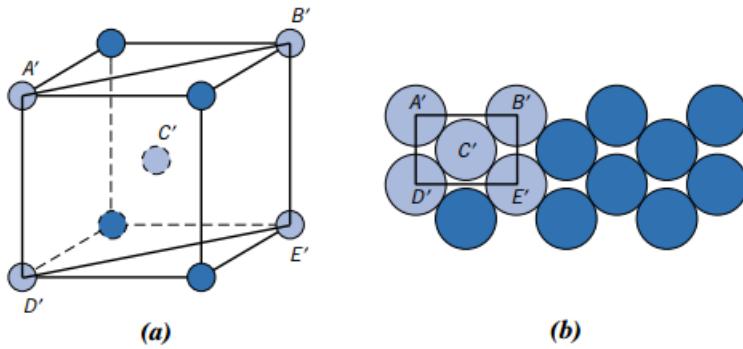
Metal	Modulus of Elasticity (GPa)		
	[100]	[110]	[111]
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

Source: R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd edition.
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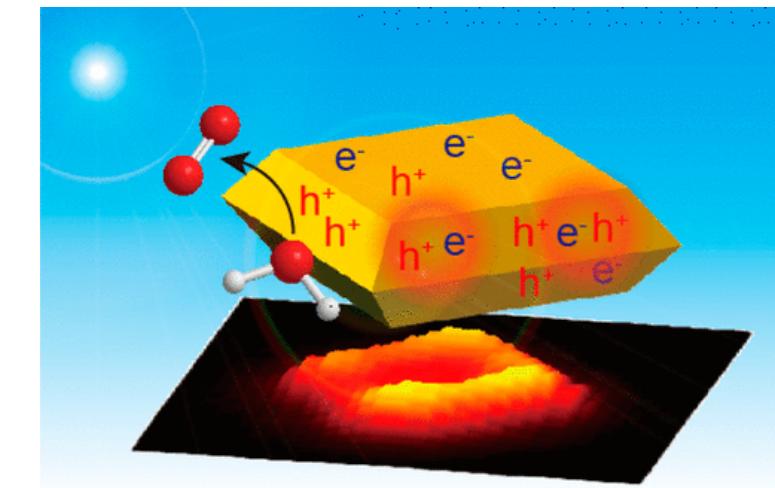
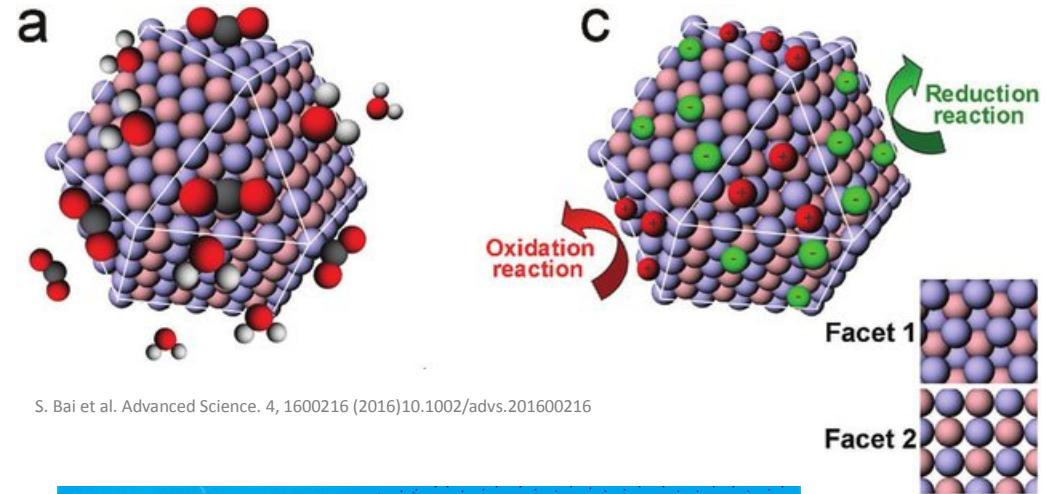
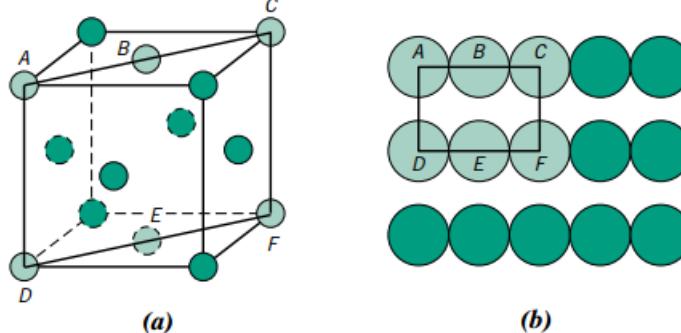


Crystallographic planes and surface facets

(110) plane for BCC

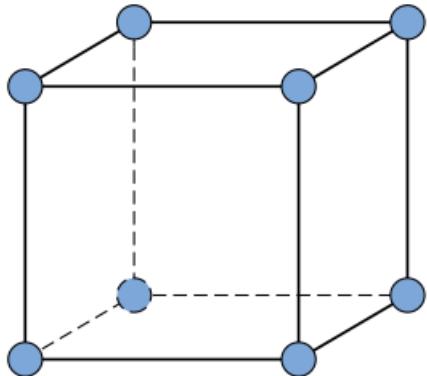


(110) plane for FCC

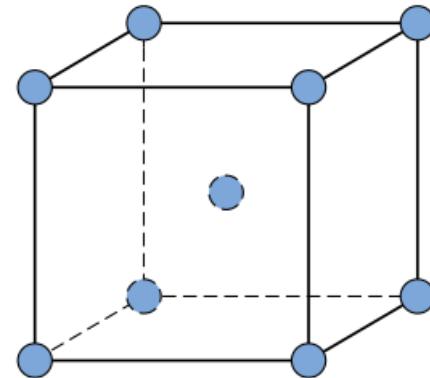


Cubic crystal structures (monoatomic)

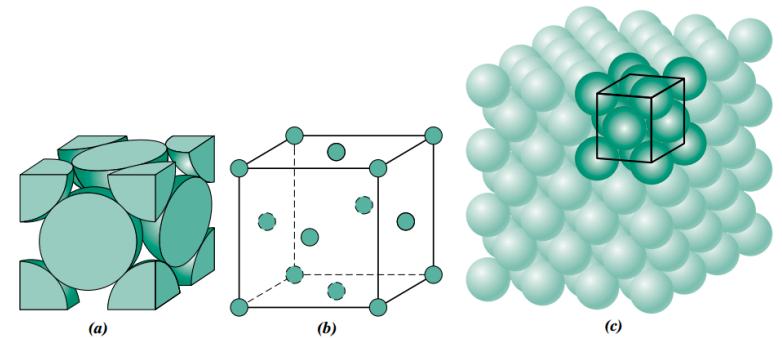
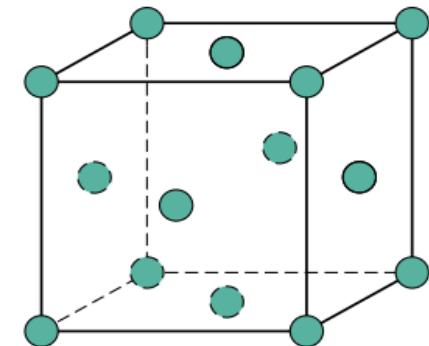
Simple Cubic



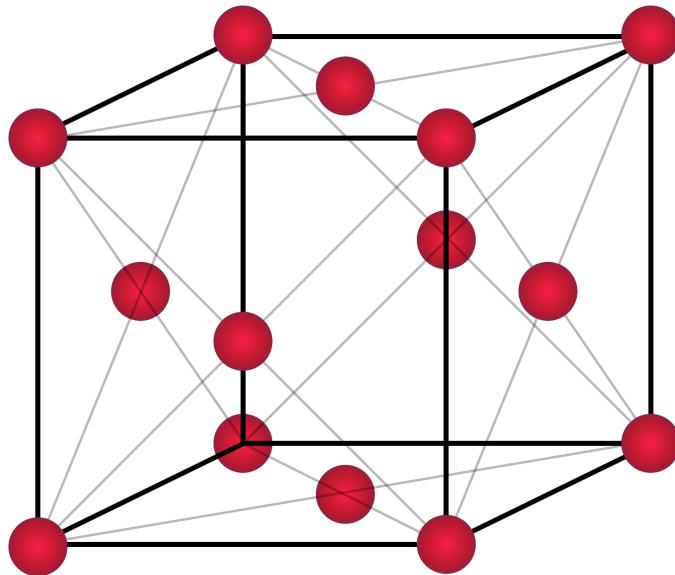
Body-Centered Cubic



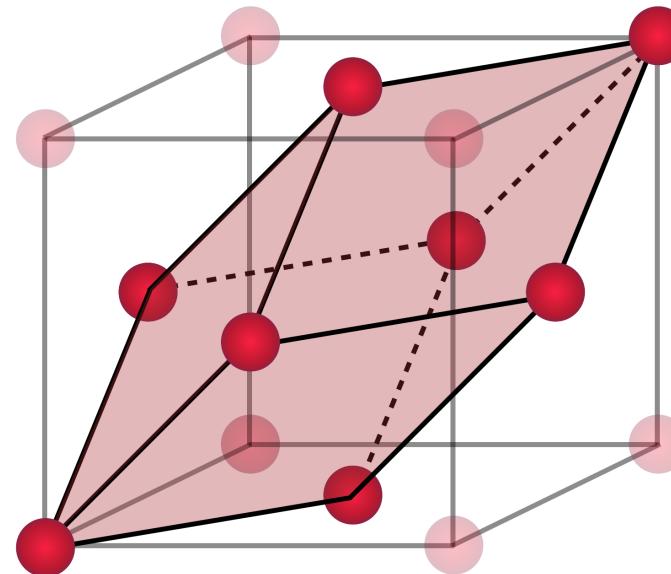
Face-Centered Cubic



Cubic crystal structures (monoatomic)



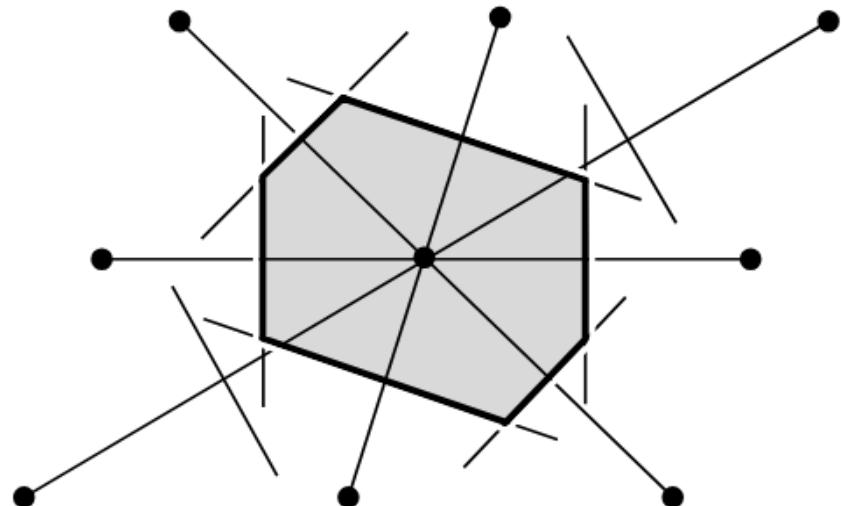
(a) conventional unit cell



(b) primitive unit cell

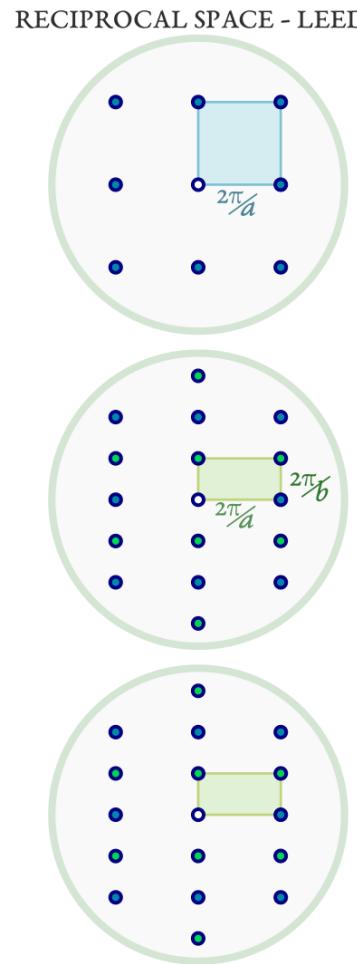
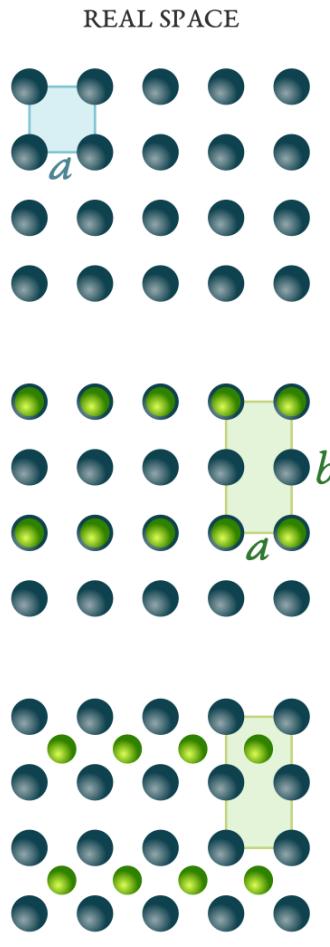
The Unit Cell

Figure 4 A primitive cell may also be chosen following this procedure: (1) draw lines to connect a given lattice point to all nearby lattice points; (2) at the midpoint and normal to these lines, draw new lines or planes. The smallest volume enclosed in this way is the Wigner-Seitz primitive cell. All space may be filled by these cells, just as by the cells of Fig. 3.



Physics: “Wigner-Seitz cell”

A side note on Reciprocal Space:

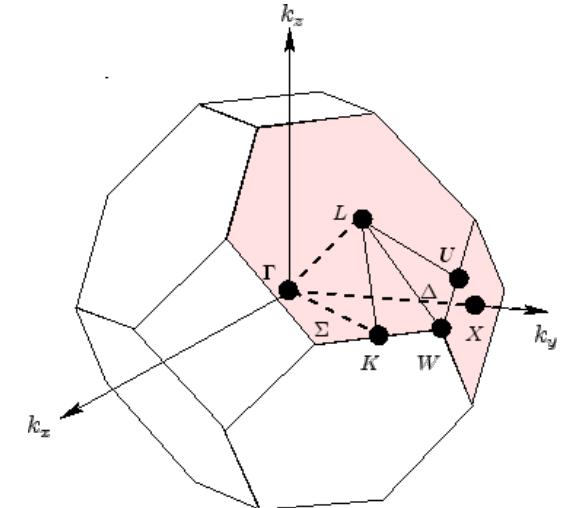


$$\mathbf{b}_1 = \frac{2\pi}{V} \mathbf{a}_2 \times \mathbf{a}_3$$

$$\mathbf{b}_2 = \frac{2\pi}{V} \mathbf{a}_3 \times \mathbf{a}_1$$

$$\mathbf{b}_3 = \frac{2\pi}{V} \mathbf{a}_1 \times \mathbf{a}_2$$

$$\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3$$



Reciprocal cell of FCC lattice,
aka first Brillouin Zone

A side note on Reciprocal Space:

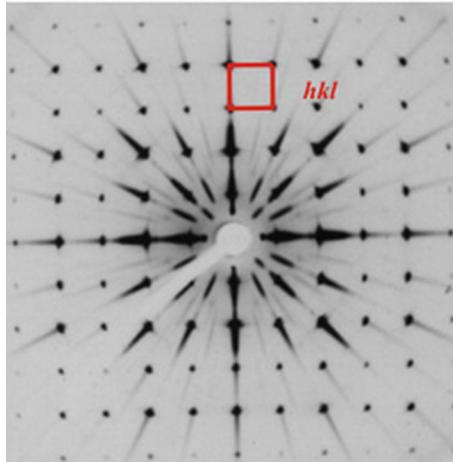
Why bother with reciprocal space?

Falls out naturally in the math (complex exponentials)

Corresponds to experimental measurements
(where you probe the sample with light or beam source)

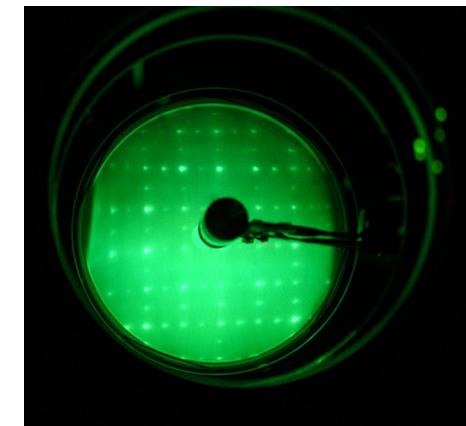
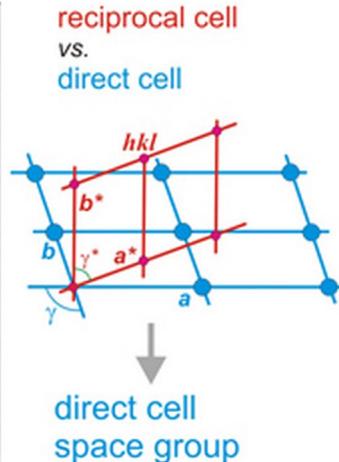
X-ray diffraction → Bulk crystal structure

Reciprocal space



Low-energy electron diffraction (LEED)

→ Surface crystal structure



How XRD works

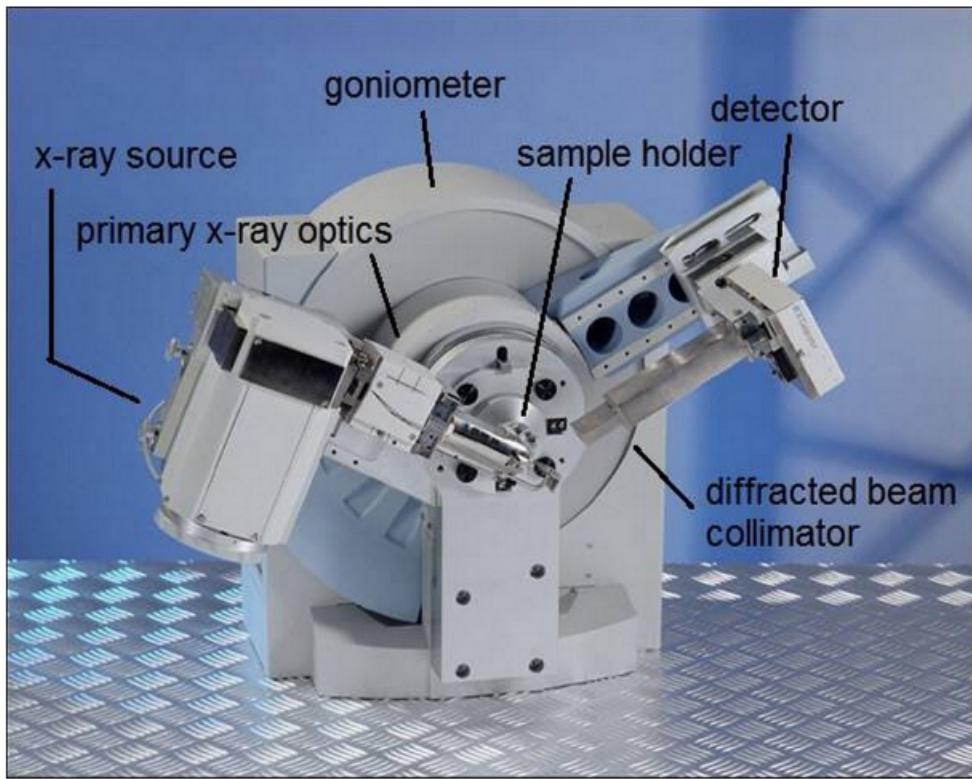


Image from [link](#)

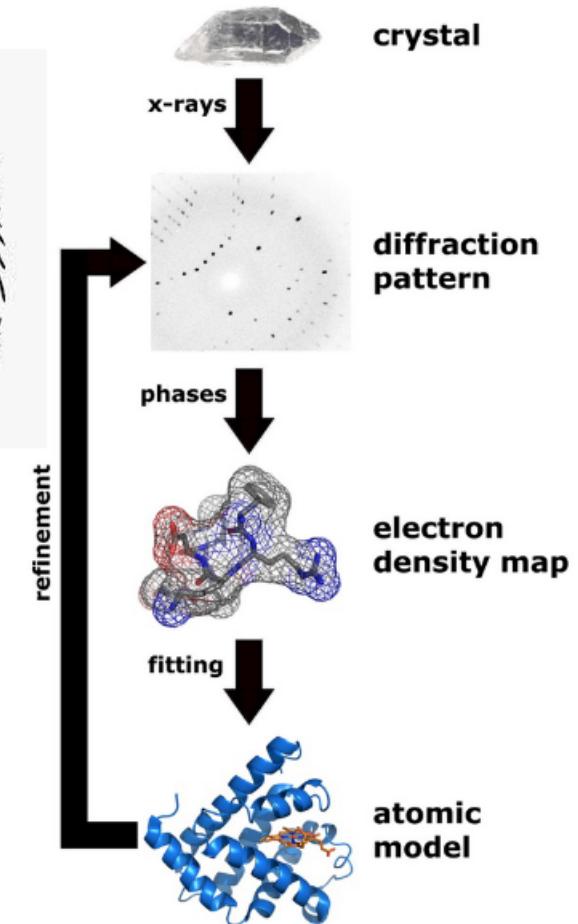


Image from [Bio Libretext, CC BY-NC-SA 3.0](#)

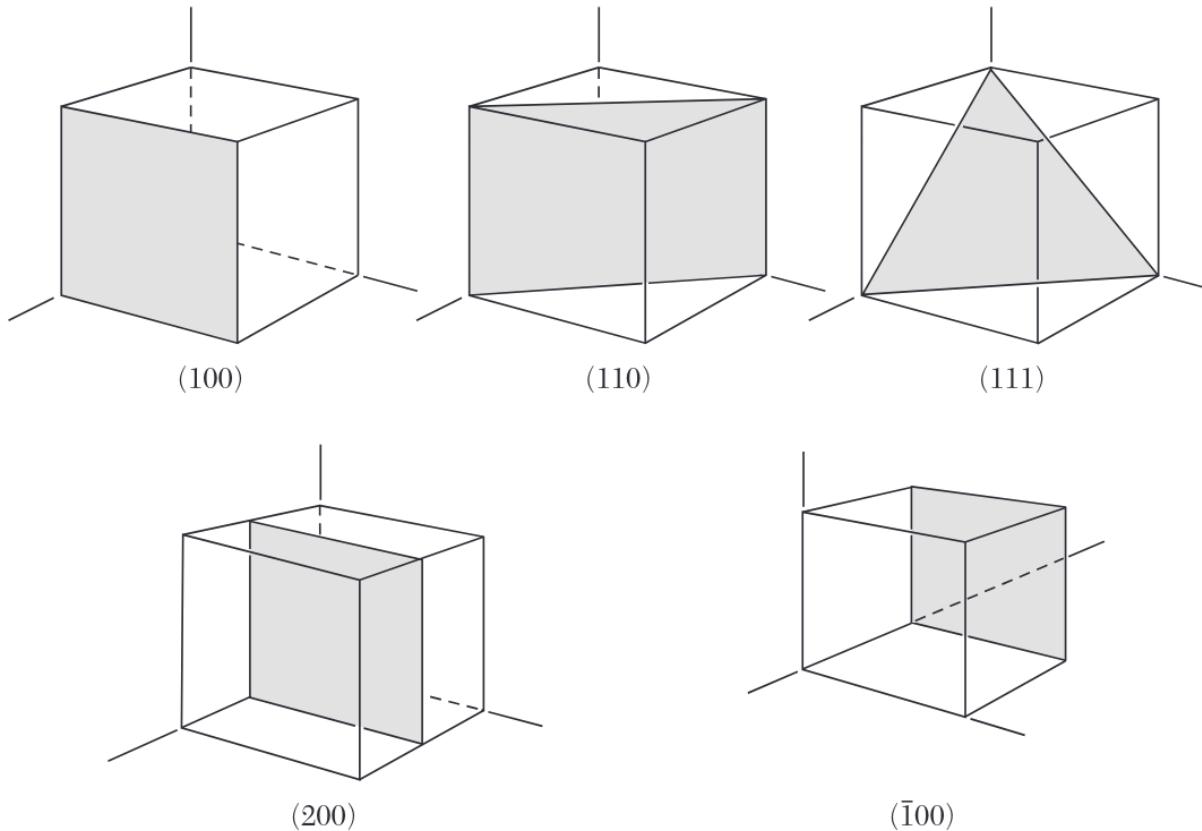


Figure 14 Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to (001) .

Lecture Outline

Sums for pair-wise interactions

Cutoffs

Periodic Boundary Conditions

Long-ranged potentials

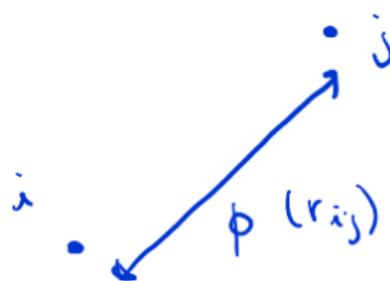
Ewald summation

Fast Multipole Method

Interacting pairs of objects

e.g., between spins, dislocations, atoms

For evaluating energies and forces → thermodynamics, kinetics



total interaction
of small sys.
4 particles

$$U = \phi(r_{12}) + \phi(r_{13}) + \phi(r_{14}) \\ + \phi(r_{23}) + \phi(r_{24}) \\ + \phi(r_{34})$$

N particles

$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \phi_{ij}(r_{ij})$$

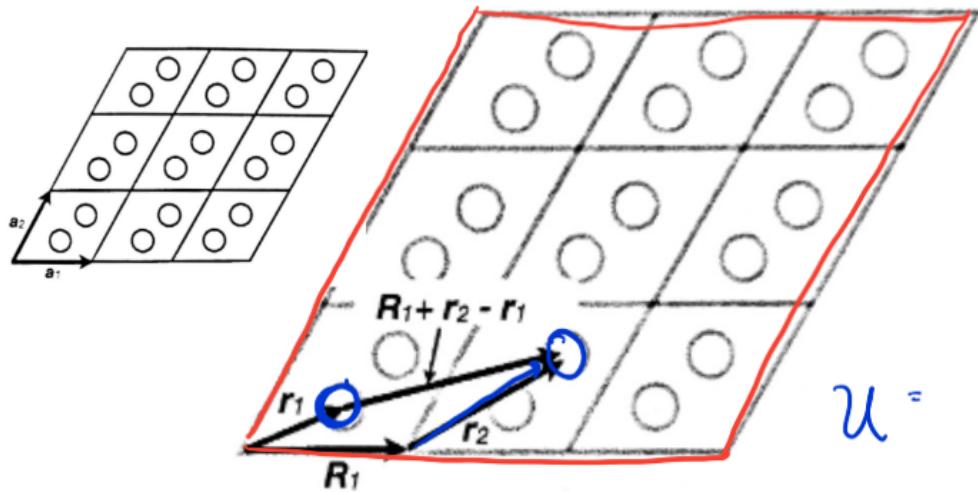
$$U = \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N \phi_{ij}(r_{ij})$$

$$U = \sum_{i=1}^{N-1} \sum_{\substack{j=i+1 \\ j=1}}^N \phi_{ij}(r_{ij})$$

$$r_{ij} = (\vec{r}_{ij} \cdot \vec{r}_{ij})^{1/2}$$

e.g., Coulomb

Perfect crystals



all interactions ψ_i
unit cell
+ simulation cell

$$U = \frac{1}{2} \sum_{\bar{R}_1} \left(\sum_{i=1}^N \sum_{j=i}^N \phi_{ij} (|\bar{R}_1 + \bar{r}_2 - \bar{r}_1|) \right)$$

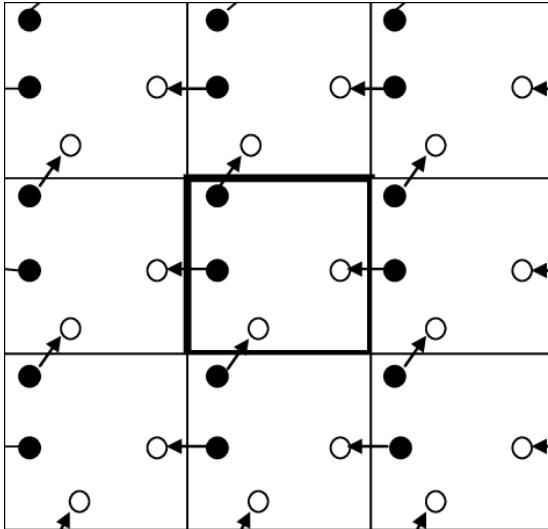
$\underbrace{\omega_i}_{\text{same unit cell}}$

$$\bar{U} = \frac{1}{N} U \quad \text{energy per particle}$$

2 atoms/unit

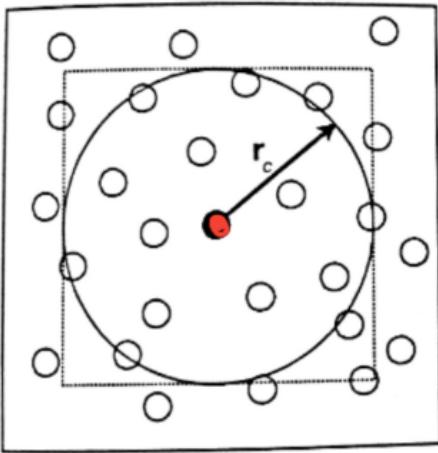
\bar{R}_1 = lattice vector - connect b/t
unit cells
(lateral dir.)

Periodic Boundary Conditions



- Mimic the real (essentially infinite) system with a finite number of objects of a manageable simulation cell
- Natural correspondence to the concept of a unit cell
- A constant concern: interactions between images
- Converge with respect to simulation cell size

Cutoffs



$$\sum_{\bar{R}} \rightarrow \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \sum_{n_3=-\infty}^{\infty}$$

$$\bar{R} = n_1 \bar{a}_1 + n_2 \bar{a}_2 + n_3 \bar{a}_3$$

$n_1, n_2, n_3 \in \mathbb{Z}$

For estimated error ΔU cutoff r_c

$$\Delta U \approx \int_{r_c}^{\infty} 4\pi r^2 \cdot \phi(r) \cdot \rho dr$$

↑ density of particles

Typical form $\phi(r) \sim \frac{1}{r^n}$

$$\approx 4\pi \rho \frac{1}{3-n} r^{3-n} \Big|_{r_c}^{\infty} = \frac{4\pi \rho}{n-3} r_c^{3-n}$$

Lennard-Jones potential

$$n \geq 4$$

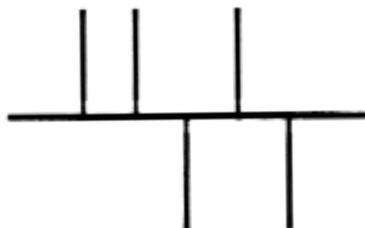
Coulomb potential

$n = 1$ "Long-range potentials"

Long-range potentials

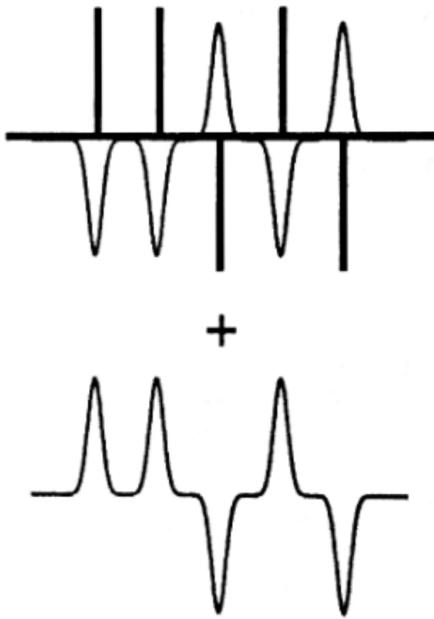
Electrostatic energy

e.g., a system of point charges



Long-range potentials

Ewald method: convert a conditionally convergent sum to convergent sum



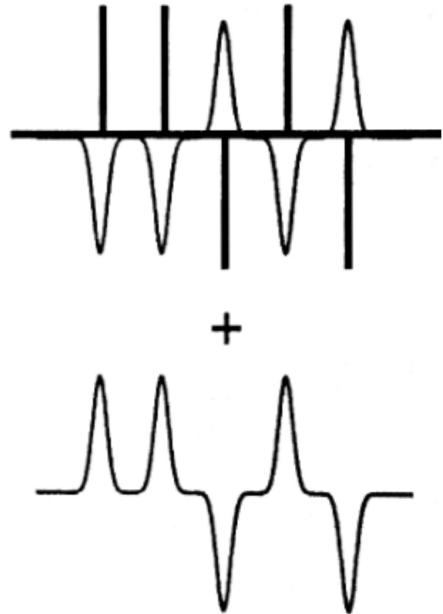
Interactions needed to compute

- 1) Coulomb potential of point particles
- 2) Electrostatic potential of Gaussian charges
- 3) Spurious self-interaction b/t Gaussian charges + point particles

Long-range potentials

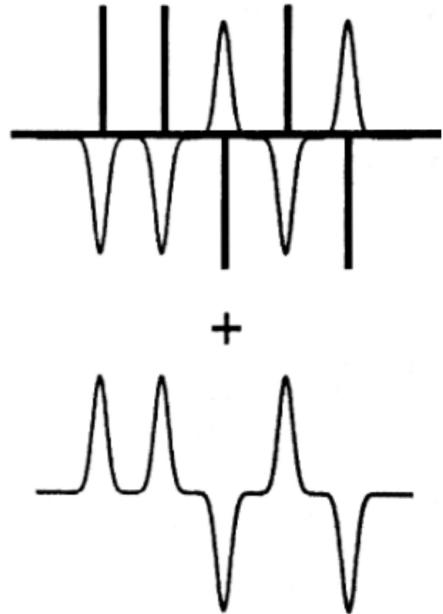
Ewald method

1) Coulomb potential of screened point particles



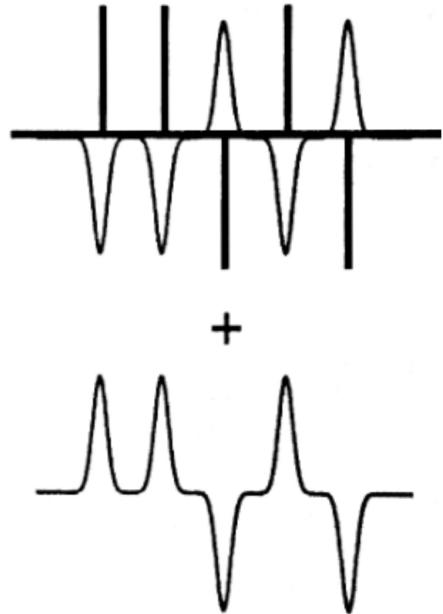
Long-range potentials

Ewald method: need to include interactions from compensating Gaussian charges



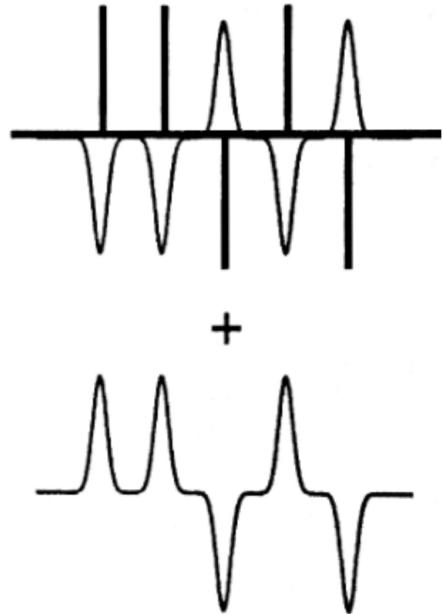
Long-range potentials

Ewald method: need to include interactions from compensating Gaussian charges



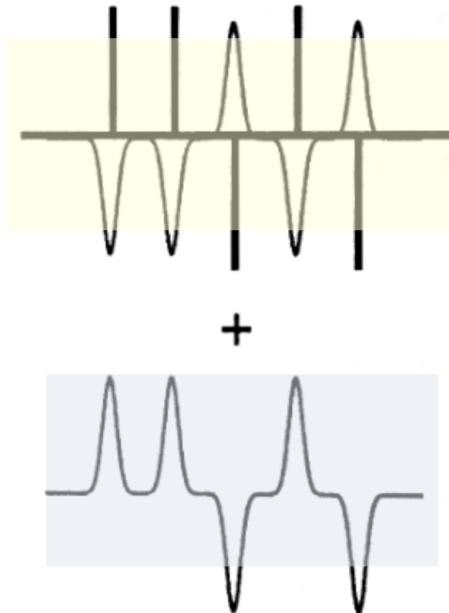
Long-range potentials

Ewald method: need to include interactions from compensating Gaussian charges



Long-range potentials

Ewald method: total energy

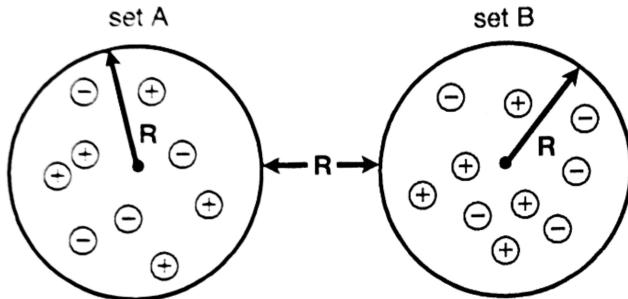


$$U_e = \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n \sum_{\mathbf{R}} \frac{q_i q_j \operatorname{erfc}(\sqrt{\alpha} |\mathbf{R} + \mathbf{r}_j - \mathbf{r}_i|)}{|\mathbf{R} + \mathbf{r}_j - \mathbf{r}_i|}$$
$$+ \frac{2\pi}{V} \sum_{k \neq 0} \frac{1}{k^2} \rho(\mathbf{k}) |^2 e^{-k^2 / 4\alpha^2}$$
$$- \left(\frac{\alpha}{\pi} \right)^{1/2} \sum_{i=1}^n q_i^2$$

Spurious self-interaction b/t
Gaussian charge and point charge

Long-range potentials

Fast Multipole Method



3	3	3	3
3	3	3	3
2	2	2	2
1	1	1	2
1	0	1	2
1	1	1	2