Welcome to
CHE 384T: Computational Methods in Materials Science

Simulating Finite Systems

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Announcements

HW2 released, due Sept 26, 11:59pm - lattice sums

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 diretionality

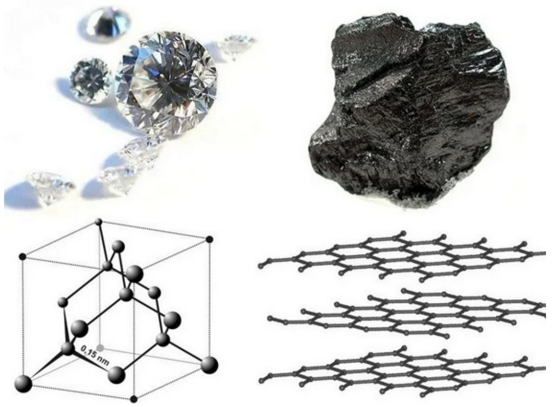
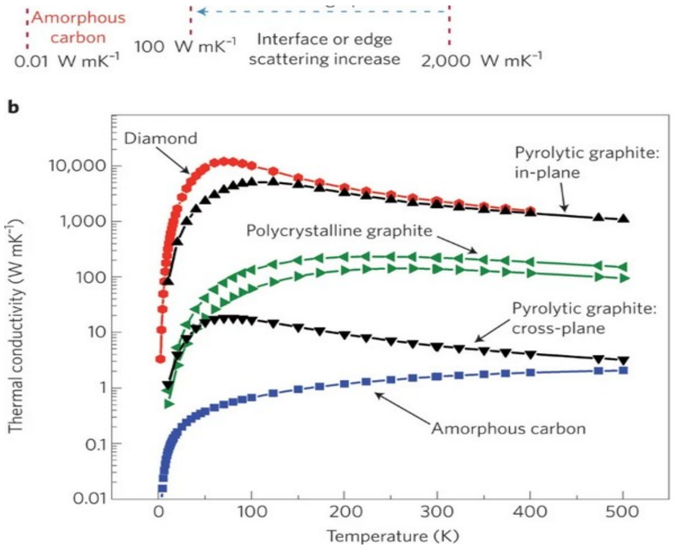


Table 3.4
Modulus of Elasticity Values for Several Metals at Various Crystallographic Orientations

	Modulus of Elasticity (GPa)		
Metal	*[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

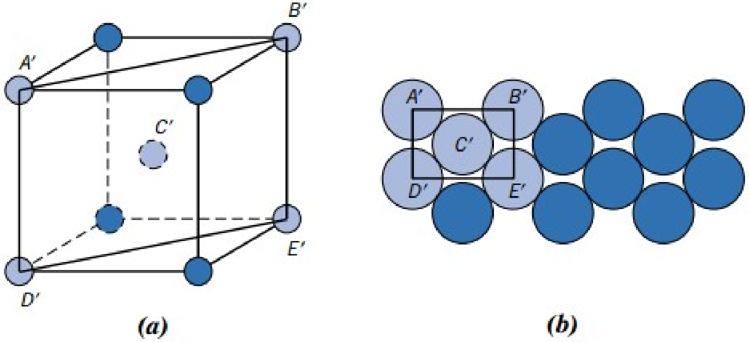
Source: R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd edition. Copyright © 1989 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.



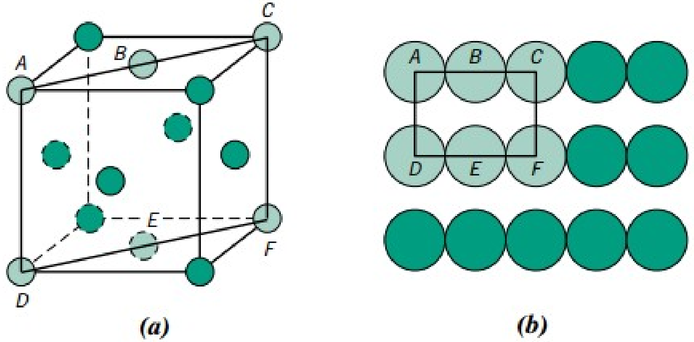
A. Balandin. Nature Mater 10, 569–581 (2011). 10.1038/nmat3064

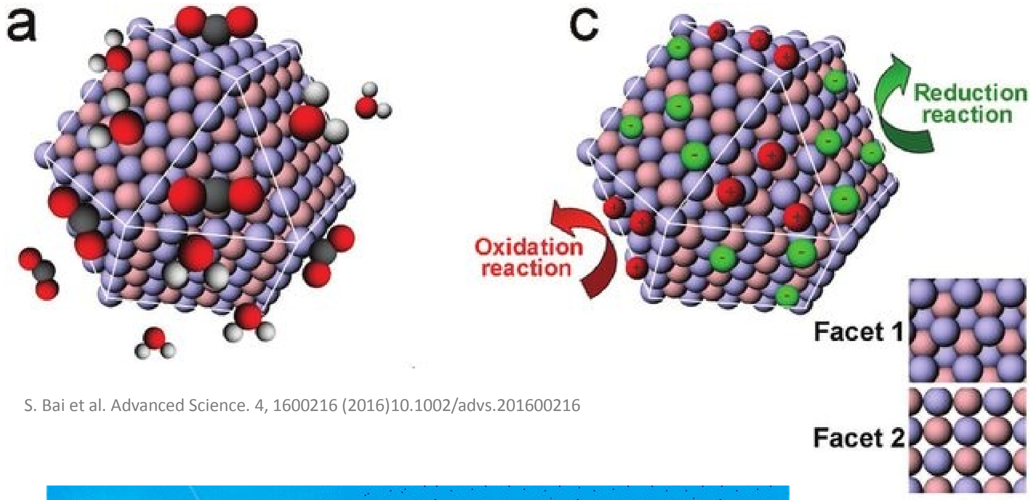
Crystallographic planes and surface facets

(110) plane for BCC

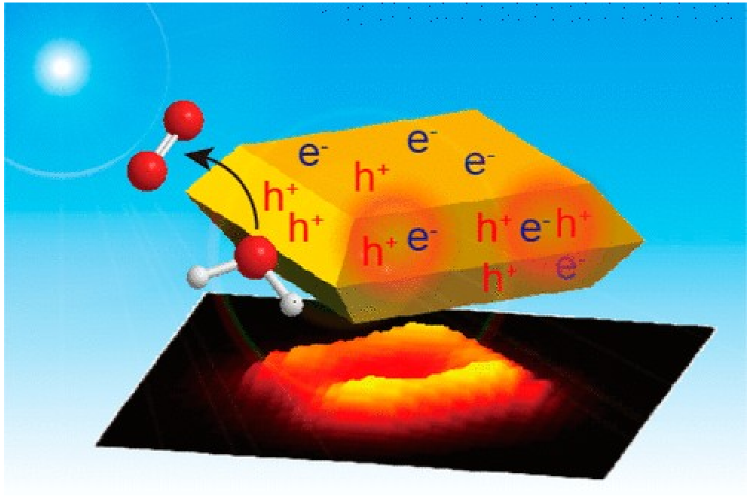


(110) plane for FCC



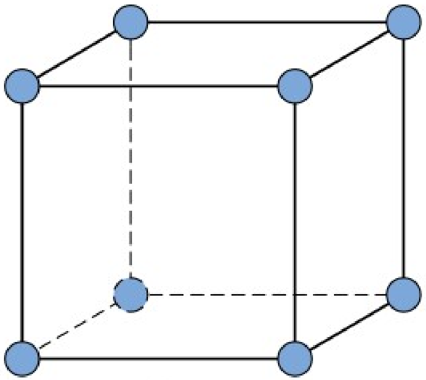


S. Bai et al. Advanced Science. 4, 1600216 (2016)10.1002/advs.201600216

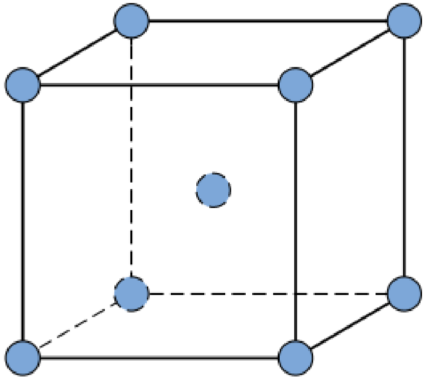


Cubic crystal structures (monoatomic)

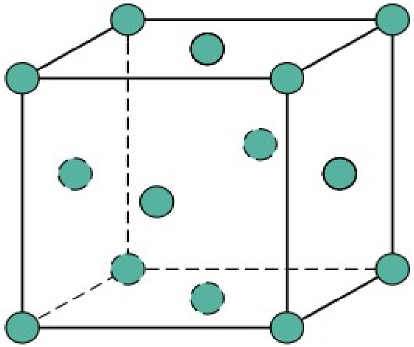
Simple Cubic

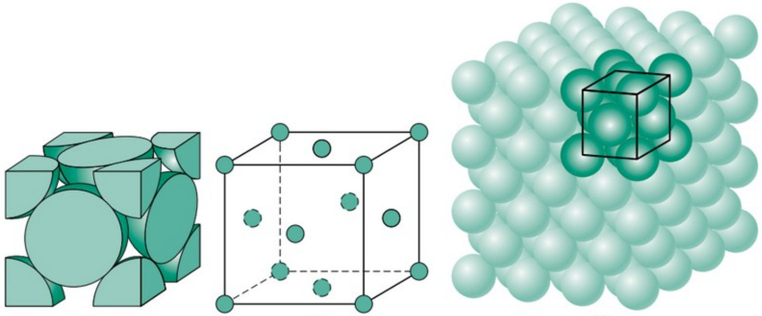


Body-Centered Cubic



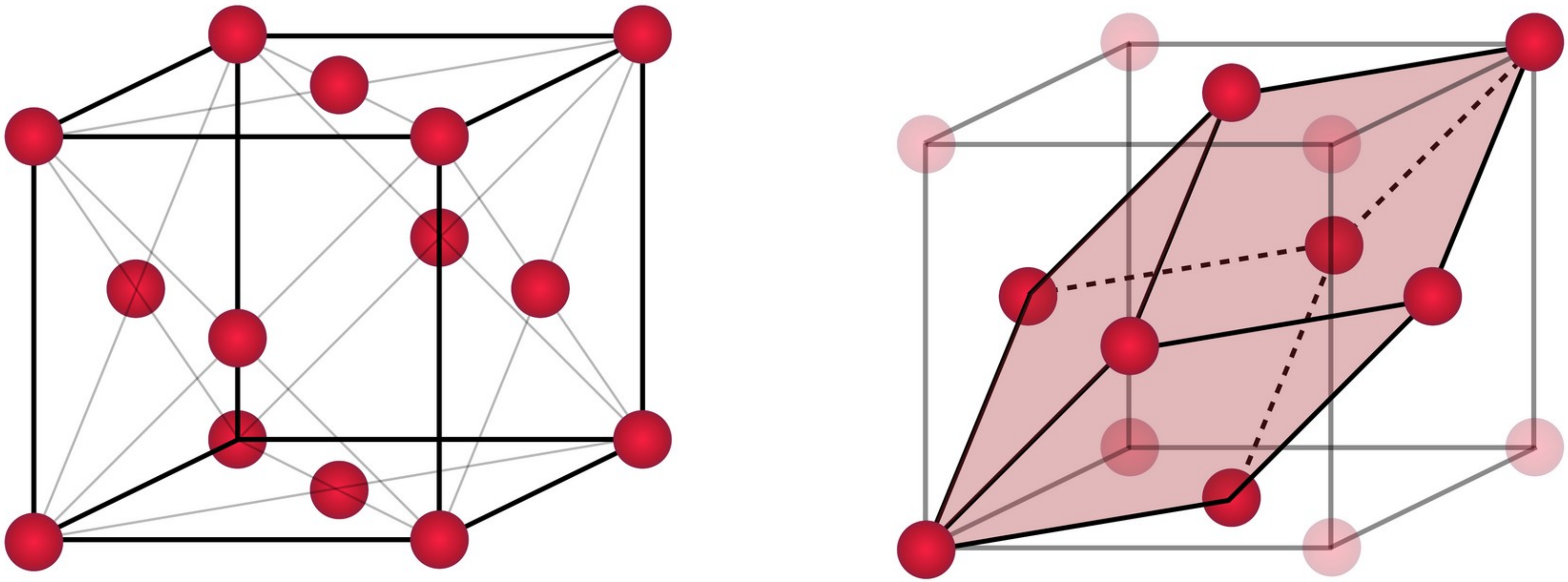
Face-Centered Cubic





(a) (b) (c)

Cubic crystal structures (monoatomic)

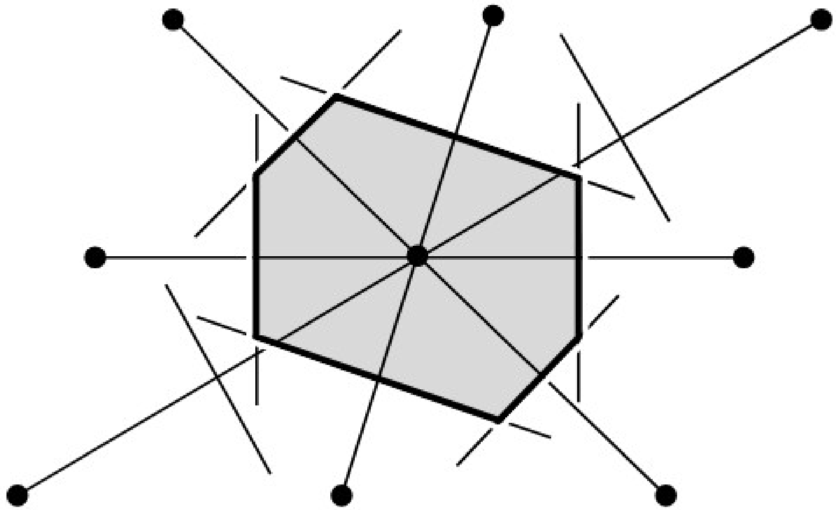


(a) conventional unit cell

(b) primitive unit cell

The Unit Cell

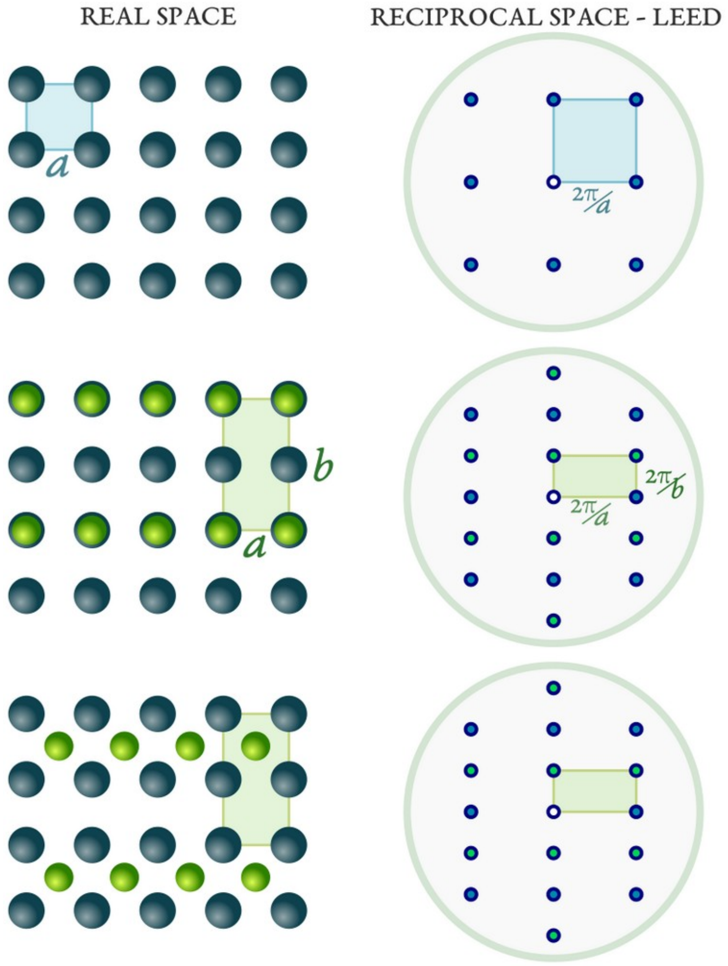
Figure 4 A primitive cell may also be chosen following this procedure: (1) draw lines to connect a given lattice point to all nearby lattice points; (2) at the midpoint and normal to these lines, draw new lines or planes. The smallest volume enclosed in this way is the Wigner-Seitz primitive cell. All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



Physics: “Wigner-Seitz cell”

Image from Kittel, Solid-state Physics

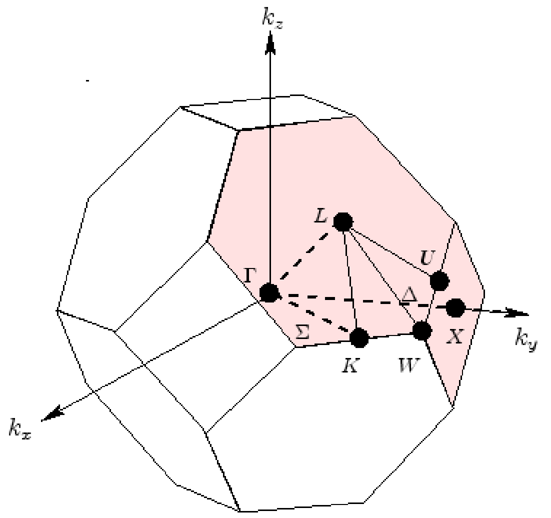
A side note on Reciprocal Space:



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

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

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



Reciprocal cell of FCC lattice, aka first Brillouin Zone

$$\mathbf{G} = v_1\mathbf{b_1} + v_2\mathbf{b_2} + v_3\mathbf{b_3}$$

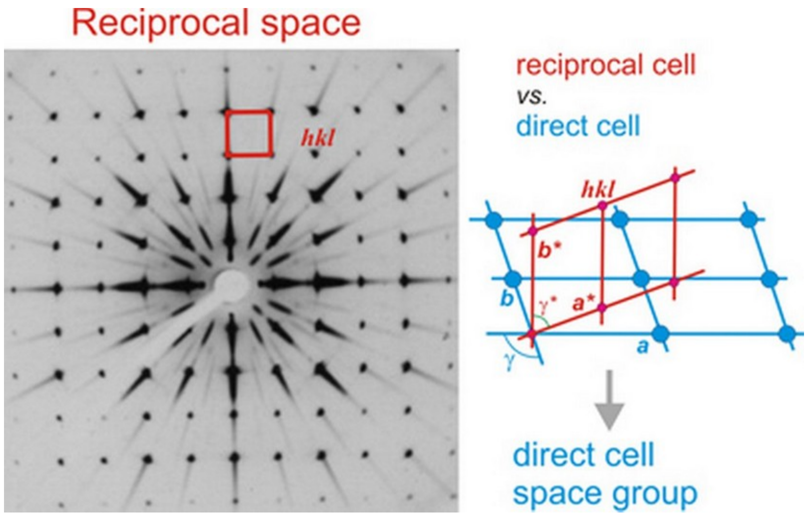
A side note on Reciprocal Space:

Why bother with reciprocal space?

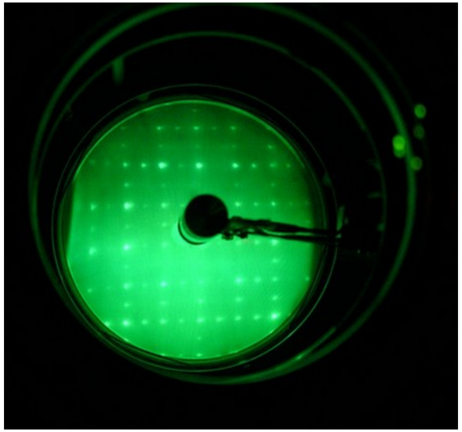
Falls out naturally in the math (complex exponentials)

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

X-ray diffraction → Bulk crystal structure



Low-energy electron diffraction (LEED)
→ Surface crystal structure



How XRD works

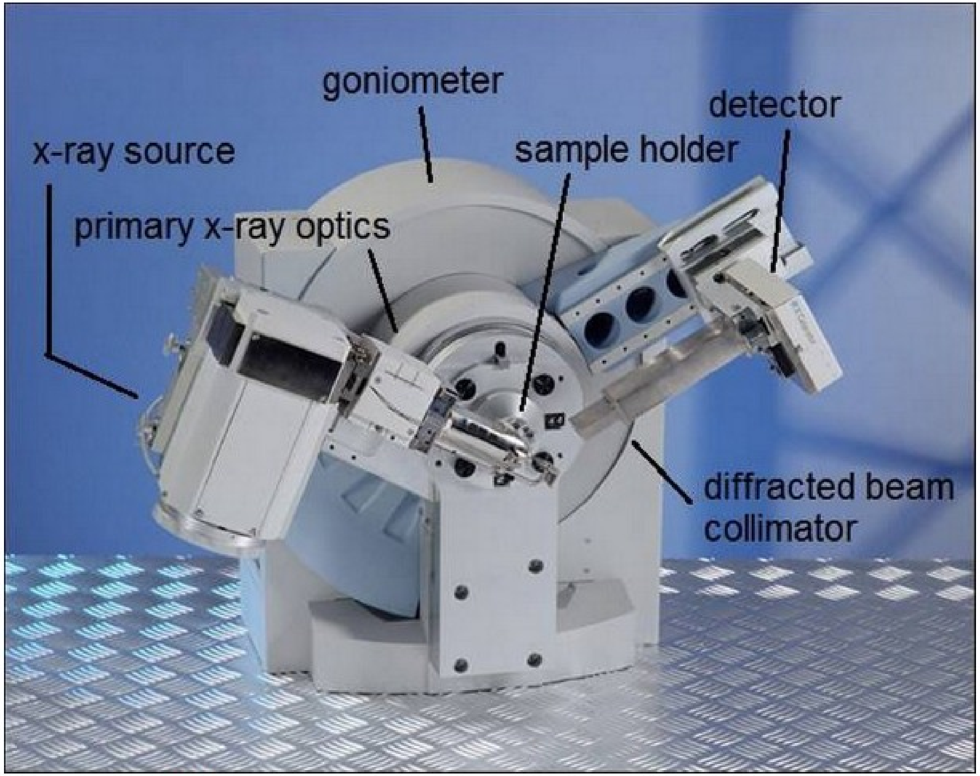


Image from link

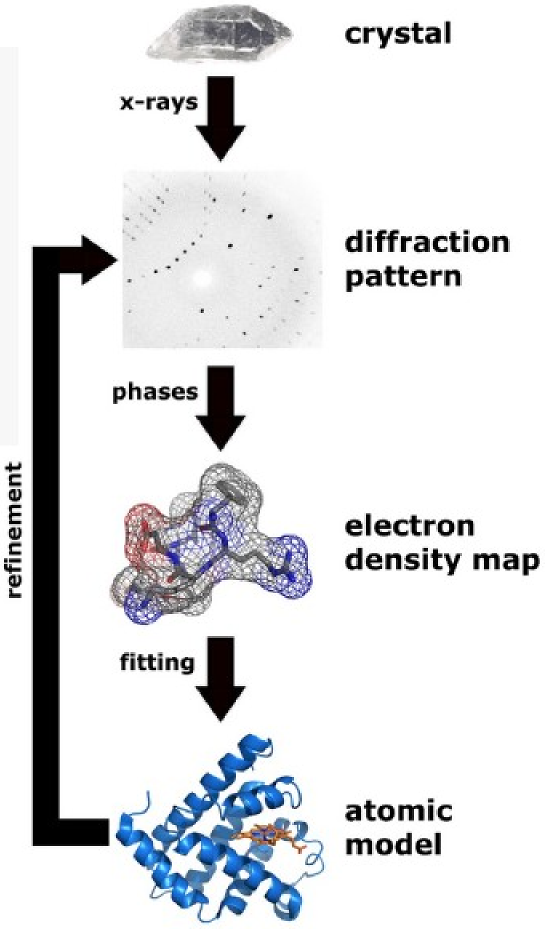


Image from Bio Libretext, CC BY-NC-SA 3.0

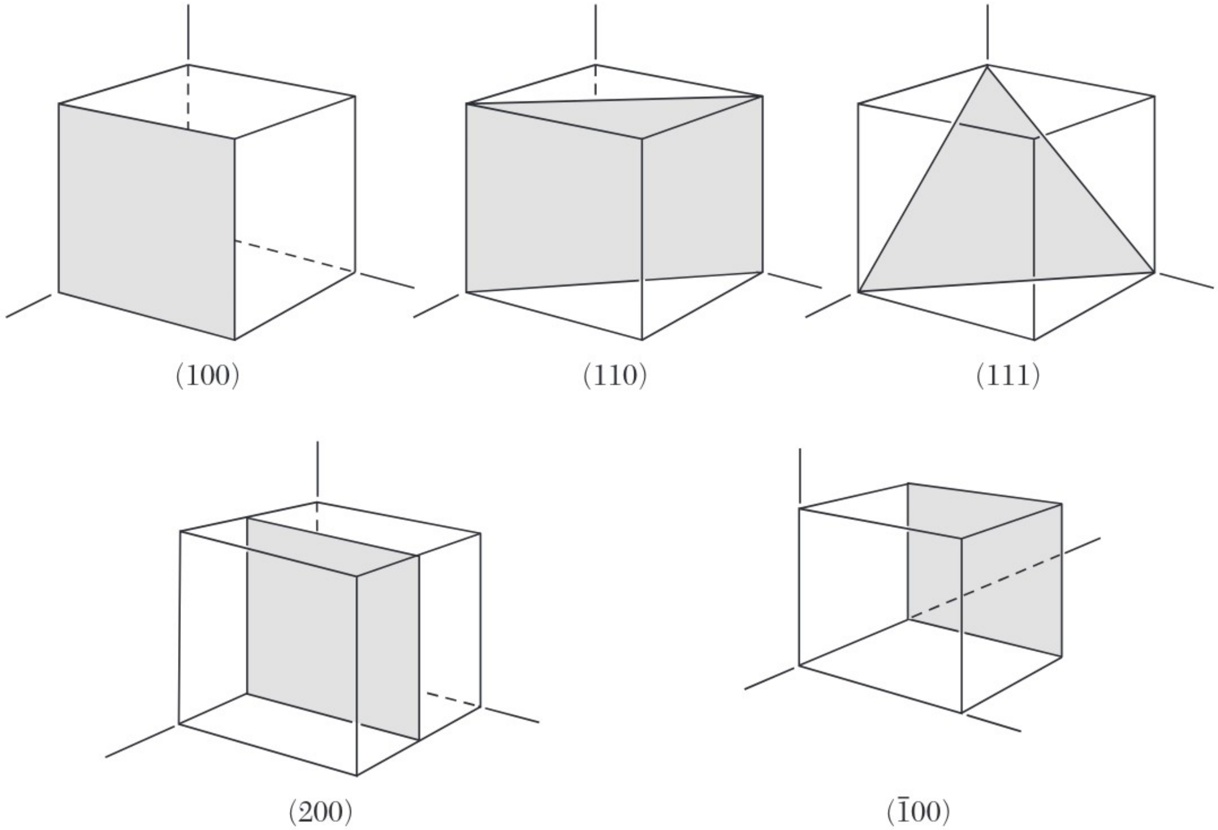


Figure 14 Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) and to (100).

Kittel, Solid-state Physics

Lecture Outline

Sums for pair-wise interactions

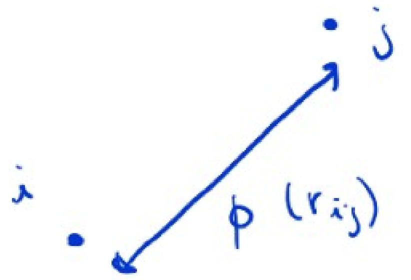
Cutoffs

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



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

e.g., Coulomb

total interaction of small sys.
4 particles

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

N particles

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

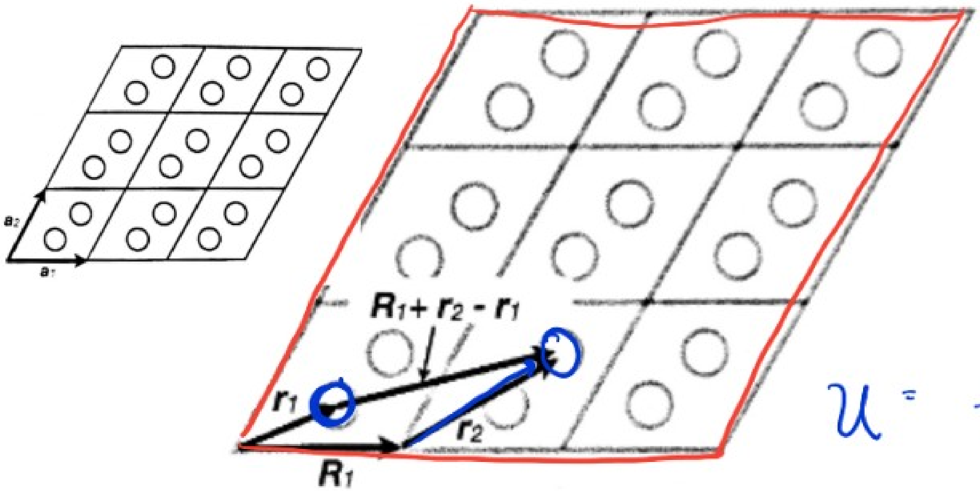
or

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

or

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

Perfect crystals



2 atoms/unit

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

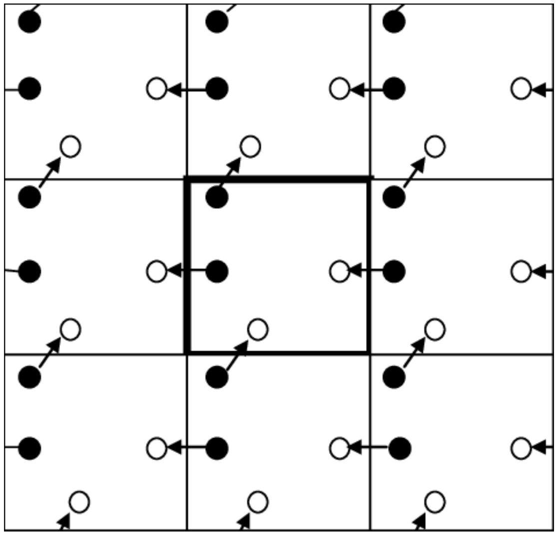
$$\mathcal{U} = \frac{1}{2} \sum_{\bar{R}_1} \sum_{i=1}^{N} \sum_{j=i}^{N}{}' \phi_{ij} \left(\left| \bar{R}_1 + \bar{r}_2 - \bar{r}_1 \right| \right)$$

w/i same unit cell

all interactions w/i unit cell + simulation cell

$$u \equiv \frac{1}{N} \mathcal{U}$$ energy per particle

Periodic Boundary Conditions



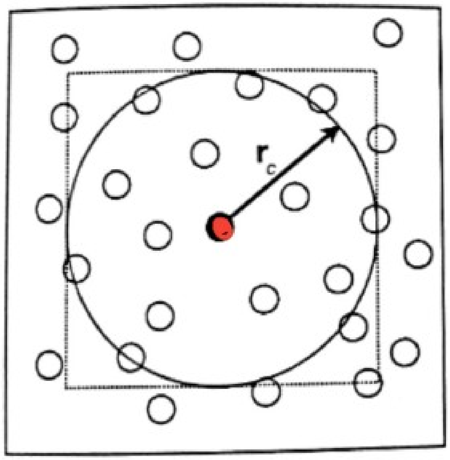
- Mimic the real (essentially infinite) system with a finite number of objects of a manageable simulation cell

- 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 4 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 $\phi(r) \sim \frac{1}{r^n}$

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

Lennard-Jones potential $n \geq 4$

Coulomb potential $n = 1$ "Long-range potentials"

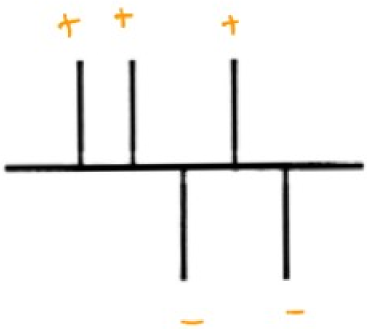
Long-range potentials

Electrostatic energy

$$\mathcal{U}_e = \frac{1}{2} \sum_{\bar{R}} \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \underbrace{\frac{q_i q_j}{|\bar{R} + \bar{r}_j - \bar{r}_i|}}_{\sim 1/r}$$

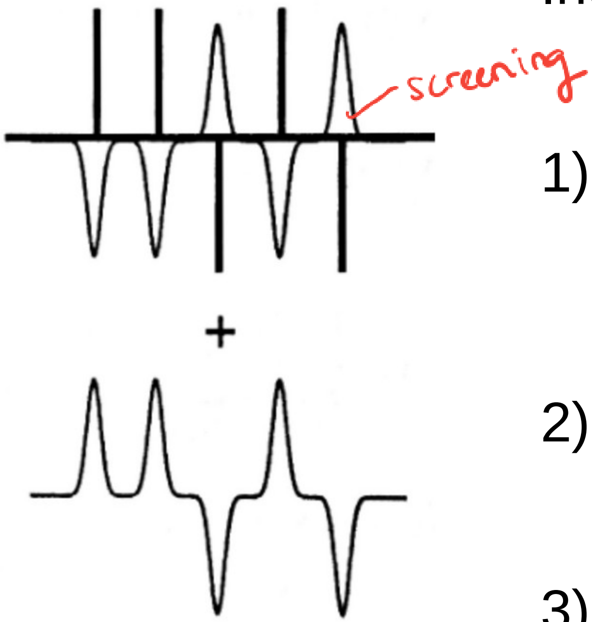
e.g., a system of point charges

$$\rho(\bar{r}) = \sum_{i=1}^{N} q_i \, \delta(\bar{r} - \bar{r}_i)$$



Long-range potentials

Ewald method: convert a conditionally convergent sum to convergen sum



Interactions needed to compute

(screened)

1) Coulomb potential of point particles

(periodic array, compensating/background)

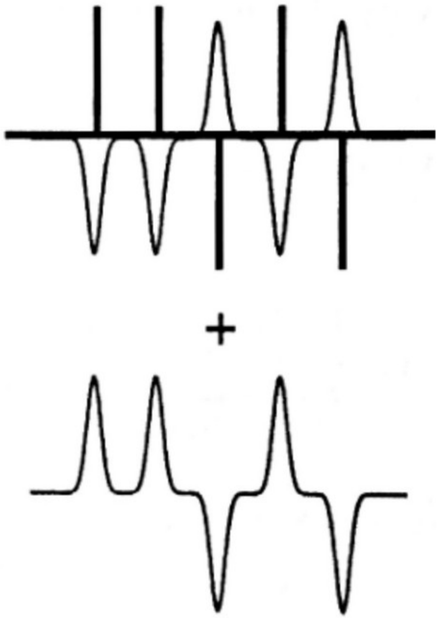
2) Electrostatic potential of Gaussian charges

(compensating/background)

3) Spurious self-interaction b/t Gaussian charges + point particles

Long-range potentials

Ewald method



1) Coulomb potential of screened point particles

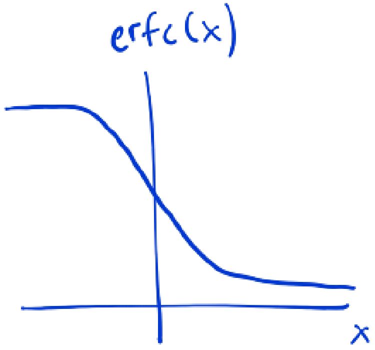
$$\rho(\bar r) = \sum_{j=1}^{n} q_j \left\{ \underbrace{\delta(\bar r - \bar r_j)}_{\text{original point charges}} - \underbrace{\left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha(\bar r - \bar r_j)^2}}_{\text{screening Gaussian charges}} \right\}$$

recall Poisson's equation (Gaussian units)

$$-\nabla^2 \phi(\bar r) = 4\pi\rho(\bar r)$$

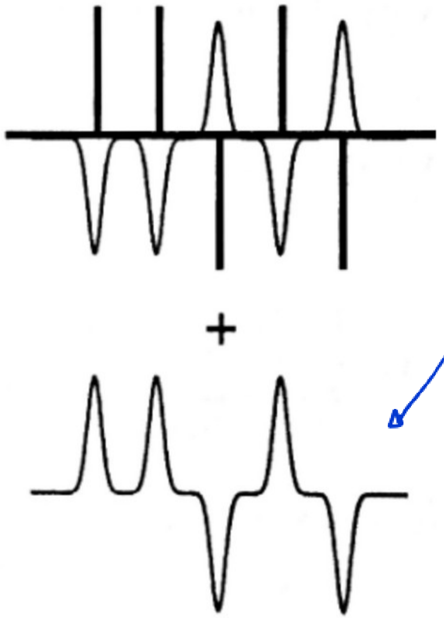
$$\Rightarrow \phi(\bar r) = \mathcal{U}^{①} = \frac{1}{2}\sum_{i\neq j} q_i q_j \frac{\operatorname{erfc}(\sqrt{\alpha}\,|\bar r_{ij}|)}{|\bar r_{ij}|}$$

short-range b/c screening



Long-range potentials

Ewald method: need to include interactions from compensating Gaussian charges



Take advantage of mathematical properties of Fourier transform of Poisson equation

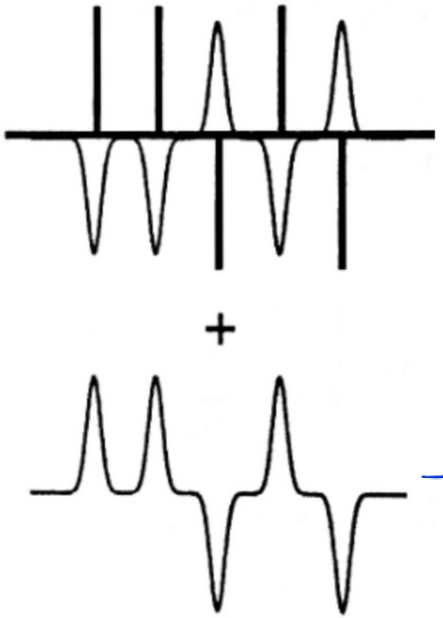
real space $-\nabla^2 \phi(\bar{r}) = 4\pi\rho(\bar{r})$

Fourier/reciprocal space $k^2 \tilde{\phi}(\bar{k}) = 4\pi\tilde{\rho}(\bar{k})$

$$\rightarrow \tilde{\phi}(\bar{k}) = \underbrace{\frac{4\pi}{k^2}}_{\text{Green's func. soln for unit point charge}} \cdot \underbrace{\tilde{\rho}(\bar{k})}_{\text{Fourier transform of collection of charge} \; = ?}$$

Long-range potentials

Ewald method: need to include interactions from compensating Gaussian charges



$$\tilde{\rho}(\bar{k}) = \int d\bar{r}\, \exp(-i\bar{k}\cdot\bar{r})\,\rho(\bar{r})$$

$$= \int d\bar{r}\, \exp(-i\bar{k}\cdot\bar{r}) \cdot \sum_{j=1}^{n} q_j \left(\frac{\alpha}{\pi}\right)^{3/2} \exp\left(-\alpha|\bar{r}-\bar{r}_j|^2\right)$$

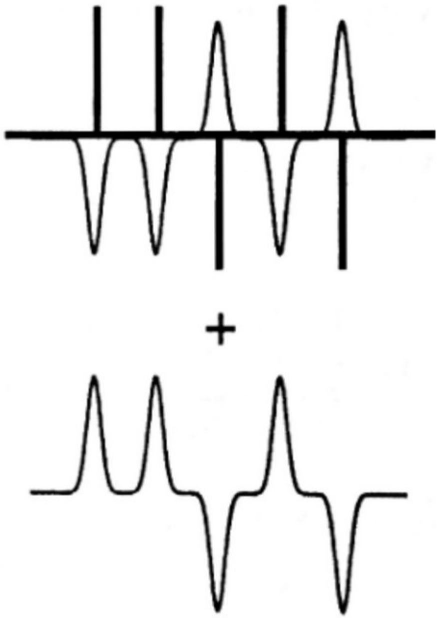
$$= \sum_{j=1}^{n} q_j \exp(-i\bar{k}\cdot\bar{r}_j)\exp\left(-k^2/4\alpha\right)$$

since $\tilde{\phi}(\bar{k}) = \frac{4\pi}{k^2}\tilde{\rho}(k) \rightarrow$

$$\rightarrow \tilde{\phi}(\bar{k}) = \frac{4\pi}{k^2} \cdot \sum_{j=1}^{n} q_j \exp(-i\bar{k}\cdot\bar{r}_j)\exp\left(-\frac{k^2}{4\alpha}\right)$$

Long-range potentials

Ewald method: need to include interactions from compensating Gaussian charges



since $\mathcal{U}^{comp} = \frac{1}{2}\sum_i q_i \, \phi_i(r_i)$

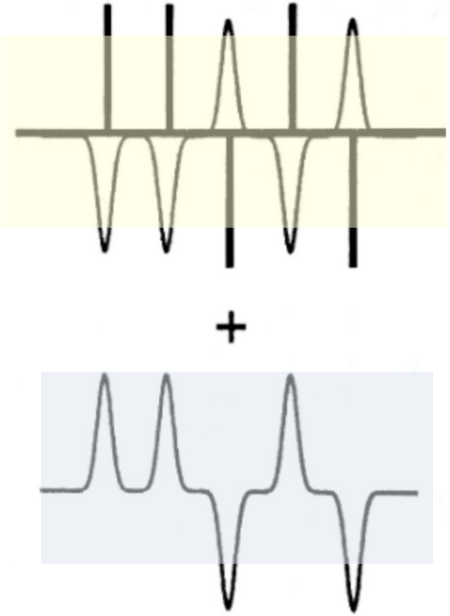
reverse FT : $\phi(\bar{r}) = \mathcal{F}^{-1}\left(\tilde{\phi}(\bar{k})\right)$

$$= \frac{1}{V}\sum_{k\neq 0} \tilde{\phi}(k)\exp(+i\bar{k}\cdot\bar{r})$$

$$\Rightarrow \mathcal{U}^{(2)} = \frac{1}{2}\sum_{k\neq 0}^{n} \frac{4\pi}{Vk^2} \underbrace{q_i q_j \exp\left(-i\bar{k}\cdot(\bar{r}_j-\bar{r}_i)\right)}_{\equiv |\rho(k)|^2} \exp(-k^2/4\alpha)$$

Long-range potentials

Ewald method: total energy



$$U_e = \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{\mathbf{R}} \frac{q_i q_j \operatorname{erfc}(\sqrt{\alpha}|\mathbf{R}+\mathbf{r}_j-\mathbf{r}_i|)}{|\mathbf{R}+\mathbf{r}_j-\mathbf{r}_i|} \quad u^{1}$$

$$+\frac{2\pi}{V}\sum_{k\neq 0}\frac{1}{k^2}\rho(\mathbf{k})|^2 e^{-k^2/4\alpha^2} \quad u^{2}$$

$$-\left(\frac{\alpha}{\pi}\right)^{1/2}\sum_{i=1}^{n} q_i^2$$

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

Long-range potentials

Fast Multipole Method