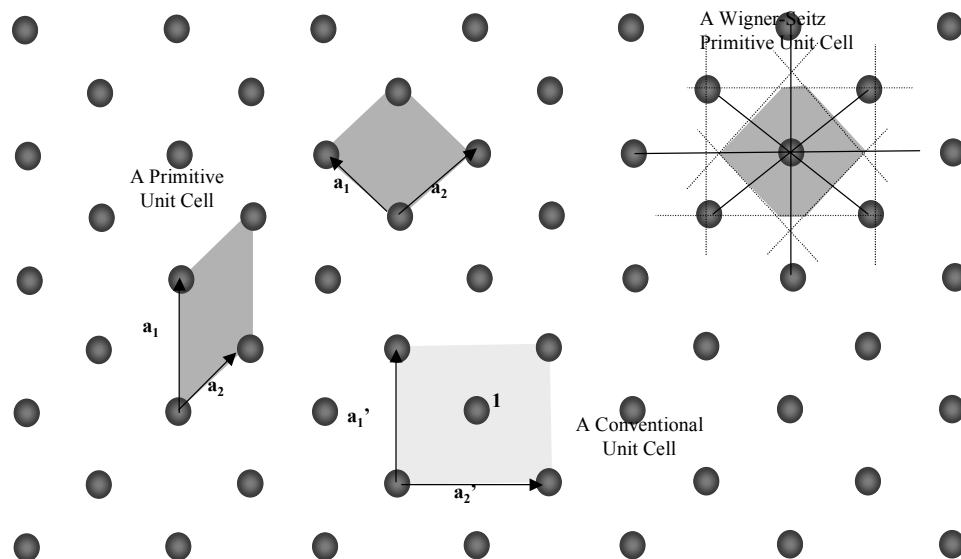


2.57 Nano-to-Macro Transport Processes
Fall 2004
Lecture 8

In the last lecture, we have talked about the **primitive unit cell**. There is only one lattice point (equivalently speaking) per primitive unit cell. The smallest space formed by all the bisecting planes is a Wigner-Seitz cell, as indicated in the figure.



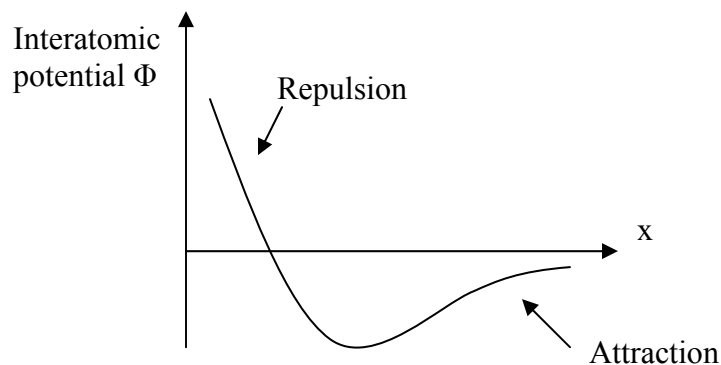
For the bonding potential, two often-used empirical expressions for the repulsive potential between the atoms separated by a distance r are

$$U_R(r) = \frac{B}{r^{12}} \quad (\text{Lennard-Jones})$$

and

$$U_R(r) = U_0 e^{-r/\zeta} \quad (\text{Born-Mayer})$$

where B , ζ , and U_0 are empirical constants determined from experimental data, such as the interatomic spacing and the binding energy.



Combining this attractive potential (van der Waals potential) with the Lennard-Jones potential for the repulsive force, we obtain the Lennard-Jones interaction potential between a pair of atoms i and j in a crystal as

$$U_{ij} = \frac{B}{r_{ij}^{12}} - \frac{A}{r_{ij}^6}.$$

What makes a crystal structure a favorable structure is that the total potential energy of the system reaches a minimum, as required by the second law of thermodynamics for a stable system.

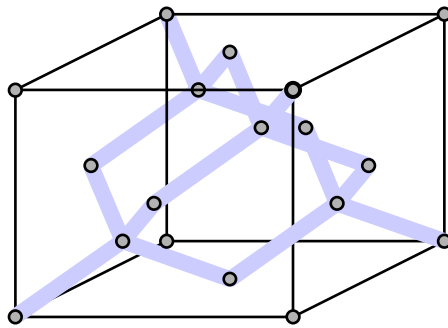
In **ionic crystals**, such as NaCl, the single valence electron in the sodium atom moves to the chlorine atom such that both Na^+ and Cl^- have closed electron-shells but meanwhile, become charged. The Coulomb potential among the ions becomes the major attractive force. The potential energy of any ion i in the presence of other ions j is then,

$$U_{i,A} = \sum_{i \neq j} \frac{\pm q^2}{4\pi\epsilon_0 r_{ij}} = -\frac{\alpha q^2}{4\pi\epsilon_0 r_0}$$

where q is the charge per ion, ϵ_0 the dielectric constant, and r_0 the nearest-neighbor separation. The parameter α is called the Madelung constant and is related to the crystal structure. This attractive potential, combined with an appropriate repulsive potential, gives a description of the potentials for ionic crystals.

Covalent bonds are formed when electrons from neighboring atoms share common orbits, rather than being attached to individual ions as in ionic crystals. Diamond, silicon, and germanium are all **covalent crystals**. Each atom has four electrons in the outer shell and forms a tetrahedral system of covalent bonds with four neighboring atoms, as indicated in the figure.

Note: For instance, in silicon the $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ atom is shared by neighboring atoms.



In certain crystals, such as GaAs, both the covalent and ionic bonding are important. Fundamentally, the covalent bonding force is still due to charge interaction. Unlike the van der Waals force in molecular crystals or the electrostatic force in ionic crystals, however, it is more difficult to write down simple expressions for the covalent crystals.

In covalent bonds, electrons are preferentially concentrated in regions connecting the nucleus, leaving some regions in the crystal with low charge concentration. Metals and their associated **metallic bonds** can be considered as an extreme case of the covalent bonds, when the covalent bonds begin to overlap and all regions of the crystal get filled up with charges. In the case of total filling of the empty space, it becomes impossible to tell which electron belongs to which atom. This can be shown by the distribution of wavefunction $\Psi(\vec{r})$, in which the probability $\Psi(\vec{r})\Psi^*(\vec{r})$ is more uniform in a metal.

3.1.4 Reciprocal lattice

If a time function $f(t)$ is periodic with a period of T (i.e. $f(t+T) = f(t)$), it can be expanded into a Fourier series as,

$$f(t) = \sum_{n=-\infty}^{\infty} \left(a_n \sin\left(\frac{2\pi n}{T}t\right) + b_n \cos\left(\frac{2\pi n}{T}t\right) \right)$$

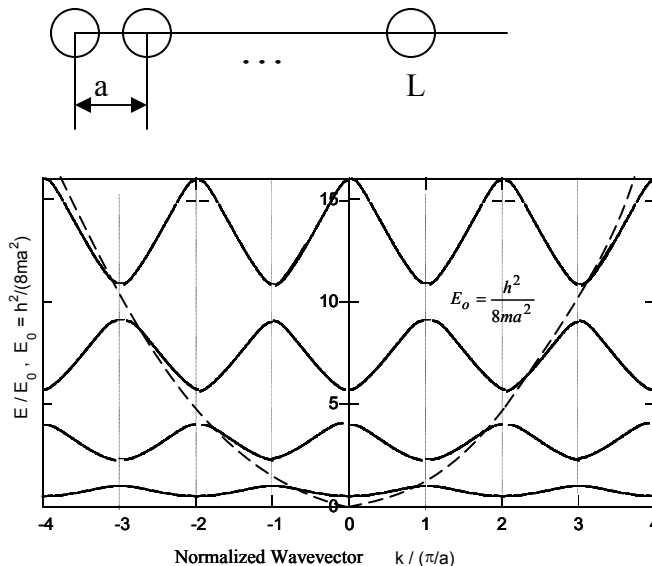
$$= \sum_{n=-\infty}^{\infty} \left(a_n 'e^{in\omega t} + b_n 'e^{-in\omega t} \right)$$

Here the angular frequency $\omega=2\pi/T$ is the Fourier conjugate of the time periodicity such that $e^{i\omega T}=1$, which ensures that $f(t)$ is periodic.

A spatial function, $f(x)$, with a periodicity a , $f(x) = f(x+a)$, can be similarly expanded into a Fourier series,

$$f(x) = \sum_{n=-\infty}^{\infty} \left(a_n 'e^{ink_x x} + b_n 'e^{-ink_x x} \right)$$

where the wavevector, $k_x=2\pi/a$, is the Fourier conjugate to spatial periodicity a .



In the above figure, the electron energy dispersion shows a period of $2\pi/a$ because of the periodic potential field $u(x+a) = u(x)$ (recall the Bloch theorem).

Note: (1) The discussed function $f(x)$ can represent not only the charge density but also other periodically distributed properties. (2) The Born-von Karman boundary condition requires that the wave functions at the two end points be equal to each other. This results in $\Delta k = \frac{2\pi}{L} = \frac{2\pi}{Na}$, not $k_x = \frac{2\pi}{a}$. (3) For personal interests, you may want to compare the process with digital signal processing (DSP), where a is in analog to the sampling period, k corresponds to the detected frequency. The highest measurable frequency is inversely proportional to a .

Now we will extend our discussion to three-dimensional cases. With a translation lattice vector $\vec{T} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$, we can reach any crystal point from the origin.

For a function $u(\mathbf{r}) = u(\mathbf{r} + \mathbf{T})$, we will first give the following answer and then show that the given Fourier expansion indeed satisfies the required periodicity,

$$u(\mathbf{r}) = \sum_{\mathbf{G}} u_{\mathbf{G}} e^{i\mathbf{r} \cdot \mathbf{G}}$$

where \mathbf{G} and the inverse transformation are given by

$$\mathbf{G} = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$$

and $(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$ are conjugated to the primitive lattice vectors $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ through

$$\mathbf{b}_1 = 2\pi(\mathbf{a}_2 \times \mathbf{a}_3) / V, \quad \mathbf{b}_2 = 2\pi(\mathbf{a}_3 \times \mathbf{a}_1) / V, \quad \mathbf{b}_3 = 2\pi(\mathbf{a}_1 \times \mathbf{a}_2) / V$$

where $V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$ is the volume of the primitive unit cell in real space. For the one-dimensional case, we have $\mathbf{G} = 2\pi n/a$, $r = x$.

With the above definitions, we can show that $u(\mathbf{r})$ is indeed invariant with any translational lattice vector in the real space, $\mathbf{T} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, where n_1, n_2, n_3 integers,

$$\begin{aligned} u(\mathbf{r} + \mathbf{T}) &= \sum_{\mathbf{G}} u_{\mathbf{G}} e^{i(\mathbf{r} + \mathbf{T}) \cdot \mathbf{G}} = \sum_{\mathbf{G}} u_{\mathbf{G}} e^{i\mathbf{r} \cdot \mathbf{G} + i\mathbf{T} \cdot \mathbf{G}} \\ &= \sum_{\mathbf{G}} u_{\mathbf{G}} e^{i\mathbf{r} \cdot \mathbf{G} + i2\pi(n_1m_1 + n_2m_2 + n_3m_3)} = \sum_{\mathbf{G}} u_{\mathbf{G}} e^{i\mathbf{r} \cdot \mathbf{G}} = u(\mathbf{r}) \end{aligned}$$

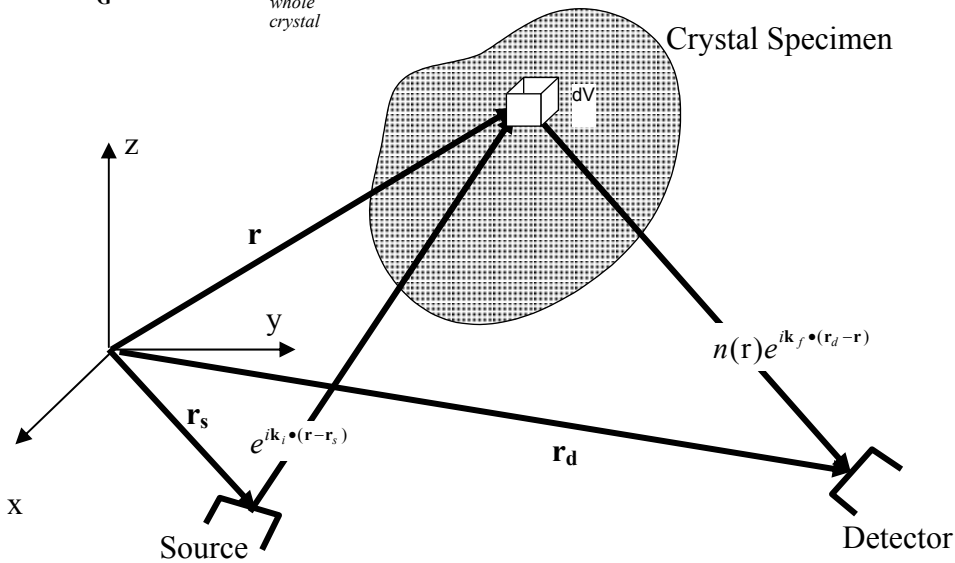
Thus, we see that the new set of vectors introduced, $(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$, which has a unit of m^{-1} , are the corresponding Fourier conjugate to the real space lattice vector $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$. We can use $(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$ to construct a new lattice called the **reciprocal lattice**. Previous definitions on real space lattices, such as unit cells and the Wigner-Seitz primitive unit cell, are equally applicable to such a reciprocal lattice. This reciprocal space is the Fourier conjugate of the real space.

Although a very abstract concept, the reciprocal lattice can actually be easily mapped out with diffraction experiments. When electron waves or X-rays (electromagnetic waves) with proper energy are shone onto a crystal, the reflection or transmission occurs only along specific directions, as shown in the following figure.

Consider an incident wave from the source along direction \mathbf{k} . The incident wave is proportional to $e^{i\mathbf{k}_i \cdot (\mathbf{r}-\mathbf{r}_s)}$, where \mathbf{r} is any point in the sample and \mathbf{r}_s is the location of the source relative to the origin of coordinates. The wave scattered into the detector is then proportional to $n(\mathbf{r})e^{i\mathbf{k}_f \cdot (\mathbf{r}_d-\mathbf{r})}$, where \mathbf{k}_f is the propagation direction of the scatter wave, $n(\mathbf{r})$ is the nuclei density, and \mathbf{r}_d is the position of the detector. Because each of the atoms may scatter wave, the total amplitude at the detector is

$$\int_{\text{whole crystal}} A e^{i\mathbf{k}_i \cdot (\mathbf{r}-\mathbf{r}_s)} n(\mathbf{r}) e^{i\mathbf{k}_f \cdot (\mathbf{r}_d-\mathbf{r})} dV = A e^{i(\mathbf{k}_f \cdot \mathbf{r}_d - \mathbf{k}_i \cdot \mathbf{r}_s)} \int_{\text{whole crystal}} n(\mathbf{r}) e^{i(\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{r}} dV$$

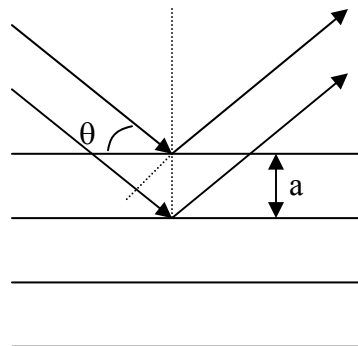
$$= A \sum_{\mathbf{G}} e^{i(\mathbf{k}_f \cdot \mathbf{r}_d - \mathbf{k}_i \cdot \mathbf{r}_s)} \int_{\text{whole crystal}} n_{\mathbf{G}} e^{i(\mathbf{G} + \mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{r}} dV$$



Because the exponential function $e^{i(\mathbf{G} + \mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{r}}$ is a rapidly varying function in the crystal with both negatives and positives, the above integral will be close to zero except when the exponent vanishes, i.e., when

$$\mathbf{G} + \mathbf{k}_i - \mathbf{k}_f = \mathbf{0}.$$

This is called the Bragg condition for diffraction. Because the wavevectors \mathbf{k}_f and \mathbf{k}_i are determined by the relative positions of the source, the sample, and the detector. The reciprocal lattice vectors \mathbf{G} , and thus the crystal structure, can be determined from diffraction experiments.



Consider the special set of crystal planes separated by a distance a as shown in the following figure and an incident wave (photon or electron) of wavelength λ at an angle θ . Constructive interference between waves reflected from crystal planes occurs when the phase difference of the waves scattered between two consecutive planes is $2\pi n$. From the figure, we see that the path difference is $2a\sin\theta$. Thus diffraction peaks will be observed when the path difference is multiples of the wavelength, i.e., $2a \sin \theta = n\lambda$.

In the following lecture, we will continue the discussion of energy dispersion for electrons and phonons. For phonons, in the acoustic waves a linear energy dispersion function is used as the approximation. For electrons, two parabolic curves are connected to approximate the energy dispersion.

