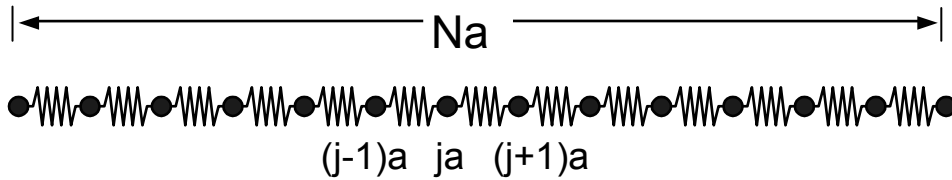


**2.57 Nano-to-Macro Transport Processes**  
**Fall 2004**  
**Lecture 7**

In the last lecture, we have talked about atoms in a one-dimensional chain. We find the solution as

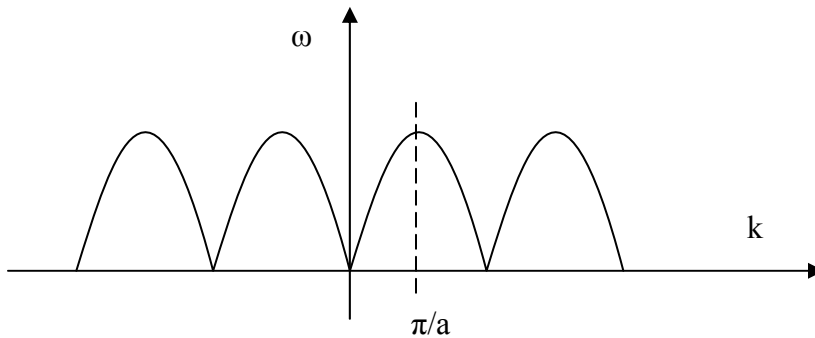
$$u_j = A \exp[-i(\omega t - kja)],$$

where the frequency is  $\omega = 2\sqrt{\frac{K}{m}} \left| \sin \frac{ka}{2} \right|$ .



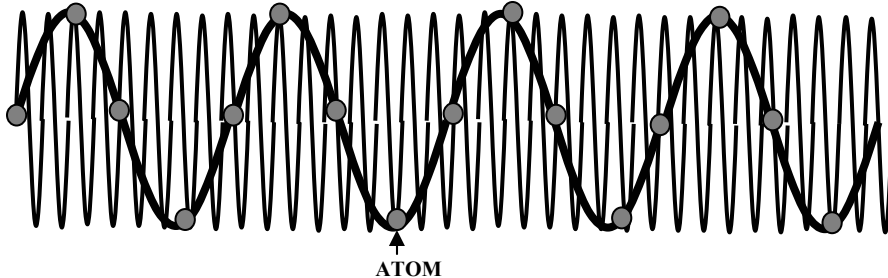
Note: When  $k$  approaches zero for large wavelength, the frequency becomes a linear function of the wavevector, i.e.  $\omega \approx 2\sqrt{\frac{K}{m}} \frac{ka}{2} = ka\sqrt{\frac{K}{m}}$ . We can calculate the sound

velocity by  $v_{\text{sound}} = \frac{d\omega}{dk}$ .



In last two lectures, we have derived the allowed  $k$  values as

$$k = \frac{2\pi n}{Na} \quad (n=0, \pm 1, \pm 2, \dots).$$



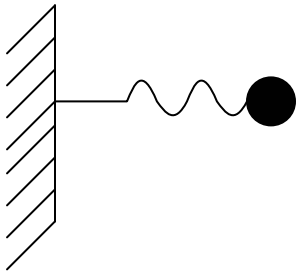
In the above figure,  $k = \pi/a$  corresponds to  $\lambda = 2a$ . However,  $k > \pi/a$  is meaningless in physics because there are no atoms vibrating between one period. Thus the allowable

wavevector for a lattice vibration is naturally confined to the first Brillouin zone ( $|k| < \pi/a$ ). Therefore, we totally have  $N$  allowable wavevectors (also wavelength) in between  $-\pi/a < k < \pi/a$ . Each of these wavevectors corresponds to one mode of the vibration of the lattice. This mode is called a **normal mode**.

For a harmonic oscillator, quantum mechanics gives

$$E_n = h\nu(n + 1/2); \nu = \frac{1}{2\pi} \sqrt{\frac{K}{m}},$$

in which the frequency is consistent with classical mechanics.



Similarly, quantum mechanics gives the energy levels for a chain with  $N$  atoms as

$$E_n = h\nu(n + \frac{1}{2})$$

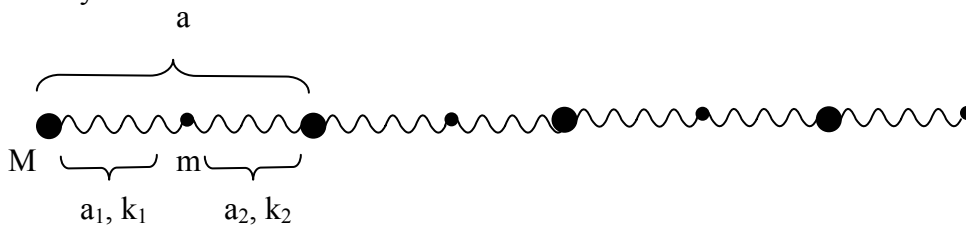
or  $E_n = \hbar\omega(n + \frac{1}{2})$  ( $n=0,1,2,3,\dots$ ),

in which  $\omega = 2\sqrt{\frac{K}{m}} \left| \sin \frac{ka}{2} \right|$ .

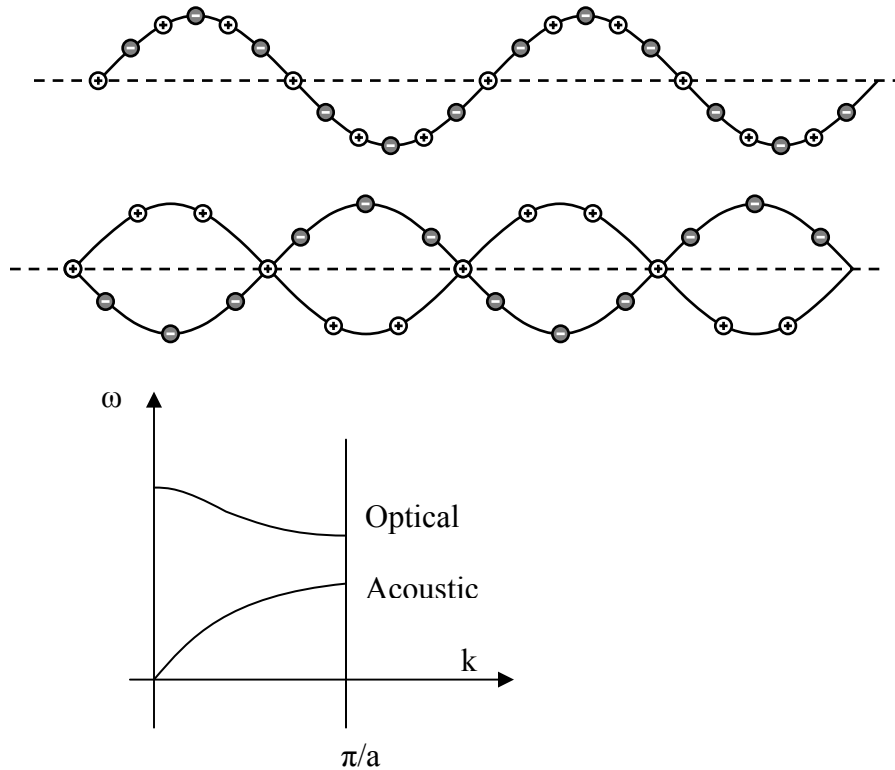
The basic vibrational energy quanta,  $h\nu$ , is called a phonon. Comparison between electrons, phonons, and photons:

- (1) Electrons obey the Pauli exclusion principle, which says that each quantum state can only have at most one electron. Photons and phonons are not limited by the Pauli exclusion principle. Each quantum state, which corresponds to one set of wavevectors, can have many phonons and photons.
- (2) Unlike electrons, phonons and photons at rest do not have mass though they have momentum and energy. They are also called fictitious particles since they are the quantization of the normal mode of a field.

### 3.3.3 Polyatomic lattice chain

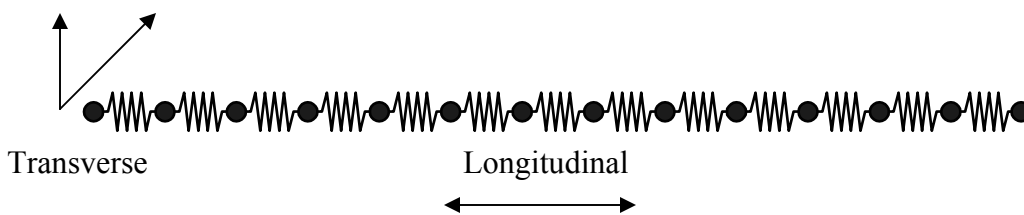


Now let us consider a chain with two atoms per period, in which two types of motions exist. In the first case, the adjacent two atoms vibrate in phase, while in the second figure the two atoms are moving out of phase. Clearly, the out-of-phase modes require more energy. Lower frequency (energy) branch is called the acoustic branch and the higher frequency one is called the optical branch, because the high frequency phonons in the optical branch can interact with electromagnetic waves more easily. In general, if there are  $m$  atoms in a basis and  $N$  lattice points in the chain, there are one acoustic branch with  $N$  acoustic modes, and  $(m-1)$  optical branches with  $(m-1)N$  optic modes.

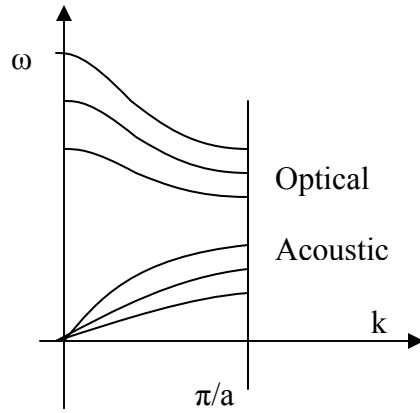


### 3.3.4 Phonons in 3D crystals

- Each direction is different
- Two transverse waves, one longitudinal wave



- For  $m$  atoms per basis, we have 3 acoustic waves and  $3(m-1)$  optical waves.
- Each  $k_x, k_y, k_z$  represents a normal mode.
- The energy dispersion (E-k relationship) can be totally different in different directions, such as  $a, \sqrt{2}a$ , and  $\sqrt{3}a$ .



Note: (1) For the out-of-phase movement, both longitudinal and transverse modes exist. (2) The transverse waves normally have lower frequencies because less energy is required for the wave propagation. (3) Normally sound (pressure waves) are longitudinal waves; electromagnetic (EM) waves are transverse waves; acoustic waves can be either type. (4) In some cases two transverse waves can overlap in the figure. (5) At  $k = \pi/a$ , all curves should be horizontal.

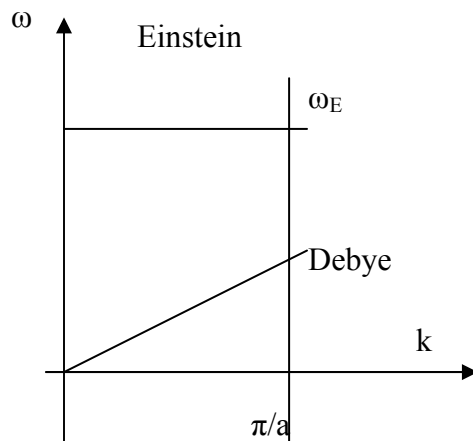
#### f. Approximation

##### (1) Debye approximation

Although the E-k curves for acoustic phonons are nonlinear, very often, the Debye approximation is used, which assumes a **linear** and **isotropic** relation between the frequency and the wavevector. This approximation is valid at low frequencies but is not a good approximation at high frequencies. In the very low frequency region, the lattice vibration carries the sound wave.

##### (2) Einstein approximation

The optical phonons are simplified as constant frequency  $\omega_E$ .



### 3.1 Crystal structures

#### (1) Basic conceptions

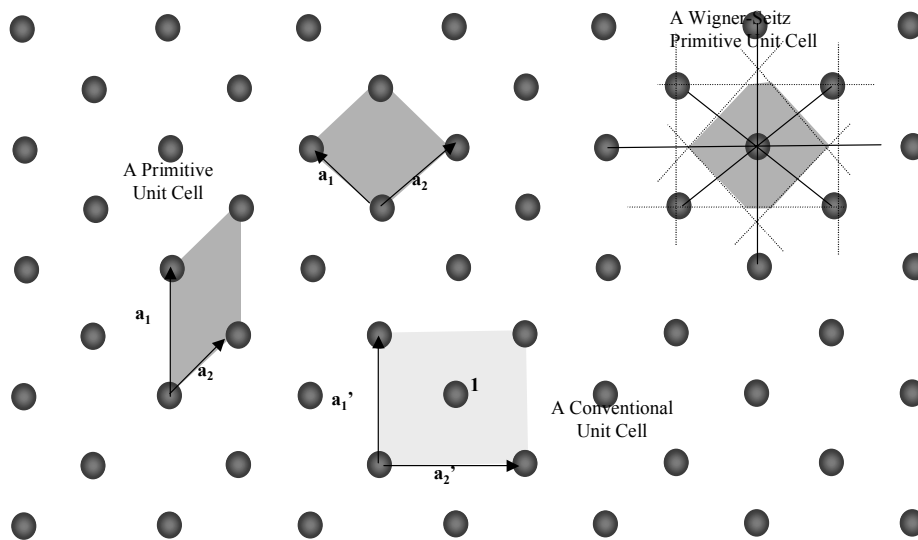
To form an actual crystal, a basis consisting of one or several atoms (or a molecule) is attached to each lattice point, i.e.

crystal = lattice + basis.

From a mathematical point of view, the location of each point can be described by a vector. Due to the periodic arrangement of lattice points, we can choose a basic set of vectors called the **primitive lattice vectors** to construct all other vectors in the lattice. In a three-dimensional lattice,  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$  are primitive lattice vectors if from any point, we could reach all other lattice points by a proper choice of integers through the following translation

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (n_1, n_2, n_3 \text{ cover all integers}).$$

The magnitudes of  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , and  $\mathbf{a}_3$  are called the lattice constants. The other set of vectors  $\mathbf{a}_1'$  and  $\mathbf{a}_2'$  are not primitive lattice vectors because we cannot use them to construct all other lattice points by a two-dimensional version of the above equation. For example we cannot reach point 1 through any linear integer combination of  $\mathbf{a}_1'$  and  $\mathbf{a}_2'$ .

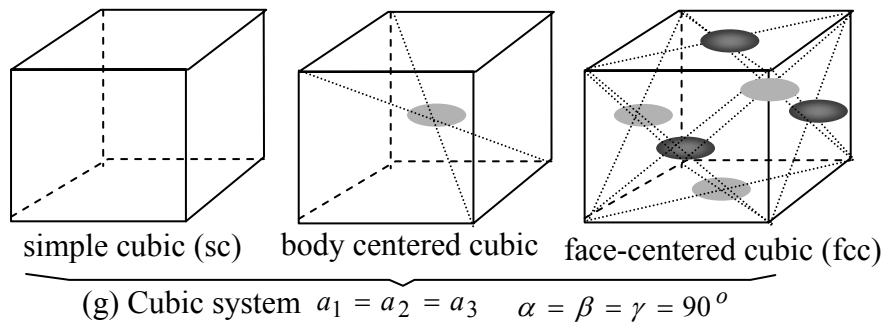


A **primitive unit cell** is the parallelepiped defined by the primitive lattice vectors. There is only one lattice point (equivalently speaking) per primitive unit cell. For example, each of the four lattice points in the two parallelograms formed by the two sets of primitive lattice vectors in above figure is shared by four unit cells and thus the number of equivalent lattice point in each parallelogram is one. These are thus primitive unit cells. On the other hand, the shaded rectangle formed by  $\mathbf{a}_1'$  and  $\mathbf{a}_2'$  are not a primitive unit cell because there are two lattice points in such a rectangle---the center point plus the four corners, each of the latter is shared by four cells. Because the choices of primitive lattice vectors are not unique, there can be different ways to draw a primitive unit cell, as the two examples in the figure. One method to construct a unit cell uniquely is the Wigner-Seitz cell, which is constructed by connecting all the neighboring points surrounding an arbitrary lattice point and drawing the bisecting plane perpendicular to each connection line. The smallest space formed by all the bisecting planes is a Wigner-Seitz cell, as indicated in the figure.

Sometimes, it is more convenient to describe a lattice by the **conventional unit cell**. For example, in the figure, the rectangle formed by  $\mathbf{a}_1'$  and  $\mathbf{a}_2'$  is more convenient than the parallelogram formed by the primitive lattice vectors. This unit cell has two lattice points and is called a conventional unit cell. The crystal can also be constructed by repeating such a conventional unit cell.

(2) Three important systems

There are totally 14 types of Bravais lattices and can be further grouped into 7 types of point symmetry operations (seven crystal systems). Here we will focus on the cubic system.



A simple cubic (sc) lattice totally encloses one atom point inside because the eight atoms at the corner are also shared by adjacent lattices. The body centered cubic (bcc) lattice has two atoms inside, while the face-centered cubic (fcc) lattice has four enclosed atoms.

Note: We can estimate the atom number for a cubic micrometer volume as

$$\left(\frac{1e-6}{5e-10}\right)^3 = 8e9,$$

which indicates the material should be similar to bulk crystal.

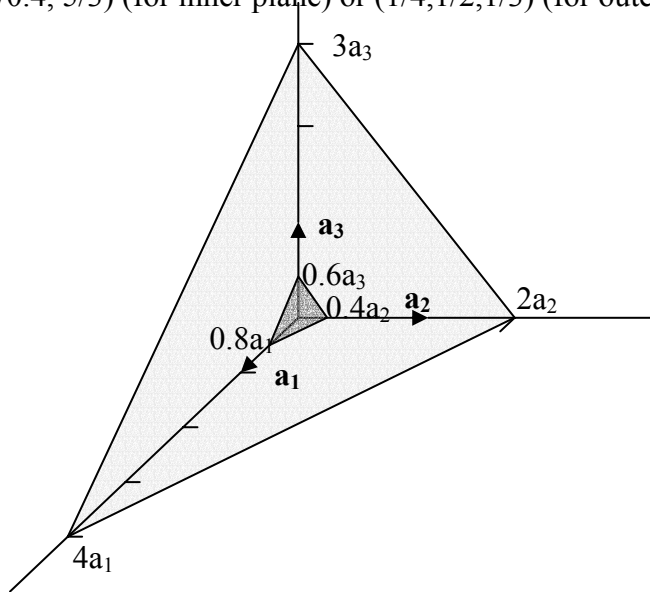
(3) Miller index

The **Miller indices of crystal planes** (hkl) are obtained in accordance with the following steps:

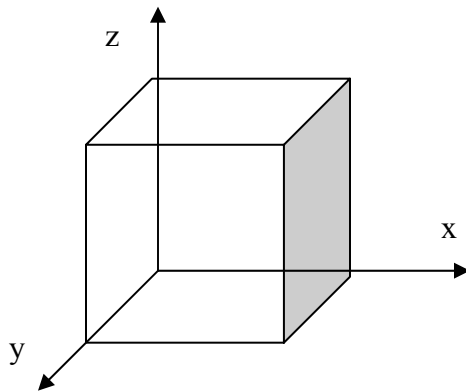
(a) Find the intercepts of the crystal plane with the axes formed by the lattice vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$  in terms of the lattice constants. The origin of the lattice vectors can be at any lattice point. One can choose any crystal plane that is convenient to use. For example, in the following figure, we have two crystallographically identical planes, one intercepts the axis at  $0.8a_1$ ,  $0.4a_2$ ,  $0.6a_3$  and the other at  $4a_1$ ,  $2a_2$ ,  $3a_3$ .

(b) Take the reciprocal of these numbers and reduce the numbers to the three smallest integers that have the same ratio as the original set. The result is enclosed in parenthesis (hkl) and this set of numbers is called the Miller indices of the plane. The above example yields

$(1/0.8, 1/0.4, 5/3)$  (for inner plane) or  $(1/4, 1/2, 1/3)$  (for outer plane)  $\rightarrow (364)$ .

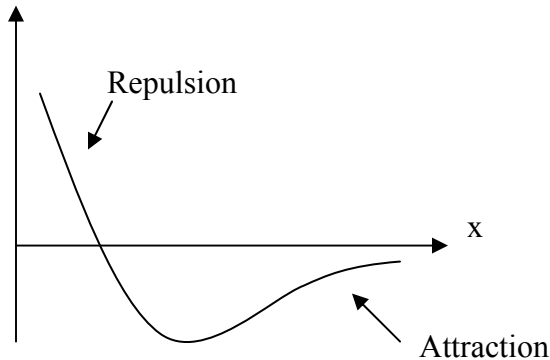


Note: Taking the reciprocal is necessary because a plane parallel to an axis will intersect it at infinity. This manipulation avoids infinity in the expression. For instance, the shaded plane in the following figure is denoted by (100). A parallel plane intersecting at  $x = -1$  is denoted by  $(\bar{1}00)$ . We can use the sign  $\{100\}$  to denote all the equivalent planes.



### 3.1.3 Bonding potential

Interatomic  
potential  $\Phi$



Recall the previous discussion about the interatomic forces. Here we will learn them in more details.

The force interaction between atoms consists of a long-range attractive force and a short-range repulsive force. The short-range repulsive force is effective when the inner-shell electrons or the nuclei begin to overlap, due to the Pauli exclusion principle. 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  $B$ ,  $\zeta$ , and  $U_0$  are empirical constants determined from experimental data, such as the interatomic spacing and the binding energy.

Note: The repulsive forces are normally very strong and the curve is sharp when the distance approaches zero.

**Molecular crystals** are characterized by the dipole-dipole interaction between atoms. An isolated atom is not polarized, but when another atom is close by, the electrical field of electrons from the neighboring atom distorts the positions of the electrons and the nucleus of the current atom, creating an induced dipole. The attractive potential between the induced dipoles of two atoms is given by

$$U_A = -\frac{A}{r^6}.$$

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

$$U = \frac{1}{2} \sum_{i \neq j} \left( \frac{B}{r_{ij}^{12}} - \frac{A}{r_{ij}^6} \right) = \frac{1}{2} \sum_{i \neq j} 4\epsilon \left( \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right)$$

reaches a minimum, as required by the second law of thermodynamics for a stable system.