1.1 Review of Hamiltonian Mechanics

Hamilton gave a very elegant and powerful formulation of classical mechanics. Before we review quantum mechanics, let's go back to classical mechanics and use them to derive equations of lattice vibrations. We are interested primarily in solids which have a crystal structure and are therefore periodic.

\[
\begin{array}{ccc}
\text{displacement from equilibrium} \\
\end{array}
\]

Hamiltonian mechanics express the laws of physics as a function of "momentum-like" coordinates $p_i$ and "space-like" coordinates $x_i$. So each coordinate in space is labeled with an index $i$ and has an equilibrium position $x_i$. Then the displacement can be denoted as $u_i = x_i - \bar{x}_i$. 
Hamiltonian equations are then
\[
\frac{dp_i}{dt} = \frac{\partial H(p_i, x_i)}{\partial x_i}
\]
\[
\frac{dx_i}{dt} = \frac{\partial H(p_i, x_i)}{\partial p_i}
\]

Some simple examples of H are

the free particle (potential energy)

\[
H = \sum_i \frac{p_i^2}{2m}
\]

Then we have \( \frac{dp_i}{dt} = 0 \) because \( \frac{\partial H}{\partial x_i} = 0 \) since it does not depend on \( x_i \). Hence \( p_i \) is constant.
This is Newton's 1st law.

If we have a potential energy which is varying in the \( x_i \) direction \( V(x_i) \) so that

\[
-\frac{\partial V}{\partial x_i} = F_i
\]

then
\[
\frac{dp_i}{dt} = -\frac{\partial V}{\partial x_i} - F_i
\]

The quantity \( F_i \) is defined as the force and \( \frac{dp_i}{dt} = F_i \) is Newton's second law in disguise.
We next consider the motion of atoms in our crystal. Since atoms are rather heavy relative to electrons, it will often suffice to treat their motion classically, while we treat the electrons quantum mechanically. Next we need to express the kinetic and potential energy of the atoms in the lattice in order to write down the Hamiltonian.

The kinetic energy can be expressed in terms of displacements/momenta as

$$T = \frac{1}{2M} \sum \phi_i^2(n)$$

Next we write the potential energy of the crystal \( U \) as a power series in the displacements \( \phi_i(n) \)

$$U = U_0 + \sum B_i^m \phi_i(n) + \frac{1}{2} \sum B_{ij}^{mn} \phi_i(n) \phi_j(m)$$

This is a Taylor expansion so the \( i \)th term is \( B_i^m = \frac{\partial U}{\partial \phi_i(n)} \) the \( i \)th derivative. Since we assume to be in equilibrium, potential
energy is at a minimum, so
\[ \frac{\partial U}{\partial u_i(n)} = 0 \text{ and } B_{ij}^m = 0 \]

Recall: \( f(x) = f(a) + f'(a)(x-a) + \frac{f''(a)}{2!}(x-a)^2 \)
We also have symmetry
\[ B_{ij}^m = \frac{\partial U}{\partial u_i(n) \partial u_j(m)} = B_{ji}^m \]

Using the displacement \( u_i(n) \) instead of position \( x_i(n) \) we can write down
\[ \dot{p}_i(n) = - \frac{\partial H(p_i, u_i)}{\partial u_i(n)} \]
\[ = - \frac{1}{2} \frac{\partial}{\partial u_i(n)} \left[ \sum_{m} B_{ij}^m u_i(n) u_j(m) \right] \]
\[ = - \sum_{m} B_{ij}^m u_j(m) \]

We also have the kinetic term
\[ \dot{u}_i(n) = \frac{\partial}{\partial p_i(n)} \left[ \frac{1}{2M} \sum_{m} \frac{p_i^2(n)}{2} \right] \]
\[ \Rightarrow M \dot{u}_i(n) = p_i(n) \]
which gives us

\[ M_i^0 (n) + \sum_{m,j} B_{ij} U_j (m) = 0 \]

The atom index \( n \) and \( m \) runs over all the atoms in the crystal, which is a large number. Let us simplify a little by considering only one dimension and allowing only first neighbor interactions so that we can drop \( i \) and have \( B_{nm} \neq 0 \) only if \( m = n \pm 1 \). Without loss of generality we can write \( n = 0 \) and have

\[ B_{0m} \neq 0 \quad \text{for} \quad m = \pm 1 \]
\[ B_{0m} = 0 \quad \text{otherwise} \]

In fact it is customary to denote this constant by \( -K \) which is the "spring" constant of the forces between neighboring atoms in the crystal. This leaves us with

\[ M \ddot{u} (n) = Ku (n-1) + K(n+1) - 2Ku (n) \]

We still have one index \( n \) going over
The atoms in the crystal so the number of equations to solve is still large, but they only couple to their "neighbors" \( n+1 \) and \( n-1 \). To further simplify, we have to assume that the crystal is periodic, with the positions of atoms always separated by a distance \( a \).

\[
M, K, M, K, M, K, M, \ldots
\]

Then we can write the displacement as

\[
u(n) = \bar{u} \exp(iqna)
\]

Plug this in to get

\[
M \bar{u} \exp(iqna) = -2K \bar{u} \exp(iqna) + K \bar{u} \exp(iq(n+1)a) + K \bar{u} \exp(iq(n-1)a) + K \bar{u} \exp(iqa) + K \bar{u} \exp(iqa)
\]

Simplify to get

\[
M \bar{u} = K \bar{u} \left[ 2\cos(qa) - 1 \right]
\]

or\[
\bar{u} = -\frac{2K}{M} \sin^2 \left( \frac{qa}{2} \right)
\]
Symbolically this can be written as
\[ u + \omega^2 u = 0 \]

with the oscillation frequency
\[ \omega(q) = 2 \sqrt{\frac{k}{m}} | \sin \left( \frac{qa}{2} \right) | \]

This relationship between the wave vector \( q \) and frequency \( \omega(q) \) is called the dispersion relationship. The librations of atoms about their equilibrium positions carry energy and are called "phonons."

Phonons are significant because they carry thermal energy and they also scatter electrons, allowing them to transfer energy to the crystal lattice and thereby cause resistance. We will treat the electron + crystal problem in a perturbative way. First we will develop the properties of electrons in a perfect crystal and then we will add in the changes resulting from the small displacements of atoms about their equilibrium positions.