

**NOTES 7: Energy of Lattice Waves and their Quantization (Phonons)****Classical Analysis**

So far we have addressed only the *mechanical behavior* of lattice waves – the description of the wave phenomenology consistent with Newton’s law and the kinematics of the crystal lattice. This led to two different types of plane waves, one (the longitudinal) polarized along the direction of wave propagation, and the other (transverse) polarized in one of the lateral directions in the perpendicular plane. Now we take the analysis one step further to understand the wave energy. In addition to being essential to the statistical mechanics, the energy also leads to a quantum mechanical description of lattice waves and the introduction of the particle *dual* of lattice waves – the *phonon*.

We start with a monatomic linear lattice of atomic mass  $m$ , spacing  $a$ , and nearest neighbor interaction (spring constant)  $C$ . We consider the longitudinal wave  $\Delta r_s = A \cos(\omega t - ska)$ . The total energy of the wave is the energy of each atom summed over all atoms. From mechanics we know that the instantaneous energy of a mass-spring system has a kinetic energy term associated with each mass and a potential energy term associated with each spring. The kinetic energy depends only on the velocity of the individual masses in motion. The potential term depends only on the force constant and the displacement of the atoms from their equilibrium positions. The kinetic energy associated with the  $sth$  mass is

$$KE_s \rightarrow \frac{1}{2} M v_s^2 = \frac{1}{2} M \left( \frac{d\Delta r_s}{dt} \right)^2$$

The potential energy associated with the  $sth$  spring (assuming nearest neighbors only)

$$PE_s \rightarrow \frac{1}{2} C (\Delta r_{s+1} - \Delta r_s)^2 = \frac{1}{2} C (\Delta r_s - \Delta r_{s+1})^2$$

By summing over all atoms we get the total energy:

$$U(t) = \frac{1}{2} M \sum_s \left( \frac{d\Delta r_s}{dt} \right)^2 + \frac{1}{2} C \sum_s (\Delta r_s - \Delta r_{s+1})^2 \quad (\text{instantaneous}) \quad (1)$$

For longitudinal wave  $\Delta r_s = A \cos(\omega t - ska)$ , we have  $\frac{d\Delta r_s}{dt} = -\omega A \sin(\omega t - ska)$  and

$$U(t) = \sum_s \left\{ \frac{1}{2} M \omega^2 A^2 \sin^2(\omega t - s k a) + \frac{1}{2} C A^2 [\cos(\omega t - s k a) - \cos(\omega t - s k a - k a)]^2 \right\}$$

The last term has the form  $[\cos(\alpha - \beta) - \cos \alpha]^2$  with  $\alpha = \omega t - s k a$ ,  $\beta = k a$ . So we can use the trigonometric identity

$$\cos(\alpha - \beta) = \cos \alpha \cos \beta + \sin \alpha \sin \beta$$

$$\begin{aligned} U(t) &= \sum_s \left[ \frac{1}{2} M \omega^2 A^2 \sin^2 \alpha + \frac{1}{2} C A^2 (\cos \alpha (\cos \beta - 1) + \sin \alpha \sin \beta) \right]^2 \\ &= \sum_s \left[ \frac{1}{2} M \omega^2 A^2 \right] \sin^2 \alpha + \frac{1}{2} C A^2 \left( \cos^2 \alpha (\cos \beta - 1)^2 + 2 \cos \alpha (\cos \beta - 1) \sin \alpha \sin \beta + \sin^2 \alpha \sin^2 \beta \right) \end{aligned}$$

To get the average, we integrate over the period of wave,  $\tau$

$$\bar{U} = \int_0^\tau U(t) dt, \quad \tau = \frac{2\pi}{\omega} = \frac{1}{f}$$

$$\int_0^\tau \sin^2 \alpha dt = \frac{\tau}{2}; \quad \int_0^\tau \cos^2 \alpha dt = \frac{\tau}{2}; \quad \int_0^\tau 2 \sin \alpha \cos \alpha dt = \int_0^\tau \sin 2\alpha dt = 0$$

So,

$$\bar{U} = \sum_s^N \left\{ \frac{1}{2} M \omega^2 A^2 \frac{\tau}{2} + \frac{1}{2} C A^2 \left[ \frac{\tau}{2} (\cos \beta - 1)^2 + \frac{\tau}{2} \sin^2 \beta \right] \right\}$$

$$\bar{U} = \sum_s^N \left\{ \frac{1}{4} M \omega^2 A^2 + \frac{1}{4} C A^2 [\cos^2 \beta - 2 \cos \beta + 1 + \sin^2 \beta] \right\}$$

$$\bar{U} = \sum_s^N \left\{ \frac{1}{4} M \omega^2 A^2 + \frac{1}{2} C A^2 [1 - \cos \beta] \right\}$$

for linear monatomic lattice, we have  $\omega^2 = \frac{2C}{M} (1 - \cos \beta)$ , so that

$$\bar{U} = \sum_s^N \left\{ \frac{1}{4} M \omega^2 A^2 + \frac{1}{4} M \omega^2 A^2 \right\} = \frac{1}{2} N \cdot M \omega^2 A^2$$

### ***Quantization of Lattice Waves (Phonons)***

#### Fourier representation of total lattice energy

Our coverage of lattice waves assumed implicitly that we could identify the atomic nuclei with sufficient accuracy to distinguish one nucleus from its neighbors. Hence we applied the classical mechanics (Newton's law) and derived the results of Chapter 2 without ever seeing Planck's constant. Remarkably, this is an acceptable approach with the atomic nuclei because, by the very definition of a solid, they maintain a fixed average position with time that is much better defined in space than the internuclear separation.

The same statements *cannot* be made about the amplitude of the lattice waves,  $\Delta r_s$ . Measurements of this amplitude cannot be made with arbitrary accuracy because of the limitations imposed by quantum mechanics. To account for this fact, we seek to quantize the amplitudes according to the method of quantum mechanics. The first step is to write out the *total* particle energy in terms of the deviations of each lattice atom from its equilibrium position:

$$U_{tot} = \frac{1}{2} m \sum_s \left( \frac{d\Delta r_s}{dt} \right)^2 + \frac{1}{2} C \sum_s (\Delta r_s - \Delta r_{s-1})^2 \quad (1)$$

The standard quantum-mechanical (Hamiltonian) approach is in terms of the canonical pair of variables, the particle momentum  $p_s$  and position  $\Delta r_s$ . We recognize that

$$m \frac{d\dot{\Delta r}_s}{dt} = m v_s = p_s. \text{ And in crystals we have the wave translation relation: } \Delta r_{s-1} = \Delta r_s e^{-jka},$$

so that  $\frac{1}{2} C \sum_s (\Delta r_s - \Delta r_{s-1})^2 = \frac{1}{2} C \sum_s \Delta r_s^2 (1 - e^{-jka})^2$ . This allows us to write (1) as

$$U_{tot} = \sum_s \frac{p_s^2}{2m} + \frac{1}{2} C \sum_s (\Delta r_s)^2 (1 - e^{-jka})^2 \quad (2)$$

We have already seen that *one* general solution to the lattice wave equation is the plane wave of wave vector  $k$  and associated circular frequency  $\omega$ ,

$$\Delta r_s = A e^{j(ksa - \omega t)}$$

By linear superposition, the sum over  $\Delta r_s$  values of all possible  $k$  and  $\omega$  values should also be a good solution and has the form of a discrete Fourier series,

$$\Delta r_s = \frac{1}{\sqrt{N}} \sum_K R_k e^{jksa} \quad R_k \rightarrow \text{complex amplitude}$$

The normalization  $1/\sqrt{N}$  leads to an inverse Fourier series  $R_k = \frac{1}{\sqrt{N}} \sum_s \Delta r_s e^{-jksa}$

We expect that because  $\mathbf{p}$  is  $\propto \frac{d\Delta r_s}{dt}$ , it can also be represented Fourier series but with a phase

shift. It turns out:  $P_s = \frac{1}{\sqrt{N}} \sum_k P_k e^{-jksa}$  and the inverse Fourier series is just

$P_k = \frac{1}{\sqrt{N}} \sum_s P_s e^{jksa}$ . Substituting these two Fourier representations into  $U_{\text{tot}}$ , we get:

$$U_{\text{tot}} = \frac{1}{2NM} \sum_{s=1}^N \sum_{k,k'} P_k P_{k'} e^{-j(k'+k)sa} + \frac{C}{2N} \sum_{s=1}^N \sum_{k,k'} R_k R_{k'} e^{j(k+k')sa} (1 - e^{-jka}) (1 - e^{-jk'a}) \quad (3)$$

where all quadratic terms, in general, require two independent wave vectors  $k$  and  $k'$  in the summation. While appearing quite formidable, there is a great simplification for any  $a$ ,

$$\sum_{s=1}^N e^{\pm j(k'+k)sa} = N \delta_{k,-k'}$$

where  $\delta$  is the Kronecker delta function defined as  $\delta_{m,n} = 1$  if  $m = n$ ;  $\delta_{m,n} \neq 0$  in  $m \neq n$ .

Substitution into (3) yields  $U_{tot} = \frac{I}{2M} \sum_k P_k P_{-k} + \frac{C}{2} \sum_k R_k R_{-k} (2 - 2 \cos ka)$

But we know for acoustical lattice waves:  $\omega_k^2 = \frac{2C}{m} (1 - \cos ka)$ , which leads to

$$U_{tot} = \frac{I}{2m} \sum_k P_k P_{-k} + \frac{m}{2} \sum_k \omega_k^2 R_k R_{-k} \quad (4)$$

We write the subscript  $k$  on  $\omega$  to remind ourselves of the dispersion relation connecting them, i.e., there is one-to-one mapping between  $\omega$  and  $k$  that remains valid (and very useful) no matter how we analyze the lattice waves and their energy.

Two final simplifying steps follow from the fact that  $\Delta r_s$  and  $p_s$  must be real quantities:

$$R_{-k} = \frac{I}{\sqrt{N}} \sum_s \Delta r_s e^{-jksa} = R_k^* \quad \text{and} \quad P_{-k} = \frac{I}{\sqrt{N}} \sum_s p_s e^{-jksa} = P_k^*$$

Substitution into (4) then yields

$$U_{tot} = \frac{I}{2m} \sum_k P_k^2 + \frac{m}{2} \sum_k \omega_k^2 R_k^2 = \sum_k U_k \quad (5)$$

where the last step is to emphasize that the total energy of the lattice atoms has been reduced to a summation over lattice wave vectors and Fourier amplitudes !

### Quantum mechanical transformation

Up to this point the analysis is entirely classical. Essentially what we have done is derive a new expression for the *total energy* of the lattice in which the atoms are decoupled entirely. In other words, the energy is now written as a sum over independent lattice-wave *modes*, each specified by  $k$  (and  $\omega$ ). While at first appearing to be purely mathematical, it justifies the next step of the analysis, which is to transform (5) according to the rules of quantum mechanics but treating the *mode*  $k$  as the

“particle”, the Fourier amplitude  $P_k$  as its momentum, and the Fourier amplitude  $R_k$  as its position.

In the “position” representation of quantum mechanics,  $R_k$  becomes the position operator, the

momentum is given by  $P_k \rightarrow -i\hbar \frac{\partial}{\partial R_k}$  and  $U_k$  becomes the energy eigenvalue for mode  $k$ . This is a

very important procedure called Second Quantization. It is the same as First Quantization you learn in an introductory quantum mechanics class except that now the momentum and position are Fourier amplitudes. Essentially, it is quantum mechanics in Fourier space, and is a pervasive technique in many-body physics and quantum-field theory.

The Second Quantization on (5) and operation on the total (lattice) wave function  $\psi$  to yield the lattice Schrodinger equation,

$$\sum_k \left( \frac{-\hbar^2}{2m} \frac{d^2}{dR_k^2} + \frac{1}{2} m \omega_k^2 R_k^2 \right) \psi = \sum_k U_k \psi \quad (6)$$

This represents a sum of independent 2<sup>nd</sup> order differential equations, each having the form,

$$\left( \frac{-\hbar^2}{2m} \frac{d^2}{dR_k^2} + \frac{1}{2} m (\omega_k R_k)^2 \right) \psi_k = U_k \psi_k$$

But this is identical in form to the harmonic oscillator Schrodinger equation

$$\frac{d^2 \psi}{dR_k^2} + \left[ \frac{2mU_k}{\hbar^2} - \left( \frac{m\omega_k R_k}{\hbar} \right)^2 \right] \psi_k = U_k \psi_k$$

Define:  $\alpha = m\omega_k/\hbar$ ,  $\beta = 2mU_k/\hbar^2$ , and we get

$$\frac{d^2 \psi}{dR_k^2} + (\beta - \alpha^2 R_k^2) \psi = 0$$

Now define dimensionless variable  $W$ .

$$W = \sqrt{\alpha} R_k \rightarrow \frac{d\psi}{dR_k} = \frac{d\psi}{dW} \frac{dW}{dR_k} = \sqrt{\alpha} \frac{d\psi}{dW}$$

and

$$\frac{d^2\psi}{dR_k^2} = \alpha \frac{d^2\psi}{dW^2}$$

So we get, 
$$\frac{d^2\psi}{dW^2} + \left(\frac{\beta}{\alpha} - W^2\right)\psi = 0$$

This is a general 2<sup>nd</sup> order equation of ODE theory.

It has the solution  $\psi(W) = A_n e^{-W^2/2} H_n(W) \dots \dots \dots H_n(W) \rightarrow$  Hermite polynomials

Required condition  $l \frac{\beta}{\alpha} = 2n + 1, \quad 2n + 1, \quad n = 0, 1, 2, \dots$  or  $U_k = \left(n + \frac{1}{2}\right) \hbar\omega_k$

n	$H_n(W)$
0	1
1	W
2	$(1 - 2W^2)$
3	$(3W - 2W^3)$
4	$(3 - 12W^2 + 4W^4)$
5	$(15 - 20W^3 + 4W^5)$

Now we can go back and write:

$$U_{tot} = \sum_k U_k = \sum_k \left(n + \frac{1}{2}\right) \hbar\omega_k$$

Where  $n \rightarrow$  # phonons

$$n = 0, 1, 2, 3 \dots, \quad k = \frac{-\pi}{a} \text{ to } \frac{\pi}{a}$$

$\omega_k \rightarrow$  phonon mode, wave vector  $k$ , frequency  $\omega_k$  and state occupancy  $n$  or  $n \rightarrow \# \text{ phonons}$

**What does this mean?**

- We started by solving for arbitrary excitation of monatomic lattice as a sum over all atoms.
- End up with a sum over all possible frequencies ( consistent with dispersion relation)

weighted by  $(n + \frac{1}{2})\hbar$

- The integer  $n$  has determined magnitude of  $\Delta r$

Note there are two  $k$ s for each  $\omega_k$  (left-going and right going waves):

$$\Delta r_0 e^{i(kx - \omega_k t)} \quad \text{and} \quad \Delta r_0 e^{-i(kx - \omega_k t)}$$

$$\begin{aligned} \ddot{A}r &= \ddot{A}r_s \cos kx \cos \omega_k t \\ \frac{KE}{vol} &= \frac{1}{2} \tilde{n} \left( \frac{d\Delta r}{dt} \right)^2 = \frac{1}{2} \tilde{n} \dot{\omega}^2 \ddot{A}r_0^2 \cos^2 kx \cos^2 \omega_k t = \frac{1}{4} \tilde{n} \dot{\omega}_k^2 \ddot{A}r_0^2 \cos^2 kx \end{aligned}$$

In a crystal of volume  $V$ , this becomes:

$$\overline{KE} = \frac{1}{4} \rho \omega_k^2 \Delta r_0^2 \int_V \cos^2 kx = \frac{1}{8} \rho \omega_k^2 \Delta r_0^2 V$$

Now in any time-averaged harmonic oscillator:

$$K.E. = P.E. = \frac{1}{2} U_K$$

So,

$$\frac{V}{8} \rho \omega_k^2 \Delta r_0^2 V = \frac{1}{2} \left( n + \frac{1}{2} \right) \hbar \omega_k \quad \text{or} \quad \Delta r_0 = 2 \sqrt{\frac{(n + \frac{1}{2}) \hbar}{\rho \omega_k}}$$

The smallest possible dilatation is:



$$\Delta r_{0,min} = 2\sqrt{\frac{\hbar}{2\rho V\omega_k}}$$

Numerical example:

Take Ge, optical branch  $\omega^2 = \frac{4C}{m}$  @  $k = 0$

$C = C_{11} \approx 1.29 \times 10^{11} \text{ N/m}^2$  (Kittel Chapter 3, Table 12)

$$\omega \approx 9 \times 10^{12} \text{ Hz} \quad \rho \approx 5.3 \times 10^3 \text{ kg/m}^3 ;$$

take  $V = 1 \text{ cm}^3 = 10^{-6} \text{ m}^3$ , so

$$\Delta r_{0,min} = 1.7 \times 10^{-22} \text{ m}$$

Better example:  $\Delta r_{0,min}$  @ smallest  $k$

$$k_{min} = \pi/L. \text{ Let } L = 1 \text{ cm or } k_{min} = 314 \text{ m}^{-1}$$

Take Aluminum:

$$\rho = 2.77 \times 10^3 \text{ Kg/m}^3$$

$$\omega_{min} = v_s k \quad v_s = 4681 \text{ m/s} = \sqrt{\frac{C_{12}}{\rho}}$$

So,

$$\omega_{min} = 1.47 \times 10^6 / \text{s} \quad \text{compressional wave}$$

$$\Delta r_{0,min} = 2\sqrt{\frac{\hbar}{2\tilde{n}V\omega_{min}}} = 2.28? \times 10^{-19} \text{ m} \quad (\text{another small number})$$