PHY 555 Fall 2007 -- Phonon Notes

The harmonic energy of any stable collection of particles is

$$H = \frac{1}{2}\langle \dot{u}|\hat{M}|\dot{u}\rangle + \frac{1}{2}\langle u|\hat{K}|u\rangle = \frac{1}{2}\langle \dot{s}|\dot{s}\rangle + \frac{1}{2}\langle s|\hat{D}|s\rangle \qquad (1)$$

where $|u\rangle$ is displacement and $|s\rangle = \hat{M}^{1/2}|u\rangle$ is mass-weighted displacement. Now diagonalize the dynamical matrix $\hat{D} = \hat{M}^{-1/2}\hat{K}\hat{M}^{-1/2}$,

$$\hat{D}|\vec{Q}j\rangle = \omega(\vec{Q}j)^2|\vec{Q}j\rangle \qquad (2)$$

The notation is that $\vec{Q}$ is the wavevector and *j* is the branch index for the *3n* branches, when there are *n* atoms in the unit cell. The eigenstates are complete, and we can use them to represent the terms in the energy expression, using

$$\sum_{\vec{Q}j}|\vec{Q}j\rangle\langle\vec{Q}j| = 1 \quad \text{and} \quad s(\vec{Q}j) = \langle\vec{Q}j|s\rangle \quad \text{and} \quad \dot{s}(\vec{Q}j) = \langle\vec{Q}j|\dot{s}\rangle \equiv \pi(\vec{Q}j).$$

The result is

$$H = \frac{1}{2}\sum_{\vec{Q}j}\left[\pi^*(\vec{Q}j)\pi(\vec{Q}j) + \omega(\vec{Q}j)^2 s^*(\vec{Q}j)s(\vec{Q}j)\right]. \qquad (3)$$

This has the form of uncoupled oscillators, but has the unfortunate aspect of introducing dynamical variables $s(\vec{Q}j)$ and $\dot{s}(\vec{Q}j)$ that are complex. Since each variable has both real and imaginary parts, there are twice as many variables as we need. There is no avoiding complex variables, but the problem of excess apparent variables is resolved by careful analysis. Notice that $\hat{D}$ is a real symmetric matrix, while the eigenstates $|\vec{Q}j\rangle$ are necessarily complex because Bloch's theorem has been exploited. However, if a complex eigenvector is found for a real matrix, it is guaranteed that the complex conjugate vector is also an eigenstate (and has the same eigenvalue). The complex conjugate of $|\vec{Q}j\rangle$ has wavevector $-\vec{Q}$. Therefore it is a new eigenvector that we can label as $|-\vec{Q}j\rangle$. Here a phase convention is being chosen, namely that the phases of $|\vec{Q}j\rangle$ and $|-\vec{Q}j\rangle$ are forced to be such that these states are complex conjugates of each other. The frequencies $\omega(\vec{Q}j)$ are square roots of the eigenvalues, and therefore $\omega(\vec{Q}j) = \omega(-\vec{Q}j)$. It also follows that

$$s(-\vec{Q}j) = \langle -\vec{Q}j|s\rangle = \langle\vec{Q}j|s\rangle^* = s(\vec{Q}j)^*$$

This shows that there are only half as many independent dynamical variables as appeared at first sight.

Classical treatment

So far, the algebra did not depend on any distinction between classical and quantum mechanics. In the classical treatment, the primitive variables $s(\vec{\ell}\alpha) = M_\alpha^{1/2}u(\vec{\ell}\alpha) = \langle\vec{\ell}\alpha|s\rangle$ are real numbers, whereas the new variables $s(\vec{Q}j)$ are complex. The notation is that $s(\vec{\ell}\alpha)$ is the mass-weighted displacement $u(\vec{\ell}\alpha)$ of the atom whose cell is denoted by $\vec{\ell}$. The additional 3n choices (n atoms in the cell and 3 Cartesian directions) are all summarized by the index α.

The general solution of Newton's law for the primitive variables is

$$u(\vec{\ell}\alpha,t) = M_\alpha^{-1/2} s(\vec{\ell}\alpha,t) = M_\alpha^{-1/2}\langle\vec{\ell}\alpha|s(t)\rangle = \sum_{\vec{Q}j} M_\alpha^{-1/2}\langle\vec{\ell}\alpha|\vec{Q}j\rangle\langle\vec{Q}j|s(t)\rangle$$

$$u(\vec{\ell}\alpha,t) = \mathrm{Re}\sum_{\vec{Q}j} M_\alpha^{-1/2}\langle\vec{\ell}\alpha|\vec{Q}j\rangle A(\vec{Q}j)\exp(i\phi(\vec{Q}j))\exp(-i\omega(\vec{Q}j)t) \qquad (4)$$

where the amplitude $s(\vec{Q}j,t) = \langle\vec{Q}j|s(t)\rangle$ of the $\vec{Q}j$ -normal mode has been written as a positive amplitude $A(\vec{Q}j)$ times a time-dependent phase factor $\exp[i\phi(\vec{Q}j) - i\omega(\vec{Q}j)t]$. The eigenvectors $|\vec{Q}j\rangle$ of the dynamical matrix have the spatial representation

$$\langle\vec{\ell}\alpha|\vec{Q}j\rangle = \varepsilon_\alpha(\vec{Q}j)\exp(i\vec{Q}\cdot\vec{\ell})/\sqrt{N}\ , \qquad (5)$$

where $\varepsilon_\alpha(\vec{Q}j)$ is called the "polarization vector." It is normalized by the equation $\sum_\alpha \varepsilon_\alpha(\vec{Q}j)^* \varepsilon_\alpha(\vec{Q}'j') = \delta(\vec{Q},\vec{Q}')\delta(j,j')$. It cannot in general be forced to be real, but is forced to obey the relation $\varepsilon_\alpha(\vec{Q}j)^* = \varepsilon_\alpha(-\vec{Q}j)$. It can be written as a real vector times a phase factor, $\varepsilon_\alpha(\vec{Q}j) = \hat{\varepsilon}_\alpha(\vec{Q}j)\exp[i\gamma_\alpha(\vec{Q}j)]$. Then the general solution of Newton's law is

$$u(\vec{\ell}\alpha,t) = (1/M_\alpha N)^{1/2}\sum_{\vec{Q}j} A(\vec{Q}j)\hat{\varepsilon}_\alpha(\vec{Q}j)\cos[\vec{Q}\cdot\vec{\ell} + \gamma_\alpha(\vec{Q}j) - \omega(\vec{Q}j)t + \phi(\vec{Q}j)]. \qquad (6)$$

Suppose it is desired to calculate an average quantity like $\langle u(\vec{\ell}\alpha,t)u(\vec{\ell}'\alpha',t')\rangle$. In thermal equilibrium, the amplitudes $A(\vec{Q}j)$ are Gaussian random numbers, distributed with probability

$$P(A(\vec{Q}j)) \propto \exp[-\omega(\vec{Q}j)^2 A(\vec{Q}j)^2/4k_B T], \qquad (7)$$

while the phases $\phi(\vec{Q}j)$ are randomly distributed between *0* and 2π. Statistical averages of products of cosines are simple.

$$\langle\cos[X+\phi(\vec{Q}j)]\cos[Y+\phi(\vec{Q}'j')]\rangle = \frac{1}{2}\cos(X-Y)\delta(\vec{Q},\vec{Q}')\delta(j,j'). \qquad (8)$$

This is proved by using $\cos(x)\cos(y) = [\cos(x+y)+\cos(x-y)]/2$, and then noting that the average of $\cos(x+\phi)$ is *0* if ϕ is random. Then the result is

$$\langle u(\vec{\ell}\alpha,t)u(\vec{\ell}'\alpha',t')\rangle = \frac{1}{N}\sum_{\vec{Q}j}\frac{k_B T}{M_\alpha\omega(\vec{Q}j)^2}\hat{\varepsilon}_\alpha(\vec{Q}j)^2\cos[\vec{Q}\cdot(\vec{\ell}-\vec{\ell}') - \omega(\vec{Q}j)(t-t')]\delta(\alpha,\alpha'). \qquad (9)$$

In particular, the average that enters the "Debye-Waller factor" in the scattering cross-section is

$$\langle u(\vec{\ell}\alpha,t)^2\rangle = \frac{1}{N}\sum_{\vec{Q}j}\frac{k_B T}{M_\alpha\omega(\vec{Q}j)^2}\hat{\varepsilon}_\alpha(\vec{Q}j)^2 \qquad (10)$$

There are *3nN* terms in the sum. *N* cancels *1/N*, and *3n* balances the squared ε-vector.

Quantum treatment:

First write the Hamiltonian in the form

$$H = \frac{1}{2}\sum_{\vec{Q}j}\left[\pi\left(-\vec{Q}j\right)\pi\left(\vec{Q}j\right) + \omega\left(\vec{Q}j\right)^2 s\left(-\vec{Q}j\right)s\left(\vec{Q}j\right)\right] \tag{11}$$

Now introduce the new variables

$$\begin{aligned} a\left(\vec{Q}j\right) &= \frac{1}{\sqrt{2\hbar\omega\left(\vec{Q}j\right)}}\left[\pi\left(-\vec{Q}j\right) - i\omega\left(\vec{Q}j\right)s\left(\vec{Q}j\right)\right] \\ a^+\left(\vec{Q}j\right) &= \frac{1}{\sqrt{2\hbar\omega\left(\vec{Q}j\right)}}\left[\pi\left(\vec{Q}j\right) + i\omega\left(\vec{Q}j\right)s\left(-\vec{Q}j\right)\right] \end{aligned} \tag{12}$$

In terms of these variables, the energy is

$$H = \frac{1}{2}\sum_{\vec{Q}j}\hbar\omega\left(\vec{Q}j\right)\left[a\left(\vec{Q}j\right)a^+\left(\vec{Q}j\right) + a^+\left(-\vec{Q}j\right)a\left(-\vec{Q}j\right)\right] \tag{13}$$

Check the commutation relations:

$$\left[a\left(\vec{Q}j\right), a^+\left(\vec{Q}j\right)\right] = \frac{1}{2\hbar\omega\left(\vec{Q}j\right)}\left[\left(\pi\left(-\vec{Q}j\right) - i\omega\left(\vec{Q}j\right)s\left(\vec{Q}j\right)\right), \left(\pi\left(\vec{Q}j\right) + i\omega\left(\vec{Q}j\right)s\left(-\vec{Q}j\right)\right)\right] = \frac{i}{\hbar}\left[\pi\left(\vec{Q}j\right), s\left(\vec{Q}j\right)\right] = 1$$

The last step follows from the fact that the variables $s\left(\vec{Q}j\right) = \left\langle \vec{Q}j \middle| s\right\rangle$, etc., are a unitary transformation of the variables $s\left(\vec{\ell}\alpha\right) = \left\langle \vec{\ell}\alpha \middle| s\right\rangle$, etc., and from the usual quantum mechanical commutation relations $\left[p\left(\vec{\ell}\alpha\right), s\left(\vec{\ell}'\alpha'\right)\right] = (\hbar / i)\delta\left(\vec{\ell}, \vec{\ell}'\right)\delta(\alpha, \alpha')$. Therefore the Hamiltonian can be written as

$$H = \sum_{\vec{Q}j}\hbar\omega\left(\vec{Q}j\right)\left[a^+\left(\vec{Q}j\right)a\left(\vec{Q}j\right) + \frac{1}{2}\right]. \tag{14}$$

Statistical averages are easily found by using

$$\left\langle a^+\left(\vec{Q}j\right)a\left(\vec{Q}'j'\right)\right\rangle = \left[\exp\left(\frac{\hbar\omega\left(\vec{Q}j\right)}{k_B T}\right) - 1\right]^{-1}\delta\left(\vec{Q}, \vec{Q}'\right)\delta(j, j'). \tag{15}$$

For example, to find the Debye-Waller factor, the first step is to invert Eqs. 12:

$$s\left(\vec{Q}j\right) = i\sqrt{\frac{\hbar}{2\omega\left(\vec{Q}j\right)}}\left[a\left(\vec{Q}j\right) - a^+\left(-\vec{Q}j\right)\right]. \tag{16}$$

Then, following equation (4)

$$u\left(\vec{\ell}\alpha\right) = M_\alpha^{-1/2}s\left(\vec{\ell}\alpha\right) = M_\alpha^{-1/2}\left\langle \vec{\ell}\alpha \middle| s\right\rangle = \sum_{\vec{Q}j} M_\alpha^{-1/2}\left\langle \vec{\ell}\alpha \middle| \vec{Q}j\right\rangle s\left(\vec{Q}j\right), \tag{17}$$

it is easy to get the quantum generalization of Eq. (10),

$$\left\langle u\left(\vec{\ell}\alpha,\right)^2\right\rangle = \frac{1}{N}\sum_{\vec{Q}j}\frac{\hbar}{M_\alpha\omega\left(\vec{Q}j\right)}\hat{\varepsilon}_\alpha\left(\vec{Q}j\right)^2\left[n\left(\vec{Q}j\right) + \frac{1}{2}\right], \tag{18}$$

where $n\left(\vec{Q}j\right)$ is the Bose-Einstein distribution given in Eq. (15).