General Formalism to Describe Lattice Vibrations in the Harmonic Approximation

We expect that the energy of the lattice increases as "jitter" of atoms and ions (we can collectively call them "basis elements") that make the crystal are introduced. Let's consider displacement field

$$\vec{u}_j(\boldsymbol{R})$$

where $\boldsymbol{R}$ is the Bravais lattice vector as usual, and j is the index for elements of basis in the unit cell (for m elements per basis, we define $j = 1, .., m$. In terms of the displacement field, the position of any element is given by

$$\boldsymbol{r}_j(\boldsymbol{R}) = \boldsymbol{R} + \boldsymbol{d}_j + \vec{u}_j(\boldsymbol{R})$$

Note that we use a different vector notation for the displacement field u, as opposed to the Bravais lattice vector ($\boldsymbol{R}$) and the basis defining vectors ($\boldsymbol{d}$). The reason for the distinction, which will be made clear soon, is that u is a dynamic variable, while other are simply indices. Let's denote the lattice energy due to the interaction of all atoms and ions in the crystal to as $U\left(\{\vec{u}_j(\boldsymbol{R})\}\right)$. By definition, we use $\{\vec{u}_j(\boldsymbol{R})\} = \{0\}$ when the crystal is in the classical ground state. Thus, $\left.\frac{\partial U}{\partial \vec{u}_j(\boldsymbol{R})}\right|_0 = 0$ where the subscript 0 means evaluation at $\{\vec{u}_j(\boldsymbol{R})\} = \{0\}$, i.e. the classical ground state. Generally, U can be considered as a function of the displacement field $\vec{u}_j(\boldsymbol{R})$, a $d \times m \times N$ dimensional variable where d is the spatial dimension, m is the number of elements in the basis, and N is the number of Bravais lattice points. Then, a Taylor expansion of the multi-variable function gives

$$U\left(\{\vec{u}_j(\boldsymbol{R})\}\right) \approx U_0 + \sum_{\boldsymbol{R},j,\boldsymbol{R}',j'} \frac{1}{2}\vec{u}^T{}_j(\boldsymbol{R})\, \overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}')\vec{u}_{j'}(\boldsymbol{R}').$$

This approximation is called "Harmonic Approximation" for the obvious reason. Note that the arrow notation for the displacement means a column vector, as usual in linear algebra. The D matrix is written in the dyadic form and is defined as

$$\overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}') = \frac{\partial^2 U}{\partial \vec{u}_j(\boldsymbol{R}) \partial \vec{u}_{j'}(\boldsymbol{R}')}$$

A few symmetry properties are worth noting.

(1) Bravais Lattice translation symmetry: $\overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}') = \overleftrightarrow{D}_{jj'}(\boldsymbol{R}-\boldsymbol{R}')$
(2) Real and symmetric, from definition: $\overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}') = \overleftrightarrow{D}^T{}_{j'j}(\boldsymbol{R}',\boldsymbol{R})$
(3) Uniform translation does not add energy: $\sum_{\boldsymbol{R},j,j'} \overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}') = 0$

(T means transpose for the dyadic part.) If the crystal is inversion symmetric, then some additional property can be written down (like 22.49 of A&M), $\sum_{j,j'} \overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}') = \sum_{j,j'} \overleftrightarrow{D}_{jj'}(\boldsymbol{R}',\boldsymbol{R})$.

The dynamics of the system is now defined by the Hamiltonian

$$H = T + U = \sum_{\boldsymbol{R},j} \frac{\vec{p}_j(\boldsymbol{R})^2}{2M_j} + \sum_{\boldsymbol{R},j,\boldsymbol{R}',j'} \frac{1}{2} \vec{u}^T{}_j(\boldsymbol{R}) \overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}') \vec{u}_{j'}(\boldsymbol{R}')$$

where $\vec{p}_j(\boldsymbol{R})$ is the conjugate momentum for $\vec{u}_j(\boldsymbol{R})$, and U_0 is simply re-defined to be 0. The Newtonian equation of motion is easy to write down:

$$M_j \ddot{\vec{u}}_j(\boldsymbol{R}) = -\sum_{\boldsymbol{R}',j'} \overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}')\, \vec{u}_{j'}(\boldsymbol{R}')$$

To solve this equation, we plug in the solution of the form (expected from Bloch's theorem – soon to cover),

$$\vec{u}_j(\boldsymbol{R}) = \vec{\varepsilon}_j \exp[i(\boldsymbol{k} \cdot \boldsymbol{R} - \omega t)]$$

where the displacement field is modulated sinusoidally by the Bravais lattice vector and the information about the "internal motion" within the basis as well as the polarization vector of the wave is contained in $\vec{\varepsilon}_j$. Thus, the general eigenvalue equation to be solved is:

$$M_j \omega^2 \vec{\varepsilon}_j = \sum_{\boldsymbol{R}',j'} \overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}') \vec{\varepsilon}_{j'} \exp[i(\boldsymbol{k} \cdot (\boldsymbol{R}' - \boldsymbol{R}))]$$

Note that the RHS appears to depend on $\boldsymbol{R}$, but it does not, due to (1) above and the summation over $\boldsymbol{R}'$. Thus, by defining $\overleftrightarrow{D}_{jj'}(\boldsymbol{k}) \equiv \sum_{\boldsymbol{R}'} \overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}') \exp[i(\boldsymbol{k} \cdot (\boldsymbol{R}' - \boldsymbol{R}))]$ we have a dm dimensional eigenvalue problem

$$M_j \omega^2 \vec{\varepsilon}_j = \sum\nolimits_{j'} \overleftrightarrow{D}_{jj'}(\boldsymbol{k}) \vec{\varepsilon}_{j'}$$

where $\overleftrightarrow{D}_{jj'}(\boldsymbol{k})$ is a Hermitian matrix in dm dimensions due to (2) above. The eigenvalues of this matrix equation should be positive as dictated by physics (as also can be shown by the classical minimum of the ground state energy). Thus there are dm branches of phonons in the crystal, while the total number of phonon modes is dmN, i.e. the total number of degrees of freedom, as one would have expected, since our assumption of N Bravais lattice (primitive, by our convention) points means that there are N distinct momentum values in the momentum space. The existence of the d acoustic branches (as required by the Goldstone theorem) can be proved by assuming that $\vec{\varepsilon}_j \equiv \vec{\varepsilon}$ (i.e. indep. of j) and summing the above equation over j: $\sum_j M_j\, \omega^2 \vec{\varepsilon} = \sum_{jj'} \overleftrightarrow{D}_{jj'}(\boldsymbol{k})\, \vec{\varepsilon}$. For small $\boldsymbol{k}$, assuming that $\overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}')$ dies off fast as $\boldsymbol{R}'$ moves away from $\boldsymbol{R}$, $\sum_{jj'} \overleftrightarrow{D}_{jj'}(\boldsymbol{k}) \approx \sum_{j,j',\boldsymbol{R}'} \overleftrightarrow{D}_{jj'}(\boldsymbol{R},\boldsymbol{R}')\,[\,1 + i(\boldsymbol{k} \cdot (\boldsymbol{R}' - \boldsymbol{R})) - (\boldsymbol{k} \cdot (\boldsymbol{R}' - \boldsymbol{R}))^2\,]$. The first term is 0, due to (3) above, and so we see that there are d solutions of $\omega \to 0$ as $\boldsymbol{k} \to 0$, corresponding to d acoustic phonon branches. Furthermore, if the crystal is inversion symmetric, then the 2nd term is 0, and $\omega = c(\hat{\boldsymbol{k}})|\boldsymbol{k}|$, as commonly happens.