THE MOMENTS OF PHONON FREQUENCY DISTRIBUTION

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A method of calculating the moments of the partial phonon frequency distribution $p\nu(\omega)$ and phonon frequency distribution $g(\omega)$ directly from force constants is given. In the proposed method the calculation and diagonalization of the dynamical matrix is omitted. Each moment consists of a sum of force constant matrix products. These products may be represented by diagrams and many of them give the same contributions. The calculations can be restricted to a description of nonequivalent diagrams and their multiples. The method of renormalization of diagrams for a cubic lattice is given. In this case the number of non-equivalent diagrams decreases.

The frequency distribution function of phonons describes the dynamic and thermodynamic properties of a crystal lattice. The distribution $g(\omega)d\omega$ is defined as the number of normal modes whose frequency lies between ω and $\omega+d\omega$. The properties of a lattice of more complex structure are very often described in terms of the partial frequency distribution function of phonons $p_\nu^3(\omega) \cdot p_\nu(\omega)$ characterizes the modes of the ν type atoms or a degree of freedom (for example, torsional modes of strongly bound atoms).

The most commonly used method of obtaining $g(\omega)$ or $p_\nu(\omega)$ is that of diagonalization of the dynamical matrix (1) which consists in computing the normal frequencies at a great number of points distributed equally inside the first Brillouin zone. The spectrum is then obtained as a histogram. An analytical method of calculating frequency distributions from their moments was proposed by Montroll [2]. The distributions expanded into a series of Legendre polynomials and the coefficients were obtained from the value of frequency distribution moments. However, this method requires great numbers of terms to be taken into account [3].

The continuous fraction method used by Deltour [4] is a modification of the Montroll method. The new method gives a satisfactory distribution of phonon frequencies and thermodynamical functions even from a small number of moments.

The moments of the frequency distribution function may be obtained from the traces of appropriate products of dynamical matrix [1]. For this method, the elements of the dynamical matrix must be known. However, it is possible to avoid calculation of the matrix elements, and the moments may be found directly from force constants. Such a method

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is proposed in this paper. This procedure may have an advantage over the dynamical matrix method in the case of short range interaction potential.

The moments will be described as a sum of several combinations of nearest-neighbour force constants. The contributions of equivalent combinations of force constants will prove to be equal. The summing process will be represented in the form of diagrams. Some of the diagrams will prove to sum up.

1. Consider a lattice for which the force constants and their symmetry are known. Introduce the reduced force constants

$$F_{\alpha\beta}\begin{pmatrix} nm \\ \nu\eta \end{pmatrix} = \frac{1}{\sqrt{M_\nu M_\eta}} \Phi_{\alpha\beta}\begin{pmatrix} nm \\ \nu\eta \end{pmatrix} \tag{1}$$

where n, m label elementary cells.

$\nu = (\nu', \nu'')$; $\eta = (\eta', \eta'')$ and ν', η' number single atoms (r) or a group of atoms (t) in the elementary cell.

ν'', η'' indicate a translational (R) or torsional (Θ) degree of freedom.

M_ν describes the mass $M_{\nu'}$ if $\nu'' = R$, or the inertia moment $I_{\nu'}$ of the ν' group if $\nu'' = \Theta$.

The force constants are transformed by elements of a point symmetry group $\overline{D}$ in the following way

$$\begin{aligned}
\overline{D}^T \overline{F}^{(RR)}\begin{pmatrix} n'm' \\ \nu'\eta' \end{pmatrix}\overline{D} &= \overline{F}^{(RR)}\begin{pmatrix} nm \\ \nu'\eta' \end{pmatrix} \\
(\det \overline{D})\,\overline{D}^T \overline{F}^{(R\Theta)}\begin{pmatrix} n'm' \\ \nu'\eta' \end{pmatrix}\overline{D} &= \overline{F}^{(R\Theta)}\begin{pmatrix} nm \\ \nu'\eta' \end{pmatrix} \\
(\det \overline{D})\,\overline{D}^T \overline{F}^{(\Theta R)}\begin{pmatrix} n'm' \\ \nu'\eta' \end{pmatrix}\overline{D} &= \overline{F}^{(\Theta R)}\begin{pmatrix} nm \\ \nu'\eta' \end{pmatrix} \\
\overline{D}^T \overline{F}^{(\Theta\Theta)}\begin{pmatrix} n'm' \\ \nu'\eta' \end{pmatrix}\overline{D} &= \overline{F}^{(\Theta\Theta)}\begin{pmatrix} nm \\ \nu'\eta' \end{pmatrix}.
\end{aligned} \tag{2}$$

The equation of motion of the atoms in the crystal lattice can be transformed into an equation for eigen-frequencies of the system,

$$\omega^2(k,j) w_\alpha^\nu(k,j) = \sum_{\beta\eta} C_{\alpha\beta}\begin{pmatrix} k \\ \nu\eta \end{pmatrix} w_\beta^\eta(k,j). \tag{3}$$

The eigenvectors diagonalize the dynamical matrix, which is a Fourier series of force constants:

$$C_{\alpha\beta}\begin{pmatrix} k \\ \nu\eta \end{pmatrix} = \sum_n F_{\alpha\beta}\begin{pmatrix} 0n \\ \nu\eta \end{pmatrix} e^{-2\pi i k\cdot(R_0^{\nu'} - R_n^{\eta'})}. \tag{4}$$

The vector $R_n^{\eta'}$ describes the position of the η' atom or group of atoms in the n-th elementary cell. The eigenvectors fulfil the ortonormalization conditions

$$\begin{aligned}
\sum_{\alpha\nu} w_\alpha^\nu(k,j) w_\alpha^{*\nu}(k,j') &= \delta_{jj'} \\
\sum_j w_\alpha^\nu(k,j) w_\beta^{*\eta}(k,j) &= \delta_{\nu\eta}\delta_{\alpha\beta}.
\end{aligned} \tag{5}$$

With the help of these eigenvectors the elements of the dynamical matrix can be expressed by the eigen-frequencies of the system. Multiplying equation (3) by an arbitrary eigenvector, summing the result over j, and using the second ortonormalization relation (5), one gets

$$C_{\alpha\beta}\begin{pmatrix} k \\ \nu\,\eta \end{pmatrix} = \sum_j \omega^2(k,j) w_\alpha^\nu(k,j) w_\beta^{*\eta}(k,j). \tag{6}$$

The partial frequency phonon distribution is defined in the following way:

$$p_\nu(\omega)d\omega = \frac{1}{3N(2t+r)} \sum_{kj\alpha}{}' |w_\alpha^\nu(\omega^2(k,j))|^2 \tag{7}$$

$$\omega < \omega(k,j) < \omega + d\omega$$

where N is the number of elementary cells, and r, and t are the number of atoms or atom groups in the elementary cell respectively. The sum runs over these values of k wave vectors and j whose frequency $\omega(k,j)$ lies between ω and $\omega+d\omega$. The distribution $p_\nu(\omega)$ describes the density of energy states for a given kind of atoms or for a given degree of freedom. Their normalization follows from the condition (5),

$$\int_0^{\omega_L} p_\nu(\omega)d\omega = \frac{1}{2t+r} \tag{8}$$

where ω_L is the maximum frequency.

The total frequency distribution is obtained by summing all partial distributions:

$$g(\omega) = \sum_\nu p_\nu(\omega); \qquad \int_0^{\omega_L} g(\omega)d\omega = 1. \tag{9}$$

2. The moment of order $2l$ of the partial frequency distribution is defined as

$$\mu_{2l}^{(\nu)} = \frac{\int_{-\omega_L}^{\omega_L} \omega^{2l} p_\nu(\omega)d\omega}{\int_{-\omega_L}^{\omega_L} p_\nu(\omega)d\omega} \tag{10}$$

and only the even moments are not equal zero because the function $p_\nu(\omega)$ is even. We see from (10) that the zero moment is $\mu_0^{(\nu)} = 1$.

It is well known that the sum of all l-th power eigenvalues of matrix $C(k)$ is equal to the trace of matrix $\overline{C}^l(k)$. Hence, using the definition of $p_\nu(\omega)$ and the expression (6) the moments may be written as follows

$$\mu_{2l}^{(\nu)} = \frac{1}{3N} \sum_{k\alpha} [\underbrace{\bar{C}(k)\ldots\bar{C}(k)}_{l-\text{times}}]_{\alpha\alpha}^{\nu\nu} \tag{11}$$

The definition of the dynamical matrix (4) and the relation

$$\frac{1}{N}\sum_{k}\exp\left[-2\pi i k\cdot(R_1-R_2)\right]=\delta(R_1-R_2)$$

permits writing the moments as a sum of the products of force constant matrices, *viz.*,

$$\mu_{2l}^{(\nu)}=\frac{1}{3}\sum_{\alpha}\sum_{\eta_1\ldots\eta_{l-1}}\sum_{\beta_1\ldots\beta_{l-1}}\sum_{n_1\ldots n_l}F_{\alpha\beta_1}\begin{pmatrix}0 & n_1\\ \nu & \eta_1\end{pmatrix}\ldots F_{\beta_{l-1}\alpha}\begin{pmatrix}0 & n_l\\ \eta_{l-1} & \nu\end{pmatrix}\times$$

$$\times\,\delta(R_{n_1}^{\eta_1'}-R_0^{\eta_1'}+\ldots R_{n_l}^{\nu'}-R_0^{\nu'}). \tag{12}$$

The δ-function restricts the summation to those combinations of force constants for which the sum of the respective vectors vanishes.

3. The number of combinations is relatively large, though the contributions from some of them are identical. How do we find these combinations? For this purpose we shall prove the following theorem: If a combination of vectors, to which the given force constants correspond, is transformed to another one with the help of the elements of the point symmetry group of the crystal, then the two combinations will give identical contributions to the moment. (A similar theorem exists for the elements of the translation symmetry group of the crystal.)

Let us consider part of expression (12):

$$\operatorname*{Tr}_{(\alpha)}\left\{\overline{F}^{\nu''\eta_1''}\begin{pmatrix}0 & n_1\\ \nu' & \eta_1'\end{pmatrix}\ldots\overline{F}^{\eta_{l-1}''\nu''}\begin{pmatrix}0 & n_l\\ \eta_{l-1}' & \nu'\end{pmatrix}\right\}\times$$

$$\times\,\delta(R_{n_1}^{\eta_1'}-R_0^{\eta_1'}+\ldots R_{n_l}^{\nu'}-R_0^{\nu'}). \tag{13}$$

The product of the same symmetry elements $\overline{D}\cdot\overline{D}=\overline{E}$ (E is the unit matrix) may be put between each pair of force constants and also the element $\overline{D}$ can be introduced into the argument of the δ-function. Then, using the cyclic permutation invariance of the trace, one gets

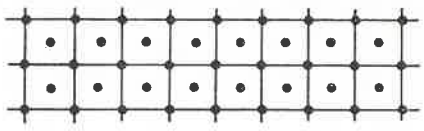
$$\operatorname*{Tr}_{(\alpha)}\left\{\overline{D}^T\overline{F}^{\nu''\eta_1''}\begin{pmatrix}0 & n_1\\ \nu' & \eta_1'\end{pmatrix}\overline{D}\ldots\overline{D}^T\overline{F}^{\eta_{l-1}''\nu''}\begin{pmatrix}0 & n_l\\ \eta_{l-1}' & \nu'\end{pmatrix}\overline{D}\right\}\times$$

$$\times\,\delta(\overline{D}R_{n_1}^{\eta_1'}-\overline{D}R_0^{\eta_1'}+\ldots\overline{D}R_{n_1}^{\nu'}-\overline{D}R_0^{\nu'}). \tag{14}$$

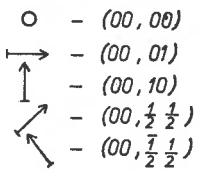
It can be shown that there is an identical number of $R\Theta$ and ΘR pairs. Therefore, the coefficients $(\det\overline{D})^2=1$ do not change the result. Thus, the two expressions (13) and (14) are equal, though they represent different combinations of force constants.

The number of considered combinations can be reduced with the help of the above proved theorem. We must find all nonequivalent combinations, *i.e.* such combinations which cannot be transformed to another by any element of crystal symmetry. Each non-equivalent combination must be multiplied by the appropriate multiple. The sum of all of them gives the value of the moments.

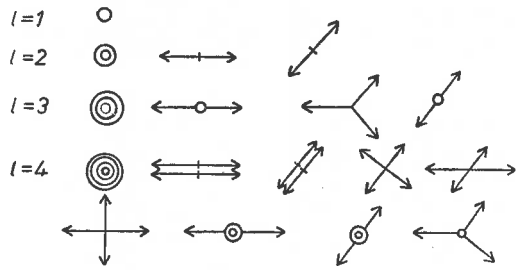
4. We will illustrate this method on the example of a two dimensional centred square lattice with the nearest and next neighbour interactions.



We introduce the following schematic description of force constants:



The force constants further than second coordinate spheres are assumed to be negligible. We may find the following non-equivalent combinations (diagrams):



where l defines the order of the moments. It may be noticed that the higher order diagrams can be obtained by multiplying those lower order diagrams for which the sum of l gives the order of the considered diagram. Therefore, we shall attempt to sum them partially.

5. For this purpose the central moment $\varepsilon_{2l}^{(\nu)}$ of the partial phonon distribution may be defined in the following way:

$$\varepsilon_{2l}^{(\nu)} = \frac{\int_{-\omega_L}^{\omega_L} (\omega^2 - \mu_2^{(\nu)})^l p_\nu(\omega) d\omega}{\int_{-\omega_L}^{\omega_L} p_\nu(\omega) d\omega}. \tag{15}$$

Expanding $(\omega^2 - \mu_2^{(\nu)})l$, the relation between the central and ordinary moments can be obtained,

$$\mu_{2l}^{(\nu)} = \varepsilon_{2l}^{(\nu)} + \binom{l}{1} \mu_{2(l-1)}^{(\nu)} \mu_2^{(\nu)} - \binom{l}{2} \mu_{2(l-2)}^{(\nu)} (\mu_2^{(\nu)})^2 -$$

$$-(-1)^s \binom{l}{s} \mu_{2(l-s)}^{(\nu)} (\mu_2^{(\nu)})^s - \ldots - (-1)^l \binom{l}{l} (\mu_2^{(\nu)})^l.$$

Hence, the ordinary moment can be calculated from the central moments and ordinary moments of lower order.

Now we shall consider the cubic lattice. Its force constant matrices for zero coordinate sphere and for $\nu = \eta$ have the diagonal form

$$F_{\alpha\beta}\begin{pmatrix}00\\ \nu\nu\end{pmatrix} = \delta_{\alpha\beta}\mu_2^{(\nu)} \tag{17}$$

where $\mu_2^{(\nu)}$ is the second moment.

Subtracting $\mu_2^{(\nu)}\delta_{\alpha\beta}\delta_{\sigma\eta}$ form the dynamical matrix (6) and using the ortonormalization condition (5) one gets

$$C_{\alpha\beta}\begin{pmatrix}k\\ \sigma\eta\end{pmatrix} - \mu_2^{(\nu)}\delta_{\alpha\beta}\delta_{\sigma\eta} = \sum_j (\omega^2(k,j) - \mu_2^{(\nu)}) w_\alpha^\sigma(k,j) w_\beta^{*\eta}(k,j). \tag{18}$$

The eigenvectors of the new matrix $(\overline{C}(k) - \mu_2^{(\nu)}\overline{E})$ and the $\overline{C}(k)$ matrix are identical, so $(\omega^2(k,j) - \mu_2^{(\nu)})^l$ are the eigenvalues of matrix $(\overline{C}(k) - \mu_2^{(\nu)}\overline{E})^l$. The use of formula (15) and the definition of the partial phonon distribution (7) yields the relation

$$\varepsilon_{2l}^{(\nu)} = \frac{1}{3N}\sum_{k\alpha}[(\overline{C}(k) - \mu_2^{(\nu)}\overline{E})^l]_{\alpha\alpha}^{II}. \tag{19}$$

Moreover, the description of the dynamical matrix (4) gives

$$C_{\alpha\beta}\begin{pmatrix}k\\ \sigma\eta\end{pmatrix} - \mu_2^{(\nu)}\delta_{\alpha\beta}\delta_{\sigma\eta} = \sum_{n\neq 0} F_{\alpha\beta}\begin{pmatrix}0n\\ \sigma\eta\end{pmatrix} e^{-2\pi i k\cdot(R_0^{\sigma'} - R_n^{\eta'})} + (\mu_2^{(\sigma)} - \mu_2^{(\nu)})\delta_{\alpha\beta}\delta_{\sigma\eta} \tag{20}$$

where

$$(\mu_2^{(\sigma)} - \mu_2^{(\nu)})\delta_{\alpha\beta}\delta_{\varrho\eta} = 0 \quad \text{if} \quad \sigma = \nu.$$

We introduce the matrices

$$A_{\alpha\beta}\begin{pmatrix}k\\ \sigma\eta\end{pmatrix} = \sum_{n\neq 0} F_{\alpha\beta}\begin{pmatrix}0n\\ \sigma\eta\end{pmatrix} e^{-2\pi i k\cdot(R_0^{\sigma'} - R_n^{\eta'})} \tag{21}$$

$$B_{\alpha\beta}\begin{pmatrix}\nu\\ \sigma\eta\end{pmatrix} = (\mu_2^{(\sigma)} - \mu_2^{(\nu)})\delta_{\alpha\beta}\delta_{\sigma\eta}. \tag{22}$$

Then,

$$\varepsilon_{2l}^{(\nu)} = \frac{1}{3N}\sum_{k\alpha}[(\overline{A}(k) + \overline{B}(\nu))^l]_{\alpha\alpha}^{\nu\nu}. \tag{23}$$

The matrices $\overline{A}(k)$ and $\overline{B}(\nu)$ do not commute. An expansion of $\overline{A}(k)$ and $\overline{B}(\nu)$ would have to consist of a set of commutators. However, we can calculate the expression (23) directly, multiplying the matrices as in the following example:

$$(\overline{A} + \overline{B})^3 = \overline{A}^3 + \overline{B}^3 + \overline{AB}^2 + \overline{B}^2\overline{A} + \overline{BAB} + \overline{BA}^2 + \overline{A}^2\overline{B} + \overline{ABA}$$

We notice that the trace of the product of an arbitrary matrix $\overline{M}$ and $\overline{B}(\nu)$ vanishes,

$$\sum_{\alpha} [\overline{B}(\nu) \cdot M]^{\nu\nu}_{\alpha\alpha} = 0; \quad \sum_{\alpha} [\overline{M} \cdot \overline{B}(\nu)]^{\nu\nu}_{\alpha\alpha} = 0; \tag{24}$$

and the central moment (23) is

$$\varepsilon^{(\nu)}_{2l} = \frac{1}{3N} \sum_{k\alpha} [\bar{A}(k)\,(\bar{A}(k)+\overline{B}(\nu))^{l-2}\bar{A}(k)]^{\nu\nu}_{\alpha\alpha}. \tag{25}$$

Carrying out the summations over k and using the definition $\overline{A}(k)$ (21) for the first few central moments, one finally gets

$$\varepsilon^{(\nu)}_{2\,1} = 0$$

$$\varepsilon^{(\nu)}_{4} = \frac{1}{3} \sum_{\alpha} \sum_{\beta} \sum_{\eta} \sum_{\substack{n_1\neq 0 \\ n_2\neq 0}} F_{\alpha\beta} \begin{pmatrix} 0 & n_1 \\ \nu & \eta \end{pmatrix} F_{\alpha\beta} \begin{pmatrix} 0 & n_2 \\ \eta & \nu \end{pmatrix} \delta(R^{\eta'}_{\eta_1} - R^{\eta'}_{0} + R^{\nu'}_{\eta_2} - R^{\nu'}_{0})$$

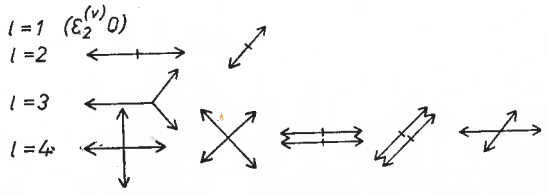
$$\varepsilon^{(\nu)}_{6} = \frac{1}{3} \sum_{\alpha} \sum_{\beta_1\beta_2} \sum_{\eta_1\eta_2} \sum_{\substack{n_1\neq 0 \\ n_2\neq 0 \\ n_3\neq 0}} F_{\alpha\beta_1} \begin{pmatrix} 0 & n_1 \\ \nu & \eta_1 \end{pmatrix} F_{\beta_1\beta_2} \begin{pmatrix} 0 & n_2 \\ \eta_1 & \eta_2 \end{pmatrix} F_{\beta_2\alpha} \begin{pmatrix} 0 & n_3 \\ \eta_2 & \nu \end{pmatrix} \times$$

$$\times \delta(R^{\eta'_1}_{n_1} - R^{\eta'_1}_{0} + R^{\eta'_2}_{n_2} - R^{\eta'_2}_{0} + R^{\nu'}_{n_3} - R^{\nu'}_{0}) +$$

$$+ \frac{1}{3} \sum_{\alpha} \sum_{\beta} \sum_{\eta} \sum_{\substack{n_1\neq 0 \\ n_2\neq 0}} (\mu^{(\eta)}_{2} - \mu^{(\nu)}_{2}) F_{\alpha\beta} \begin{pmatrix} 0 & n_1 \\ \nu & \eta \end{pmatrix} F_{\beta\alpha} \begin{pmatrix} 0 & n_1 \\ \eta & \nu \end{pmatrix} \times$$

$$\times \delta(R^{\eta'}_{n_1} - R^{\eta'}_{0} + R^{\nu'}_{n_2} - R^{\nu'}_{0}). \tag{26}$$

6. The non-equivalent contributions to $\varepsilon^{(\nu)}_{2l}$ for the abovementioned two dimensional lattice would be represented by the following diagrams.



7. This method may be used for a quick estimation of the frequency phonon distributions $p_\nu(\omega)$ and $g(\omega)$ for crystals with a short interatomic interacion potential. The calculation of the first few moments is not very difficult, even for a more complicated lattice, and the shape of the phonon distribution and the magnitude of thermodynamical functions can be easily found by the continuous fraction method.

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