Multiple oscillator model for Lattice vibrations:

If more than one lattice vibrational frequency is significant, then one uses the multiple oscillator model described by

\[ \varepsilon(\omega) = \varepsilon_0 + \sum_j \frac{\omega_{ij}^2}{\omega_j^2 - \omega^2 - i\omega \gamma_j}, \]  

(21)

where, as before, \( \varepsilon_0 \) represents the contributions from all oscillators well removed to higher frequencies, and \( \omega_{ij} \) correspond to various lattice vibrational frequencies. Note that, if all oscillators (i.e., electronic as well as lattice vibration) were included in the sum, then \( \varepsilon_0 = \varepsilon(\omega = \infty) = 1 \); also, \( \lambda_i \) and \( k \) must be calculated after performing the sum.

A simple application of the two oscillator model is MgO in the low frequency region where lattice vibration is of importance. The experimental reflectance in the region 200 cm\(^{-1}\) to 1200 cm\(^{-1}\) can be fit reasonably well with the set of parameters: \( \varepsilon_0 = 3.01, \omega_{11} = 401 cm^{-1}, \gamma_1 = 7.62 cm^{-1}, \omega_{p1}/\omega_{t1}^2 = 6.6, \omega_{t2} = 640 cm^{-1}, \gamma_2 = 102.4 cm^{-1}, \) and \( \omega_{p2}/\omega_{t2}^2 = 0.045. \)

Note that the second oscillator is weak (i.e., \( \omega_{p2}^2 \) is small). Detailed quantum mechanical treatment shows that this oscillator corresponds to the excitation of two phonons by a photon. In order to conserve the momentum, two phonons with almost equal and opposite momenta must be created, since a photon has negligible momentum compared with phonon momenta. Such two-phonon transitions have smaller probability (and hence small \( \omega_{p2}^2 \)), but they usually occur in ionic crystal.

In MgO, there is a rather large difference between the transverse optical mode frequency (at \( \omega_{11} = 401 cm^{-1} \)) where \( \varepsilon'' \) is maximum and the longitudinal optical mode frequency (at \( \omega_1 \approx 730 cm^{-1}, \) for which there is no simple formula) where \( \varepsilon' = 0. \) This is illustrated in Fig. 3.6 and Fig. 3.7 for optical constants. The negative \( \varepsilon' \) region, which extends between \( \omega_1 \) and \( \omega_{11}, \) is of importance for optical absorption in small (nano) particles. Because of the extent of this frequency region in MgO, its small particle absorption spectrum can be quite different from that of its thin films.
Model for Anisotropic solids:

Fig. 3.6: n, k and R vs. $\omega/\omega_{t1}$ for MgO.
In general, especially for anisotropic solids, the fields $\vec{D}$ and $\vec{E}$ are related by the dielectric tensor: $\vec{D} = \varepsilon_o \vec{E}$. The dielectric tensor is often symmetric, so that a coordinate system can be found in which it is diagonal:

$$
\begin{pmatrix}
  \varepsilon_1 & 0 & 0 \\
  0 & \varepsilon_2 & 0 \\
  0 & 0 & \varepsilon_3
\end{pmatrix}
$$

where $\varepsilon_1$, $\varepsilon_2$, and $\varepsilon_3$ are the principal dielectric functions. This means that if the electric field $\vec{E}$ is applied along one of the principal axes, then $\vec{D}$ and $\vec{E}$ are parallel.

Consider now the propagation of plane wave $E_o \exp(i\mathbf{q} \cdot \mathbf{r} - iw t)$ in an anisotropic medium, where for simplicity, assume $\mu = \mu_0$. Recall that the Maxwell equations for plane waves are:

$$
\vec{q} \cdot (\vec{E} \times \vec{E}_o) = 0,
\quad \vec{q} \times \vec{H}_o = 0,
$$

$$
\vec{q} \times \vec{E}_o = \omega \mu \vec{H}_o,
\quad \vec{q} \times \vec{H}_o = -\omega \varepsilon \varepsilon_o (\vec{E} \times \vec{E}_o),
$$

from the third and fourth equation one can write

$$
\vec{q} \times (\vec{q} \times \vec{E}_o) = \omega \mu \vec{q} \times \vec{H}_o = -\omega \varepsilon \varepsilon_o (\vec{E} \times \vec{E}_o),
$$

which (using $\vec{A} \times (\vec{B} \times \vec{C}) = \vec{B}(\vec{A} \cdot \vec{C}) - \vec{C}(\vec{A} \cdot \vec{B})$) leads to
This equation and the equation \( \vec{q} \cdot (\vec{E} \cdot \vec{E}_o) = 0 \) are the two relevant equations now.

Consider now the special case where \( \vec{q} \) is along one of the principal axes, say, the \( x \)-axis. Then if \( \vec{E}_o \) is referred to principal axis, these equations reduce to

\[
\begin{align*}
q^2 - \frac{\omega^2}{c^2} \varepsilon_1 & = 0, \\
q^2 - \frac{\omega^2}{c^2} \varepsilon_2 & = 0,
\end{align*}
\]

and

\( \varepsilon_3 E_{ax} = 0. \)

If \( \varepsilon_3 \neq 0 \), then \( E_{ax} = 0 \), i.e., the wave is transverse, the remaining component having the solutions,

\[
q^2 = \frac{\omega^2}{c^2} \varepsilon_1, \quad E_{ox} \neq 0, \quad E_{oy} = 0,
\]

\[
q^2 = \frac{\omega^2}{c^2} \varepsilon_2, \quad E_{ox} = 0, \quad E_{oy} \neq 0,
\]

so that the plane wave can propagate along the \( z \)-axis without a change in polarization if they are either \( x \)-polarized or \( y \)-polarized. The complex refractive indices for these two types of waves are different

\[
n_1 + ik_1 = \sqrt{\varepsilon_1}, \quad n_2 + ik_2 = \sqrt{\varepsilon_2}.
\]

Here it is assumed that the coordinate transformation to principal axes diagonalizes the real as well as the imaginary parts of

If \( \varepsilon_1 = \varepsilon_2 \), then the direction of propagation (\( z \)-axis) is called Optic axis or c- axis.

The frequency region where \( k_1 \) and \( k_2 \) are small, and \( n_1 \) and \( n_2 \) are different, one gets the phenomenon of double refraction; this is widely used for wave retarders such as quarter wave plates; incident light linearly polarized with equal \( z \)- and \( y \)- field components is phase shifted on transmission because of the two different phase velocities \( c_1 n_1 \) and \( c_1 n_2 \). This phenomenon is also known as (linear) birefringence.

If \( k_1 \) and \( k_2 \) are appreciable, then the attenuation of waves will depend on polarization, a phenomenon known as (linear) dichroism.

One can use the classical oscillator model by assigning three different sets of oscillator parameter appropriate to \( \varepsilon_1, \varepsilon_2 \) and \( \varepsilon_3 \) of the anisotropic solid.

The symmetry of the crystal lattice in a solid leads to the following general forms:

1. Isotropic, e.g., cubic crystals, amorphous solids and most liquids for which \( \varepsilon_1 = \varepsilon_2 = \varepsilon_3 = \varepsilon \):

\[
\begin{pmatrix}
\varepsilon' + i\varepsilon'' & 0 & 0 \\
0 & \varepsilon' + i\varepsilon'' & 0 \\
0 & 0 & \varepsilon' + i\varepsilon''
\end{pmatrix}
\]
2. Uniaxial e.g., tetragonal, hexagonal and trigonal crystals where $\epsilon_1 = \epsilon_2 \neq \epsilon_3$:

$$
\begin{pmatrix}
\epsilon_1' + i\epsilon_1'' & 0 & 0 \\
0 & \epsilon_1' + i\epsilon_1'' & 0 \\
0 & 0 & \epsilon_2' + i\epsilon_3''
\end{pmatrix}
$$

3. Biaxial e.g., orthorhombic crystals where $\epsilon_1 \neq \epsilon_2 \neq \epsilon_3$:

$$
\begin{pmatrix}
\epsilon_1' + i\epsilon_1'' & 0 & 0 \\
0 & \epsilon_2' + i\epsilon_2'' & 0 \\
0 & 0 & \epsilon_3' + i\epsilon_3''
\end{pmatrix}
$$

4. Biaxial e.g., triclinic and monoclinic crystals where the principal axes of the real and imaginary parts are different:

$$
\begin{pmatrix}
\epsilon_1' & 0 & 0 \\
0 & \epsilon_2' & 0 \\
0 & 0 & \epsilon_3'
\end{pmatrix}
\quad \text{Or} \quad
\begin{pmatrix}
\epsilon_1'' & 0 & 0 \\
0 & \epsilon_2'' & 0 \\
0 & 0 & \epsilon_3''
\end{pmatrix}
$$

As an example, Spitzer and Kleinman listed (also given in the book of Bohren and Huffman) the relevant parameters with seven oscillators for infra-red spectra of quartz, where the sets of parameters are different for electric field along c-axis than for those for electric field perpendicular to c-axis.