Elastic constants.

Elastic constants characterise the ability of a material to deform under any small stresses. They can be described by a fourth-rank tensor $C_{ijkl}$, relating the second-rank stress tensor $\sigma_{ij}$ to the (also second-rank) strain tensor $e_{kl}$ via the generalised Hooke’s law:

$$\sigma_{ij} = C_{ijkl}\eta_{kl} \quad \{1\}$$

where multiplication follows the rules of tensor multiplication (see Nye, 1998). Equation \{1\} can be simplified using the Voigt notation (Nye, 1998), which represents the fourth-rank tensor $C_{ijkl}$ by a square 6*6 matrix $C_{mn}$. In these notations, indices ‘11’, ‘22’, ‘33’, ‘12’, ‘13’, ‘23’ are represented by only one symbol – 1, 2, 3, 6, 5, and 4, respectively. These notations significantly simplify all equations. So we write instead of \{1\}:

$$\sigma_{i} = C_{ij}\eta_{j} \quad \{2\}$$

Note that infinitesimal strains are being used; in this limit all definitions of strain (e.g., Eulerian, Lagrangian, Hencky, etc.) become equivalent. Under a small strain, the lattice vectors $a_{ij}'$ of the strained crystal is obtained from the old lattice vectors $a_{ij}$ and the strain tensor $e_{ij}$ using the relation:

$$a_{ij}' = (\delta_{ij} + e_{ij})a_{ij} \quad \{3\}$$

In the original tensor notation and in the Voigt notation (Nye, 1998), the $(\delta_{ij}+e_{ij})$ matrix is represented as follows:

$$
\begin{pmatrix}
1+\eta_{11} & \eta_{12} & \eta_{13} \\
\eta_{12} & 1+\eta_{22} & \eta_{23} \\
\eta_{13} & \eta_{23} & 1+\eta_{33}
\end{pmatrix}
= \begin{pmatrix}
1+\eta_{11} & \eta_{12}/2 & \eta_{13}/2 \\
\eta_{12}/2 & 1+\eta_{22} & \eta_{23}/2 \\
\eta_{13}/2 & \eta_{23}/2 & 1+\eta_{33}
\end{pmatrix}
$$

\{4\}

The Voigt notation allows one to write elastic constants conveniently as a symmetric 6*6 matrix. Voigt notation is sufficient in most situations; only in rare situations such as a general transformation of the coordinate system the full fourth-rank tensor representation must be used to derive the transformed elastic constants.

One can define the inverse tensor $S_{ijkl}$ (or, in Voigt notations, $S_{ij}$ \(^1\)), often called the elastic compliance tensor:

$$\{S_{ijkl}\} = \{C_{ijkl}\}^{-1} \quad \text{or} \quad \{S_{ij}\} = \{C_{ij}\}^{-1} \quad \{5\}$$

The $S_{ij}$ tensor can be defined via the generalised Hooke’s law in its equivalent formulation:

$$\eta_{i} = S_{ij}\sigma_{j} \quad \{6\}$$

There are two groups of experimental methods of measuring the elastic constants: 1) static and low-frequency methods (based on determination of stress-strain relations for static stresses) and 2) high-frequency, or dynamic, methods (e.g., ultrasonic methods, Brillouin spectroscopy, etc.). High-frequency methods generally enable much higher accuracy. Static measurements yield isothermal elastic constants (timescale of the experiment allows thermal equilibrium to be attained within the sample), high-frequency measurements give adiabatic constants (Belikov \textit{et al.}, 1970). The difference, which is entirely due to anharmonic effects (see below), vanishes at 0 K. Adiabatic $C_{ij}$ are larger;

\(^1\) Note that in Voigt notation $C_{ijkl} = C_{mn}$, but $S_{ijkl} = S_{mn}$ only when $m$ and $n = 1,2,3$; when either $m$ or $n = 4,5$, or 6: $2S_{ijkl} = S_{mn}$, when both $m$ and $n = 4,5$, or 6: $4S_{ijkl} = S_{mn}$ (Nye, 1998).
usually by a few percent. The following thermodynamic equation gives the difference in terms of thermal pressure tensor $b_{ij}$ (Wallace, 1998):

$$ C_{ijkl}^S = C_{ijkl}^T + \frac{TV}{C_V} b_{ij} b_{kl}, $$  \quad \{7\}

where $b_{ij} = \left( \frac{\partial \sigma_{ij}}{\partial T} \right)_T$ is related to the thermal expansion tensor. For the bulk modulus:

$$ K_S = K_T (1 + \alpha \gamma T) = K_T (1 + \frac{\alpha^2 K_T V}{C_V}) $$  \quad \{8\}

where $\alpha$ and $\gamma$ are the thermal expansion and Grüneisen parameter, respectively.

At constant $P,T$ the elastic constants describing stress-strain relations \{1\} are given by:

$$ C_{ijkl}^T = \frac{1}{V} \left( \frac{\partial^2 G}{\partial \eta_{ik} \partial \eta_{kl}} \right)_T $$  \quad \{9\}

while at constant $P,S$ they are given by

$$ C_{ijkl}^S = \frac{1}{V} \left( \frac{\partial^2 H}{\partial \eta_{ik} \partial \eta_{kl}} \right)_S $$  \quad \{10\}

Now let us derive from \{9\} an expression for the elastic constants in terms of the second derivatives of the internal energy; in this derivation we follow Ackland and Reed (2003). The unit cell of a crystal can be represented by a matrix $\vec{V} = (a_1, a_2, a_3, \ldots)$, and the volume of the equilibrium unit cell is then $V_0 = \text{det} \vec{V}$. Using \{4\}, for the volume $V$ of a strained cell we obtain:

$$ \frac{V}{V_0} = \frac{\text{det} \vec{V}}{\text{det} \vec{V}_0} = 1 + \eta_1 + \eta_2 + \eta_3 + \eta_1 \eta_2 + \eta_1 \eta_3 + \eta_2 \eta_3 - \frac{\eta_4^2}{4} - \frac{\eta_5^2}{4} - \frac{\eta_6^2}{4} + \eta_1 \eta_2 \eta_3 - \frac{\eta_1 \eta_4^2}{4} - \frac{\eta_2 \eta_5^2}{4} - \frac{\eta_3 \eta_6^2}{4} + \eta_4 \eta_5 \eta_6 $$  \quad \{11\}

Then one has in the standard tensor notation:

$$ \frac{\Delta V}{V_0} = \eta_{ik} + \frac{1}{4} (2 \delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}) \eta_{ij} \eta_{kl} + O(e^3) $$  \quad \{12\}

The change of the Gibbs free energy associated with strain is then to the second order:

$$ \Delta G = \Delta F + P e_a + \frac{PV}{4} (2 \delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}) \eta_{ij} \eta_{kl} $$  \quad \{13\}

From this one has:

$$ C_{ijkl}^T = \frac{1}{V} \left( \frac{\partial^2 F}{\partial \eta_{ik} \partial \eta_{kl}} \right)_T + \frac{P}{2} (2 \delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}) $$  \quad \{14a\}

and, by analogy,

$$ C_{ijkl}^S = \frac{1}{V} \left( \frac{\partial^2 F}{\partial \eta_{ik} \partial \eta_{kl}} \right)_S + \frac{P}{2} (2 \delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}) $$  \quad \{14b\}

It is well known (Barron & Klein, 1965; Wallace, 1998) that under non-zero stresses there can be several different definitions of elastic constants. The constants $B_{ijkl}^T$ and $B_{ijkl}^S$ defined by equations \{14ab\} are those appearing in stress-strain relations and in the conditions of mechanical stability of crystals (see below), whereas the long-wavelength
limit of lattice dynamics is controlled by \( \frac{1}{V} \left( \frac{\partial^2 E}{\partial \eta_{ij} \partial \eta_{kl}} \right)_S \). These two definitions (via stress-strain relations and from long-wavelength lattice dynamics) become identical at zero pressure. Calculating the second derivatives with respect to the finite Lagrangian strains, different equations are obtained (Wallace, 1998).

**ABINIT implementation.** In ABINIT, the so-called “proper” elastic constants are calculated as follows:

\[
C_{ijkl}^{\text{proper}} = \frac{1}{V_0} \frac{d}{d \eta_{kl}} (V \sigma_{ij}) ,
\]

where \( V_0 \) is the volume of the undeformed crystal at given pressure (stress), and \( V \) is the volume changed by strain \( \eta_{kl} \). Here we have only the first derivative, so only first-order changes of \( V \) are important (to first order, \( \frac{V}{V_0} = \frac{\det V}{\det V_0} = 1 + \eta_1 + \eta_2 + \eta_3 \)). These “proper” elastic constants do not correspond to the stress-strain definition \{1\}.

\[
C_{ijkl}^{\text{proper}} = \frac{1}{V_0} \frac{d}{d \eta_{kl}} (V \sigma_{ij}) = \frac{1}{V_0} \frac{d}{d \eta_{kl}} [V_0 (1 + \eta_{kl} \delta_{kl})(\sigma_{ij}^0 + C_{ijkl} \eta_{kl})] = \frac{1}{V_0} \frac{d}{d \eta_{kl}} [\sigma_{ij}^0 + \sigma_{ij}^0 \eta_{kl} \delta_{kl} + O(\eta^2)] = \]

\[
= C_{ijkl}^{\text{proper}} + \frac{d}{d \eta_{kl}} (\sigma_{ij}^0 \eta_{kl} \delta_{kl}) = C_{ijkl}^{\text{proper}} + \sigma_{ij}^0 \delta_{kl} ,
\]

where \( \sigma_{ij}^0 \) is the stress in the reference structure (for which the elastic constants are being calculated). From \{16\} the stress-strain defined elastic constants are:

\[
C_{ijkl} = C_{ijkl}^{\text{proper}} - \sigma_{ij}^0 \delta_{kl}
\]

In case of hydrostatic pressure (\( P = -\sigma_{11} = -\sigma_{22} = -\sigma_{33} \)) we obtain corrections only for \( C_{11}, C_{22}, C_{33}, C_{12}, C_{13}, C_{23} \), e.g.: \( C_{11} = C_{11}^{\text{proper}} + P \), \( C_{12} = C_{12}^{\text{proper}} + P \).

At non-hydrostatic conditions, the situation becomes more complicated, in particular the Voigt symmetry (\( C_{ij} = C_{ji} \)) will be kept only by the “proper” constants – while for stress-strain constants it will be broken, as originally noted by Barron and Klein (1965). For example, from \{17\} \( C_{41} \) will involve a stress correction, while \( C_{14} \) will not.

For a systematic treatment of the strain, stress, electrical field and polarisation, see related document “vanderbilt-anaddb-notes.pdf”.

**REFERENCES:**

