Introduction to ab-initio lattice dynamics and vibrational thermodynamics

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Outline

Within the *Born-Oppenheimer adiabatic approximation* the nuclei move in a potential energy given by the total energy of the electron system calculated (for instance within DFT) at fixed nuclei. We call

$$E_{tot}(\mathbf{R}_I + \mathbf{u}_I)$$

this energy. The electrons are assumed to be in the ground state for each nuclear configuration.
If $|\mathbf{u}_I|$ is small, we can expand E_{tot} in a Taylor series with respect to $\mathbf{u}_I$. Within the *harmonic approximation*:

$$E_{tot}(\mathbf{R}_I+\mathbf{u}_I) = E_{tot}(\mathbf{R}_I)+\sum_{I\alpha} \frac{\partial E_{tot}}{\partial \mathbf{u}_{I\alpha}}\mathbf{u}_{I\alpha}+\frac{1}{2}\sum_{I\alpha,J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha}\partial \mathbf{u}_{J\beta}}\mathbf{u}_{I\alpha}\mathbf{u}_{J\beta}+...$$

where the derivatives are calculated at $\mathbf{u}_I = 0$ and α and β indicate the three cartesian coordinates.

Equations of motion

At equilibrium $\frac{\partial E_{tot}}{\partial \mathbf{u}_{I\alpha}} = 0$, so the Hamiltonian of the ions becomes:

$$H = \sum_{I\alpha} \frac{\mathbf{P}_{I\alpha}^2}{2M_I} + \frac{1}{2} \sum_{I\alpha, J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{I\alpha} \mathbf{u}_{J\beta}$$

where $\mathbf{P}_I$ are the momenta of the nuclei and M_I their masses. The classical motion of the nuclei is given by the $N \times 3 \times N_{at}$ functions $\mathbf{u}_{I\alpha}(t)$. These functions are the solutions of the Hamilton equations:

$$\begin{aligned} \dot{\mathbf{u}}_{I\alpha} &= \frac{\partial H}{\partial \mathbf{P}_{I\alpha}} \\ \dot{\mathbf{P}}_{I\alpha} &= -\frac{\partial H}{\partial \mathbf{u}_{I\alpha}} \end{aligned}$$

Equations of motion-II

With our Hamiltonian:

$$\begin{aligned} \dot{\mathbf{u}}_{I\alpha} &= \frac{\mathbf{P}_{I\alpha}}{M_I} \\ \dot{\mathbf{P}}_{I\alpha} &= -\sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta} \end{aligned}$$

or:

$$M_I \ddot{\mathbf{u}}_{I\alpha} = -\sum_{J\beta} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{I\alpha} \partial \mathbf{u}_{J\beta}} \mathbf{u}_{J\beta}$$

The phonon solution

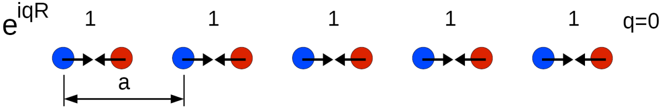
We can search the solution in the form of a phonon. Let's introduce a vector **q** in the first Brillouin zone. For each **q** we can write:

$$\mathbf{u}_{\mu s\alpha}(t) = \frac{1}{\sqrt{M_s}} \mathrm{Re}\left[\mathbf{u}_{s\alpha}(\mathbf{q}) e^{i(\mathbf{q}\mathbf{R}_\mu - \omega_\mathbf{q} t)}\right]$$

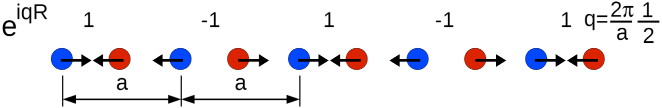
where the time dependence is given by simple phase factors $e^{\pm i\omega_\mathbf{q} t}$ and the displacement of the atoms in each cell identified by the Bravais lattice $\mathbf{R}_\mu$ can be obtained from the displacements of the atoms in one unit cell, for instance the one that corresponds to $\mathbf{R}_\mu = 0$: $\frac{1}{\sqrt{M_s}}\mathbf{u}_{s\alpha}(\mathbf{q})$.

Characteristic of a phonon in one dimension - I

A phonon at $q = 0$ has the same displacements in all unit cells:

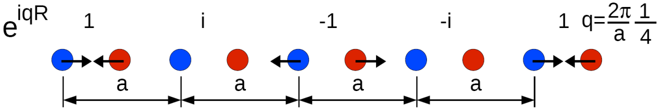


A zone border phonon with $q_{ZB} = \frac{\pi}{a} = G/2$, where $G = \frac{2\pi}{a}$ is a reciprocal lattice vector, has displacements which repeat every two unit cells:

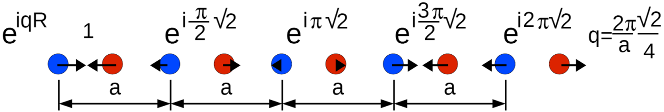


Characteristic of a phonon in one dimension - II

A phonon with $q = q_{ZB}/2$ has displacements which repeat every four unit cells:



A phonon at a general wavevector q could be incommensurate with the underlying lattice:



The phonon solution

Inserting this solution in the equations of motion and writing $I = (\mu, s)$, $J = (\nu, s')$ we obtain an eigenvalue problem for the $3 \times N_{at}$ variables $\mathbf{u}_{s\alpha}(\mathbf{q})$:

$$\omega^2_{\mathbf{q}} \mathbf{u}_{s\alpha}(\mathbf{q}) = \sum_{s'\beta} D_{s\alpha s'\beta}(\mathbf{q}) \mathbf{u}_{s'\beta}(\mathbf{q})$$

where:

$$D_{s\alpha s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}(\mathbf{R}_\nu - \mathbf{R}_\mu)}$$

is the dynamical matrix of the solid.

Within DFT the ground state total energy of the solid, calculated at fixed nuclei, is:

$$E_{tot} = \sum_i \langle\psi_i| - \frac{1}{2}\nabla^2|\psi_i\rangle + \int V_{loc}(\mathbf{r})\rho(\mathbf{r})d^3r + E_H[\rho] + E_{xc}[\rho] + U_{II}$$

where $\rho(\mathbf{r})$ is the density of the electron gas:

$$\rho(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

and $|\psi_i\rangle$ are the solution of the Kohn and Sham equations. E_H is the Hartree energy, E_{xc} is the exchange and correlation energy and U_{II} is the ion-ion interaction. According to the Hellmann-Feynman theorem, the first order derivative of the ground state energy with respect to an external parameter is:

$$\frac{\partial E_{tot}}{\partial\lambda} = \int \frac{\partial V_{loc}(\mathbf{r})}{\partial\lambda}\rho(\mathbf{r})d^3r + \frac{\partial U_{II}}{\partial\lambda}$$

Deriving with respect to a second parameter μ:

$$\begin{aligned}\frac{\partial^2 E_{tot}}{\partial\mu\partial\lambda} &= \int \frac{\partial^2 V_{loc}(\mathbf{r})}{\partial\mu\partial\lambda}\rho(\mathbf{r})d^3r + \frac{\partial^2 U_{II}}{\partial\mu\partial\lambda} \\ &+ \int \frac{\partial V_{loc}(\mathbf{r})}{\partial\lambda}\frac{\partial\rho(\mathbf{r})}{\partial\mu}d^3r\end{aligned}$$

So the new quantity that we need to calculate is the charge density induced, at first order, by the perturbation:

$$\frac{\partial\rho(\mathbf{r})}{\partial\mu} = \sum_i \left[\frac{\partial\psi_i^*(\mathbf{r})}{\partial\mu}\psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r})\frac{\partial\psi_i(\mathbf{r})}{\partial\mu}\right]$$

To fix the ideas we can think that $\lambda = \mathbf{u}_{\mu s\alpha}$ and $\mu = \mathbf{u}_{\nu s'\beta}$

The wavefunctions obey the following equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

where $V_{KS} = V_{loc}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})$. $V_{KS}(\mathbf{r},\mu)$ depends on μ so that also $\psi_i(\mathbf{r},\mu)$, and $\varepsilon_i(\mu)$ depend on μ. We can expand these quantities in a Taylor series:

$$\begin{aligned}
V_{KS}(\mathbf{r},\mu) &= V_{KS}(\mathbf{r},\mu=0) + \mu\frac{\partial V_{KS}(\mathbf{r})}{\partial\mu} + \dots \\
\psi_i(\mathbf{r},\mu) &= \psi_i(\mathbf{r},\mu=0) + \mu\frac{\partial\psi_i(\mathbf{r})}{\partial\mu} + \dots \\
\varepsilon_i(\mu) &= \varepsilon_i(\mu=0) + \mu\frac{\partial\varepsilon_i}{\partial\mu} + \dots
\end{aligned}$$

Inserting these equations and keeping only the first order in μ we obtain:

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) - \varepsilon_i\right] \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} = -\frac{\partial V_{KS}}{\partial \mu}\psi_i(\mathbf{r}) + \frac{\partial \varepsilon_i}{\partial \mu}\psi_i(\mathbf{r})$$

where: $\frac{\partial V_{KS}}{\partial \mu} = \frac{\partial V_{loc}}{\partial \mu} + \frac{\partial V_H}{\partial \mu} + \frac{\partial V_{xc}}{\partial \mu}$ and

$$\begin{aligned} \frac{\partial V_H}{\partial \mu} &= \int \frac{1}{|\mathbf{r}-\mathbf{r}'|} \frac{\partial \rho(\mathbf{r}')}{\partial \mu} d^3 r' \\ \frac{\partial V_{xc}}{\partial \mu} &= \frac{dV_{xc}}{d\rho} \frac{\partial \rho(\mathbf{r})}{\partial \mu} \end{aligned}$$

depend self-consistently on the charge density induced by the perturbation.

The induced charge density depends only on $P_c \frac{\partial \psi_i}{\partial \mu}$ where $P_c = 1 - P_v$ is the projector on the conduction bands and $P_v = \sum_i |\psi_i\rangle\langle\psi_i|$ is the projector on the valence bands. In fact:

$$\begin{aligned}\frac{\partial \rho(\mathbf{r})}{\partial \mu} &= \sum_i \left[P_c \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mu} \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \right] \\ &+ \sum_i \left[P_v \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mu} \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) P_v \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \right]\end{aligned}$$

$$\begin{aligned}\frac{\partial \rho(\mathbf{r})}{\partial \mu} &= \sum_i \left[P_c \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mu} \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \right] \\ &+ \sum_{ij} \psi_j^*(\mathbf{r}) \psi_i(\mathbf{r}) \left(\langle \frac{\partial \psi_i}{\partial \mu} | \psi_j \rangle + \langle \psi_i | \frac{\partial \psi_j}{\partial \mu} \rangle \right)\end{aligned}$$

DFPT

Therefore we can solve the self-consistent linear system:

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}(\mathbf{r}) - \varepsilon_i\right] P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} = -P_c \frac{\partial V_{KS}}{\partial \mu} \psi_i(\mathbf{r})$$

where

$$\frac{\partial V_{KS}}{\partial \mu} = \frac{\partial V_{loc}}{\partial \mu} + \frac{\partial V_H}{\partial \mu} + \frac{\partial V_{xc}}{\partial \mu}$$

and

$$\frac{\partial \rho(\mathbf{r})}{\partial \mu} = \sum_i \left[P_c \frac{\partial \psi_i^*(\mathbf{r})}{\partial \mu} \psi_i(\mathbf{r}) + \psi_i^*(\mathbf{r}) P_c \frac{\partial \psi_i(\mathbf{r})}{\partial \mu} \right]$$

Practical calculations

The program `ph.x` solves this self-consistent linear system for $3 \times N_{at}$ perturbations at a fixed vector $\mathbf{q}$. With $\frac{\partial \rho(\mathbf{r})}{\partial \mu}$ for all the perturbations it calculates the dynamical matrix

$$D_{s\alpha s'\beta}(\mathbf{q})$$

at the given $\mathbf{q}$. Diagonalizing this matrix we obtain $3 \times N_{at}$ frequencies $\omega_{\mathbf{q},\nu}$. By repeating this procedure for several $\mathbf{q}$ we could plot $\omega_{\mathbf{q},\nu}$ as a function of $\mathbf{q}$ and display the phonon dispersions. However, it is more convenient to adopt a different approach that requires the calculation of the dynamical matrix in a small set of points $\mathbf{q}$.

The dynamical matrix of the solid:

$$D_{s\alpha s'\beta}(\mathbf{q}) = \frac{1}{\sqrt{M_s M_{s'}}} \sum_{\nu} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}} e^{i\mathbf{q}(\mathbf{R}_\nu - \mathbf{R}_\mu)}$$

is a periodic function of $\mathbf{q}$ with $D_{s\alpha s'\beta}(\mathbf{q}+\mathbf{G}) = D_{s\alpha s'\beta}(\mathbf{q})$ for any reciprocal lattice vector $\mathbf{G}$. Furthermore, due to the translational invariance of the solid it does not depend on μ. Eq.1 is a Fourier expansion of a three dimensional periodic function. We have Fourier components only at the discrete values $\mathbf{R}_\nu$ of the Bravais lattice and we can write:

$$\frac{1}{\sqrt{M_s M_{s'}}} \frac{\partial^2 E_{tot}}{\partial \mathbf{u}_{\mu s\alpha} \partial \mathbf{u}_{\nu s'\beta}} = \frac{\Omega}{(2\pi)^3} \int d^3\mathbf{q} D_{s\alpha s'\beta}(\mathbf{q}) e^{-i\mathbf{q}(\mathbf{R}_\nu - \mathbf{R}_\mu)} \quad (1)$$

We can use the properties of the discrete Fourier transform and sample the integral in a uniform mesh of points **q**. This will give the interatomic force constants only for a certain range of values of $\mathbf{R}_\nu$ neighbors of $\mathbf{R}_\mu$. The code `q2r.x` reads a set of dynamical matrices calculated in a uniform mesh of **q** points and calculates, using Eq. 1, the interatomic force constants for a shell of neighbors of the point $\mathbf{R}_\mu = 0$.

Therefore, if the dynamical matrix is a sufficiently smooth function of **q** and the interatomic force constants decay sufficiently rapidly in real space, we can use Eq. 1 to calculate the dynamical matrix at arbitrary **q**, limiting the sum to a few $\mathbf{R}_\nu$ neighbors of $\mathbf{R}_\mu = 0$. The program `matdyn.x` reads the interatomic force constants calculated by `q2r.x` and calculates the dynamical matrices at an arbitrary **q** using Eq. 1.

The canonical partition function

The vibrational energy of a solid whose phonon modes have frequencies $\omega_{\mathbf{q},\nu}$ depends on the number of phonons $n_{\mathbf{q},\nu}$ in each mode:

$$E_i = \sum_{\mathbf{q},\nu} \left(n_{\mathbf{q},\nu} + \frac{1}{2} \right) \hbar\omega_{\mathbf{q},\nu},$$

where i indicates the set of integer numbers $n_{\mathbf{q},\nu}$. At a given temperature T the probability that the solid has a certain energy E_i can be calculated by statistical methods and it is:

$$\frac{1}{Z} e^{-\beta E_i}$$

where Z is the canonical partition function defined as

$$Z = \sum_i e^{-\beta E_i},$$

the sum is over all the possible sets of integers $n_{\mathbf{q},\nu}$ and $\beta = 1/K_B T$ (K_B is the Boltzmann constant). We can write

$$Z = \sum_i e^{-\beta E_i} = \prod_{\mathbf{q},\nu} \left(\sum_{n=0}^{\infty} e^{-(n+1/2)\beta\hbar\omega_{\mathbf{q},\nu}} \right)$$

Making the sum over n and taking the logarithm gives:

$$\begin{aligned} \ln Z &= \sum_{\mathbf{q},\nu} \ln \left[\frac{e^{-\frac{1}{2}\beta\hbar\omega_{\mathbf{q},\nu}}}{1 - e^{-\beta\hbar\omega_{\mathbf{q},\nu}}} \right] = -\sum_{\mathbf{q},\nu} \ln \left[2\sinh(\frac{\beta\hbar\omega_{\mathbf{q},\nu}}{2}) \right] \\ &= -\beta \sum_{\mathbf{q},\nu} \frac{\hbar\omega_{\mathbf{q},\nu}}{2} - \sum_{\mathbf{q},\nu} \ln \left[1 - e^{-\beta\hbar\omega_{\mathbf{q},\nu}} \right]. \end{aligned}$$

The thermodynamic functions

The energy per unit volume of the solid is:

$$u = \frac{1}{V}\frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = -\frac{1}{V}\frac{\partial \ln Z}{\partial \beta}.$$

The Helmholtz free energy per unit volume ($f = u - Ts$ where s is the entropy per unit volume), is given by:

$$f = -\frac{1}{V}\frac{1}{\beta}\ln Z.$$

Using the expression of $\ln Z$ in terms of the phonon frequencies, we have:

$$u = \frac{1}{V}\sum_{\mathbf{q},\nu}\frac{\hbar\omega_{\mathbf{q},\nu}}{2} + \frac{1}{V}\sum_{\mathbf{q},\nu}\frac{\hbar\omega_{\mathbf{q},\nu}}{e^{\beta\hbar\omega_{\mathbf{q},\nu}} - 1}.$$

The phonon density of states

Introducing the phonon density of states:

$$g(\omega) = \frac{1}{V}\sum_{\mathbf{q},\nu} \delta(\omega - \omega_{\mathbf{q},\nu})$$

we can write the thermodynamic fuctions as one dimensional integrals over the frequencies:

$$f = \int_0^\infty d\omega\; g(\omega) \ln\left[2\sinh(\frac{\beta\hbar\omega}{2})\right],$$

$$u = \int_0^\infty d\omega\; g(\omega)\frac{\hbar\omega}{2} + \int_0^\infty d\omega\; g(\omega)\frac{\hbar\omega}{e^{\beta\hbar\omega}-1},$$

$$s = \frac{1}{T}(u - f).$$

The thermodynamic functions

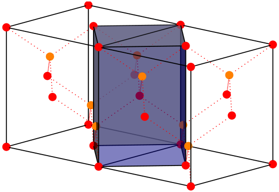
The small program `print_thermo.x` reads as input a file with the phonon dos and gives as output f, u, and s as a function of T. Moreover it writes the isochoric specific heat:

$$\begin{aligned} c_v = \frac{\partial u}{\partial T} &= K_B \int_0^\infty d\omega\, g(\omega) \left[\frac{\beta\hbar\omega/2}{\sinh(\frac{\beta\hbar\omega}{2})} \right]^2 \\ &= K_B \int_0^\infty d\omega\, g(\omega) e^{\beta\hbar\omega} \left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1} \right]^2 . \end{aligned}$$

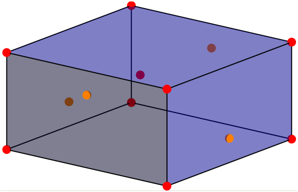
See also the QHA package in the QE distribution for a similar functionality.

The α-β structural transition in Tin - I

The structure of Tin in the α phase ($T < 13C$) is the diamond structure (note a centered tetragonal unit cell with $c = \sqrt{2}a$):

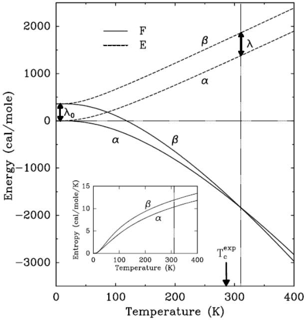


The structure of Tin in the β phase ($T > 13C$) ($c \approx 0.55a$):



The α-β structural transition in Tin - II

Phase stability is studied comparing the Helmholtz free energies at different temperatures:



P. Pavone, S. Baroni, and S. de Gironcoli, Phys. Rev. B **57**, 10421 (1998).