Phonons Calculations

Fundamental Maths

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1. Thermodynamics of Composition: Ordered Solids

At $T > 0$, there are thermal fluctuations through electronic excitations and lattice vibrations

$$(1) \qquad F = E_0 + F_{elec} + F_{vib}$$

For now, we will assume that electron-phonon interactions are negligible.

E_0: DFT energy at 0 Temp
F_{elec}: Electronic free energy contribution
F_{vib}: Vibrational free energy contribution

Electronic Free Energy

$$(2) \qquad F_{elec}(T) = E_{elec}(T) - E_{elec}(0) - TS_{elec}(T)$$

Here we will assume that the density of electronic states (DOS) near Fermi level slowly varies relative to the Fermi distribution. The electronic free energy can be reduced to the Sommerfeld model:

$$(3) \qquad F_{elec}(T) = \frac{-\pi^2}{6}k_B^2 T^2 g(\epsilon_F)$$

$g(\epsilon_F)$: DOS at Fermi level at 0 K

Lattice Vibration Free Energy

The quantum treatment of lattice vibrations in the harmonic approximation provides a reliable description of thermal vibrations in many solids for low to moderately high temperatures [1].

In the harmonic approximation, the energy of the vibrating atoms ($F_{vib,ha}$) are written as ...

$$(4) \qquad F_{vib,ha} = T + U_{ha}$$

T: Kinetic energy
U_{ha}: Potential energy in harmonic approximation

U_{ha} is the potential energy expanded as Taylor series, where higher order terms ($n > 2$) are assumed to be negligible.

$$(5) \qquad U_{ha}(\vec{q} + \Delta\vec{q}) = U(\vec{q}) + \sum_{i=1}^{3N} \frac{\partial U}{\partial q_i}\Delta\vec{q_i} + \frac{1}{2}\Delta\vec{q}^T \hat{H}\Delta\vec{q}$$

q: coordinate vector

$$(6) \qquad \hat{H} = \begin{bmatrix} \frac{\partial^2 U}{\partial q_1^2} & \frac{\partial^2 U}{\partial q_1 \partial q_2} & \cdots \\ \frac{\partial^2 U}{\partial q_2 \partial q_1} & \frac{\partial^2 U}{\partial q_2^2} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix}$$

In this model we consider that each atom only feels the force of its immediate neighbor. If the energy between two neighbors at a distance of a is $\phi(a)$, the total energy of a chain of N atoms when each atom is at rest is $U = N\phi(a)$. As a first approximation, we assume the atoms can move about a little. In cases that Δq is small in comparison to a, i.e. the kinetic energy of the "chain" of atoms is small, the harmonic approximation is good enough to capture the principal characteristics of the system with minimum effort.

To simplify the equation, we assume that the current position will have zero potential energy and that we are at equilibrium (so $\frac{\partial U}{\partial q_i} = 0$).

$$(7) \qquad U_{ha}(\vec{q} + \Delta\vec{q}) = \frac{1}{2}\Delta\vec{q}^T \hat{H} \Delta\vec{q}$$

Meanwhile, the kinetic energy (T) is well known:

$$(8) \qquad T(\Delta\vec{q}) = \frac{1}{2}\sum_{i=1}^{3N} m_i(\Delta\dot{q}_i)^2$$

Right now we have a summation term of m_i and $\dot{q}_i$. A coordinate change to make the mass term disappear (so that the equation is in terms of only one variable) can be done. We express the displacement as a mass-weighted cartesian displacement η.

$$(9) \qquad \eta_i = \sqrt{m_i}\Delta q_i$$

$$(10) \qquad F_{vib,ha} = \sum \frac{1}{2}\dot{\vec{\eta}}^2 + \frac{1}{2}\vec{\eta}^T \left(\frac{1}{\sqrt{m_i}}\hat{H}\frac{1}{\sqrt{m_j}} \right) \vec{\eta}$$

The Hessian matrix is transformed to $\hat{\tilde{H}} = \frac{1}{\sqrt{m_i}}\hat{H}\frac{1}{\sqrt{m_i'}}$. Since the Hessian matrix is a Hermitian (square, symmetric) matrix, the matrix can be decomposed to transformation matrices (called a unitary matrix) and a diagonal matrix. We can later then rewrite this as an eigenvalue problem and solve it as such.

The decomposition is:

$$(11) \qquad \hat{\tilde{H}} = \hat{\Phi}\hat{\Omega}^2\hat{\Phi}^T$$

Where $\hat{\Omega}^2 = diag(\cdots, \omega^2, \cdots)$ and $\hat{\Phi}$ is the unitary matrix composed of column vectors which are the eigenvectors of the Dynamical matrix. The unitary matrix is a transformation matrix which follows the requirement: $\hat{\Phi}^T\hat{\Phi} = \hat{I}$.

Now re-expressing $F_{vib,ha}$ (in matrix form) by expanding the decomposed $\hat{D}$:

$$(12) \qquad F_{vib,ha} = \sum \frac{1}{2}\dot{\vec{\eta}}^T\dot{\vec{\eta}} + \frac{1}{2}\vec{\eta}^T\left(\hat{U}\hat{\Omega}^2\hat{\Phi}^T\right)\vec{\eta}$$

$$(13) \qquad F_{vib,ha} = \sum \frac{1}{2}(\hat{\Phi}^T\dot{\vec{\eta}})^T(\hat{\Phi}^T\dot{\vec{\eta}}) + \frac{1}{2}\vec{\eta}^T\left(\hat{U}\hat{\Omega}^2\hat{\Phi}^T\right)\vec{\eta}$$

$$(14) \qquad \hat{Q} = \hat{\Phi}^T\vec{\eta}$$

$$(15) \qquad F_{vib,ha} = \sum \frac{1}{2}\hat{Q}^T\hat{Q} + \frac{1}{2}\hat{Q}^T\hat{\Omega}^2\hat{Q}$$

We define $\hat{Q}$ to be the normal coordinates.

Eigenvalue Problem

As a feature of a Hermitian matrix, we can re-express Equation 11 as an eigenvalue problem:

$$(16) \qquad \hat{\tilde{H}}\hat{\Phi} = \hat{\Omega}^2\hat{\Phi}$$

or in summation terms

$$(17) \qquad \sum_{l'k'a'} \tilde{H}_{lka,l'k'a'}\Phi_{l'k'a'}(\xi) = \omega_\xi^2\Phi_{lka}(\xi)$$

Where l, k, a are lattice point, equilibrium positions of atoms, and Cartesian index number respectively. $\Phi_{l'k'a'}$ is the individual eigenvector that make up the matrix $\hat{\Phi}$. The subscript ξ denotes the index of the normal mode. Each eigenvalue-eigenvector pair correspond to a normal mode of the lattice vibration. The solution form of $\Phi_{l'k'a'}$, i.e. the eigenvector, has a well-known form, based on Bloch theorem, and is written in terms of the wave vector $\mathbf{q}$ (we make this vector bold for ease of reading)

$$(18) \qquad \Phi = \frac{1}{N}W(\mathbf{r})e^{i\cdot\mathbf{q}\cdot\mathbf{r}}$$

Where $W(\mathbf{r})$ is a periodic function of the crystal lattice. The dynamical matrix is officially defined after multiplying both sides of equation by $\frac{1}{N}e^{i\cdot\mathbf{q}\cdot\mathbf{r}}$. It is still Hermitian by construction.

The vibrational frequencies at each mode are obtained as the square roots of the eigenvalues, and the eigenvectors give the pattern of atomic displacements belonging to each mode.

$$(19) \qquad\qquad D_{ka,k'a'}(\mathbf{q})W_{ka}(\mathbf{q}\nu) = \omega^2_{\mathbf{q}\nu}W_{ka}(\mathbf{q}\nu)$$

$$(20) \qquad\qquad D_{ka,k'a'}(\mathbf{q}) = \frac{1}{\sqrt{m_k m'_k}}\sum_{l'}\Phi_{0ka,l'k'a'}e^{i\cdot\mathbf{q}\cdot(\mathbf{r}_{l'}-\mathbf{r}_0)}$$

A structure is stable if all the eigenvalues are positive.

Since D($\mathbf{q}$) is a Hermitian matrix (i.e. $D^T(\mathbf{q}) = D(\mathbf{q})$), it is diagonizable with real eigenvalues $\omega^2_{q\nu}$ as well:

$$(21) \qquad\qquad \hat{D}\hat{\Phi} = \hat{\Omega}^2\hat{\Phi}$$

Then there are equations from QM to determine the number of phonons per normal mode and the density of states.

Supercell Finite-Displacement Set-Up

The harmonic force constants Φ are obtained by solving simultaneous equations of atomic forces and small displacements. To isolate the interaction between each two atoms and to eliminate self-interactions between periodic atoms, we need to make sure that the atoms are not interacting with its periodic image atoms. We do this by calculating the force constants of atoms within a supercell (see Figure 1). Any atomic displacement $u = \Delta q$ generates forces f:

$$(22) \qquad\qquad \vec{f} = -\frac{\partial F_{vib}}{\partial \vec{r}}$$

Based on the symmetry of the crystal, we impose finite displacements on specific atoms and calculate the force constants between each pair of atoms using Equation 22.

$$(23) \qquad\qquad -f_{lka} = \sum_{l'k'a'}\hat{H}_{lka,l'k'a'}u_{l'k'a'}$$

Equation 23 expresses the sum of the displacements between each atom in the supercell and the displaced atom within the supercell as well as the displaced atom in the periodic images of the supercell. This is called the cummulant force constant. At a large enough supercell, however, the interaction between each atom and the displacement of the "moved" atom's image would be so small it would be effectively zero. And that leaves you effectively with:

$$(24) \qquad\qquad \hat{H}_l = \sum_{L}\hat{H}_{l'+L}$$
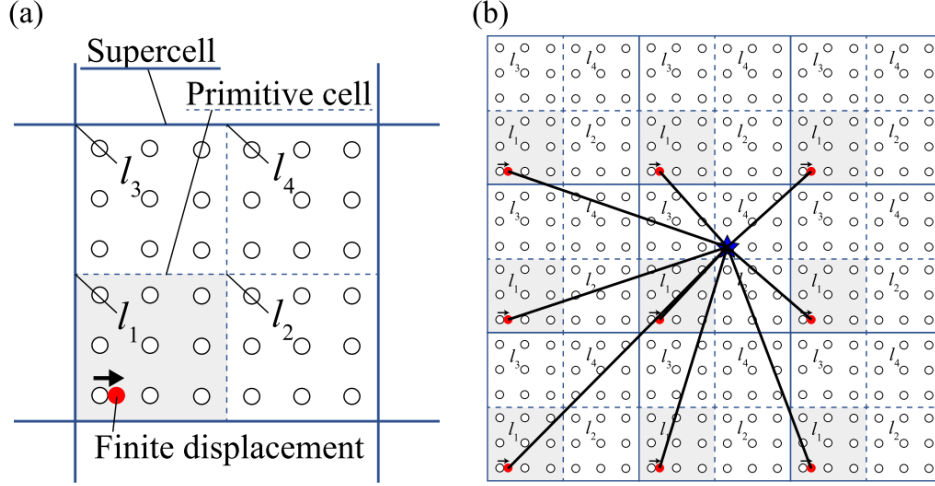
Fig. 5. (Color online) (a) A supercell contains $|P_{p\rightarrow s}|$ primitive cells, where atoms are depicted by circles. A finite displacement is introduced in one of the primitive cells. l_1, l_2, l_3, and l_4 are the indices of the lattice points (or primitive cells) in the supercell. The displacement in the supercell breaks the periodicity inside the supercell. (b) Forces in the supercell are calculated under the periodic boundary condition of the supercell. The atom near the center of the figure (filled star symbol) feels the displacements in all mirror images of the supercell.

FIGURE 1. Caption

Thermal Properties at Constant Volume

Under the harmonic approximation, the phonon partition function has the simple form:

$$(25) \qquad Z_{ha} = \prod_{\mathbf{q}\nu} \frac{e^{-\hbar\omega_{\mathbf{q}\nu}/2k_BT}}{1 - e^{-\hbar\omega_{\mathbf{q}\nu}/k_BT}}$$

From the partition function, we can calculate Hemholtz free energy $F_{gen,ha}$ and entropy $S_{gen,ha}$:

$$(26) \qquad U_{vib,ha} = F_{gen,ha} = \frac{1}{2}\sum_{\mathbf{q}\nu}\hbar\omega_{\mathbf{q}v} + k_BT\sum_{\mathbf{q}\nu}ln[1 - e^{-\hbar\omega_{\mathbf{q}\nu}/k_BT}]$$

$$(27) \qquad S_{gen,ha} = \frac{1}{2T}\sum_{\mathbf{q}\nu}\hbar\omega_{\mathbf{q}\nu}coth(\hbar\omega_{\mathbf{q}\nu}/2k_BT) - k_B\sum_{\mathbf{q}\nu}ln[2sinh(\hbar\omega_{\mathbf{q}\nu}/2k_BT)]$$

The heat capacity at constant volume:

$$(28) \qquad C_{V,ha} = \frac{1}{2T}\sum_{\mathbf{q}\nu}\hbar\omega_{\mathbf{q}v}coth(\hbar\omega_{\mathbf{q}\nu}/2k_BT) - k_B\sum_{\mathbf{q}\nu}ln[2sinh(\hbar\omega_{\mathbf{q}\nu}/2k_BT)]$$

Quasi-Harmonic Phonon (QHA) Calculation

At higher temperatures, crystal lattices start to expand and phonon frequency can show more anharmonic character. Therefore a more natural energy is the Gibbs free energy (constant pressure rather than cosntant volume). One way we can easily take into account anharmonicity due to thermal expansion is through this QHA approach. The Gibbs free energy is given by the following thermodynamic relation:

$$(29) \qquad G(T, P) = min_{V_c}[E_el(V_c) + F_{vib,ha}(V_c; T) + pV_c]$$

Where p denotes the pressure. In this aprpoach, energy functions are calculated at sampling points of unit cell volumes and then the energies are fitted to a nice smooth function such as equation of states. At $p = 0$ the lowest energy of the curve is the Gibbs free energy.
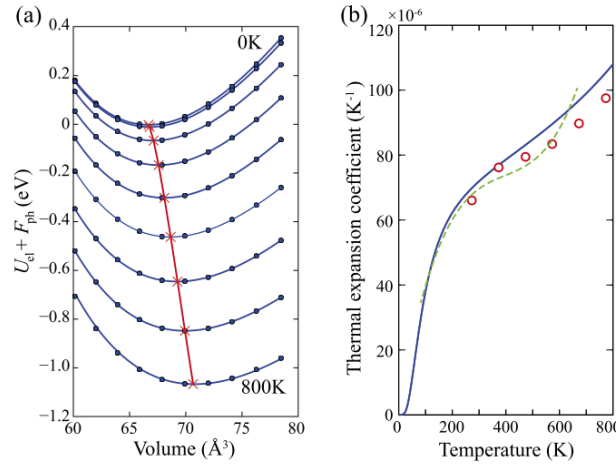
Fig. 13. (Color online) These figures are obtained from Ref. 26 licensed under CC-BY-4.0. (a) Calculated values of $U_{el}(V_c) + F_{ha}(V_c; T)$ of Al with respect to unit cell volumes at temperatures. $U_{el}(V_c) + F_{ha}(V_c; T)$ at each temperature (filled circle symbols) was fitted to the Vinet equation of states[77] (solid curves). Bottoms of the energy curves correspond to Gibbs free energies at the temperatures at $p = 0$ that are marked by cross symbols. Equilibrium volumes are obtained simultaneously. (b) Solid curve depicts calculated volumetric thermal expansion coefficients of Al at temperatures. Circle symbols[78] and dashed curve[79] are the experimental values.

FIGURE 2. Caption

We join the Gibbs free energy at increasing temperature (the red cross symbols in Figure 2. The equilibrium unit cell volume at (T, p) is obtained likewise:

$$(30) \qquad V_c^{eq}(T, p) = arg_{V_c}min[E_{el}(V_c) + F_{vib,ha}(V_c; T) + pV_c]$$

The heat capacity is calculated using the thermodynamic relation:

$$(31) \qquad C_P(T,p) = -T\frac{\partial^2 G(T,p)}{\partial T}$$

References

(1) Maradudin, A. A.; Montroll, E. W.; Weiss, G. H.; Ipatova, I., *Theory of lattice dynamics in the harmonic approximation*; Academic press New York: 1963; Vol. 3.