Ab initio methods in solid state physics

XIII. Lattice Thermodynamics

Przemysław Piekarz   Paweł T. Jochym

Department of Computational Material Science

Institute of Nuclear Physics, Polish Academy of Sciences

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Thermodynamics of lattices

- This is *not* a thermodynamics lecture
- Basic thermodynamics of crystals
  - Harmonic phonons
  - Anharmonic perturbation
- Thermodynamic properties
  - Thermodynamic functions
  - Thermal displacements
  - Heat capacity
  - Thermal expansion
  - Heat conductance
  - Phase transitions

Thermodynamics of crystals

The thermodynamics in the statistical mechanics formulation is founded on probability distribution and partition function Z:

$$Z = \sum e^{-E/k_B T}$$

The remining thermodynamic functions are defined in relation to Z. For example Helmholtz free energy F:

$$F = -k_B T \ln Z,$$

also entropy, pressure, stresses, heat capacity are defined in terms of various functions of Z.

Calculation of Z requires knowledge of the energy levels of the system E. The energy can be expanded in the small parameter $\epsilon = \sqrt{\langle u^2 \rangle} / \langle R \rangle$ where u is a displacement and R is an interatomic distance. Thus, terms in Hamiltonian H can be ordered in the powers of ϵ:

$$H = H_0 + H_2 + H_3 + H_4 + \ldots$$

Harmonic phonons

If we keep just two first terms in the Hamiltonian, the energy levels written in the *occupation number* formulation will take the form:

$$E_2(\ldots, n_k, \ldots) = \sum_k \hbar\omega_k \left(n_k + \frac{1}{2}\right)$$

which leads to the harmonic partition function Z_H:

$$Z_H = \sum_{(\ldots, n_k, \ldots)} e^{-\sum_k \hbar\omega_k (n_k + \frac{1}{2})/k_B T} = \prod_k \frac{e^{-\hbar\omega_k/2k_B T}}{1 - e^{-\hbar\omega_k/k_B T}}$$

giving harmonic free energy F_H:

$$F_H = \sum_k \left[\frac{1}{2}\hbar\omega_k + k_B T \ln\left(1 - e^{-\hbar\omega_k/k_B T}\right)\right]$$

Anharmonic perturbation

Sustaining fourth order term in the Hamiltonian ($H = H_0 + H_2 + H_4$) leads to the anharmonic partition function Z:

$$Z = e^{-E_0/k_BT} \sum e^{-(E_2+E_4)/k_BT} = e^{-E_0/k_BT} Z_H \left[1 - Z_H^{-1} \sum \frac{E_4}{k_BT} e^{-E_2/k_BT} \right]$$

$$Z = e^{-E_0/k_BT} Z_H \left[1 - \frac{\langle E_4 \rangle_H}{k_BT} \right]$$

giving free energy F:

$$F = E_0 - k_BT \ln Z_H + \langle E_4 \rangle_H = E_0 + F_H + F_A$$

Anharmonic free energy

After rather lenghty calculations the anharmonic free energy term becomes:

$$\begin{aligned}F_A =& 12\sum_{k,k'}\Phi_{k,-k,k',-k'}(n_k+1/2)(n_{k'}+1/2)\\ &-\frac{18}{\hbar}\sum_{k,k',k''}\Bigg\{|\Phi_{kk'k''}|^2\left[\frac{n_kn_{k'}+n_k+1/3}{(\omega_k+\omega_{k'}+\omega_{k''})_p}+\frac{2n_kn_{k''}-n_kn_{k'}+n_{k''}}{(\omega_k+\omega_{k'}-\omega_{k''})_p}\right]\\ &+2\Phi_{k,-k,k''}\Phi_{k',-k',k''}\frac{n_kn_{k'}+n_k+1/4}{(\omega_{k''})_p}\Bigg\}\end{aligned}$$

which can be used to calculate further termodynamic functions (entropy, heat capacity, forces, stresses, etc.). The formulas for harmonic parts are reasonably compact, e.g. C_V:

$$C_V=\left(\frac{\partial U}{\partial T}\right)_V=-T\frac{\partial^2 F}{\partial T^2}=\sum_{\mathbf{q}\nu}k_{\mathrm{B}}\left(\frac{\hbar\omega(\mathbf{q}\nu)}{k_{\mathrm{B}}T}\right)^2\frac{\exp(\hbar\omega(\mathbf{q}\nu)/k_{\mathrm{B}}T)}{[\exp(\hbar\omega(\mathbf{q}\nu)/k_{\mathrm{B}}T)-1]^2}$$

Expectation value of the squared atomic displacement:

$$\langle|u^\alpha(jl,t)|^2\rangle=\frac{\hbar}{2Nm_j}\sum_{\mathbf{q},\nu}\omega_\nu(\mathbf{q})^{-1}(1+2n_\nu(\mathbf{q},T))|e^\alpha_\nu(j,\mathbf{q})|^2,$$

Thermal expansion

$$F_H = \sum_k \left[\frac{1}{2}\hbar\omega_k + k_B T \ln\left(1 - e^{-\hbar\omega_k / k_B T}\right) \right]$$

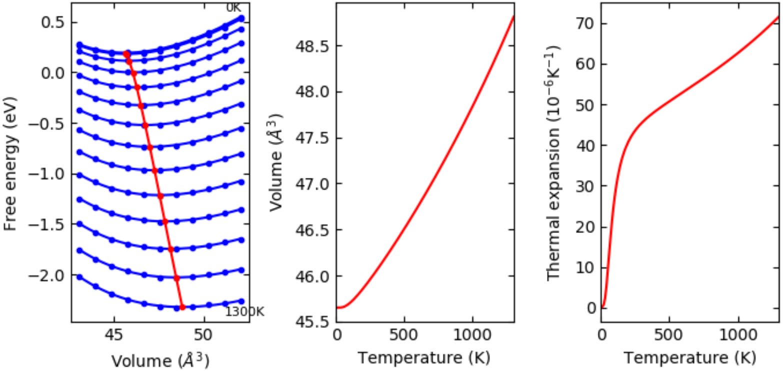
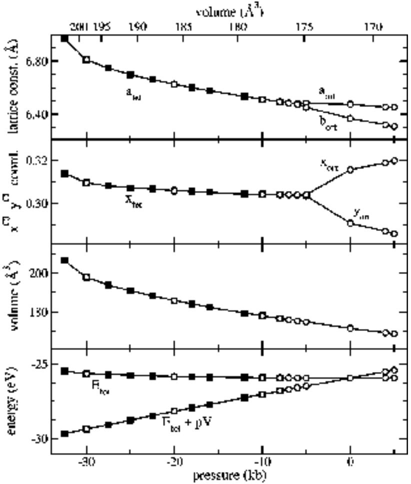
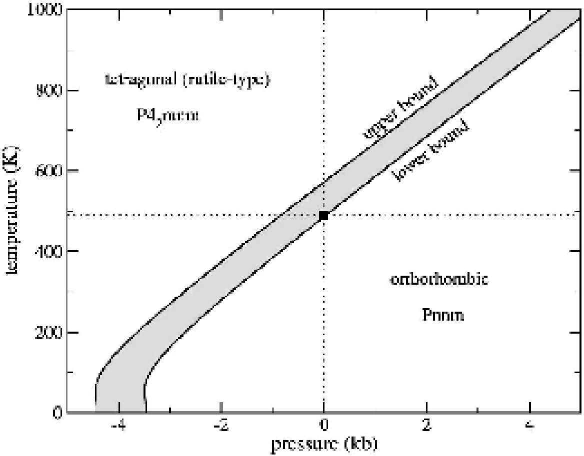


Figure 1: *Figure from documentation of Phonopy package*

Phase transitions





J. Łażewski, P. T. Jochym, P. Piekarz, and K. Parlinski; Phys. Rev. B **70** (2004) 104109