

Ab initio methods in solid state physics

X. Lattice dynamics - anharmonicity

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Anharmonic lattice dynamics

- Harmonic oscillator
- Why anharmonicity?
- Quartic oscillator
- Anharmonic perturbation theory
- Phonon life times
- Lattice thermal conductivity

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¹A. A. Maradudin, *Theory of Lattice Dynamics in the Harmonic Approximation* / (New York :, 1963.)

²M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, 1988)

Harmonic oscillator

Classic harmonic oscillator with mass m and frequency ω is governed by the quadratic potential:

$$V(u) = \frac{m\omega^2}{2}u^2$$

where u is the displacement from the equilibrium position. The solution of the equation of motion for this potential is an oscillating motion $u(t) = A \sin(\omega t + \phi)$, where frequency and phase (ϕ) are *constant* and are independent from amplitude (A). This solution is just a single, constant Fourier component (delta) when transformed to frequency domain. This reminds us of the solution of the harmonic approximation for the crystal from the previous lecture:

$$\omega^2(\mathbf{q})\varepsilon_{i\alpha} = \sum_{i'\alpha'} D_{i\alpha}^{i'\alpha'}(\mathbf{q})\varepsilon_{i'\alpha'}$$

where the dynamical matrix $D_{i\alpha}^{i'\alpha'}(\mathbf{q})$ is a function of wave vector \mathbf{q} .

Why we need anharmonicity?

$$\omega^2(\mathbf{q})\varepsilon_{i\alpha} = \sum_{i'\alpha'} D_{i\alpha}^{i'\alpha'}(\mathbf{q})\varepsilon_{i'\alpha'}$$

Consequences:

- phonon modes are *independent*,
- frequencies are constant with temperature,
- no interaction between modes \Rightarrow **no thermal equilibrium (!!)**,
- “ballistic” thermal transport without resistance,
- no phase transitions.

There are no harmonic crystals in nature!

$$V(u) = \frac{m\omega^2}{2}u^2 + \frac{\lambda}{4}u^4,$$

which leads to the equation of motion:

$$m\ddot{u} + m\omega^2u + \lambda u^3 = 0.$$

which has a solution:³ $u(t) = A\text{cn}(t\Omega, \mu)$, where cn is an elliptic Jacobi function and

$$\Omega = \sqrt{\omega^2 + \frac{\lambda}{m}A^2} \quad ; \quad \mu = \sqrt{\frac{\lambda}{2m} \left(\frac{A}{\Omega}\right)^2}$$

³P.T. Jochym, J. Łażewski, W. Szuszkiewicz; Scientific Reports 10, 19783 (2020)]

```

from scipy.special import ellipj
from numpy import linspace, exp, cos
from matplotlib.pyplot import plot, legend, figure
from ipywidgets import interact, fixed

x = linspace(0,20,100)
@interact(u=fixed(x), m=(0,1,0.01))
def ejf(u,m):
    figure(figsize=(10,7))
    plot(u, cos(u), ':', label='cos(t)')
    l = 1-exp(1-1/(1-m))
    plot(u, ellipj(u,l)[1], label=f'cn(t,{1:5.3f})')
    legend(loc='lower left');

```

Energy of the crystal

Potential energy of the lattice can be expanded as a function of the atomic displacements $s_{ni\alpha}$, where $\alpha = x, y, z$, (assuming small vibrations and negligible quantum effects):

$$V(s) = V_0 + \frac{1}{2} \sum_{ni\alpha} \sum_{n'i'\alpha'} \left. \frac{\partial^2 V}{\partial s_{ni\alpha} \partial s_{n'i'\alpha'}} \right|_{s=0} s_{ni\alpha} s_{n'i'\alpha'} + O(s^3)$$

The linear term vanishes due to the equilibrium point assumption. The quadratic term determines the behavior of the crystal in the small-vibrations regime investigated previously. The $O(s^3)$ is the subject of our following considerations. If $U(s) = V(s) - V_0$:

$$U(s) = \sum_{p=2}^{\infty} U_p = \sum_{p=2}^{\infty} \frac{1}{p!} \sum_{[n,i,\alpha]} \Phi(n_1 i_1 \alpha_1; \dots; n_p i_p \alpha_p) s_{n_1 i_1 \alpha_1} \cdots s_{n_p i_p \alpha_p}$$

Anharmonic perturbation theory

If U_3, U_4 are small compared to U_2 complete Hamiltonian $H = H_0 + H'$ may be treated as perturbation of the non-interacting Hamiltonian H_0 :

$$H \approx H_0 + U_2 + U_3$$

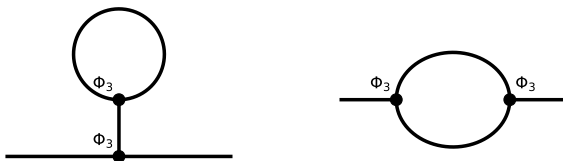
If $\mathbf{G}_q(\omega)$ is a one-phonon Green's function for the full Hamiltonian and $\mathbf{G}_q^0(\omega)$ is a Green's function for the non-interacting Hamiltonian H_0 , then we can write following Dyson equation:

$$[\mathbf{G}_q(\omega)]^{-1} = [\mathbf{G}_q^0(\omega)]^{-1} - \boxtimes_q(\omega)$$

where $\boxtimes_q(\omega_q)$ is an anharmonic self-energy. If this correction is sufficiently small and $\hbar\omega_q \gg |\Sigma_q(\omega_q)|$ the changes in phonon spectrum may be described by frequency shift Δ_q and linewidth Γ_q :

$$\Delta_q = -\frac{1}{\hbar} \text{Re } \Sigma_q(\omega_q) ; \quad \Gamma_q = \frac{1}{\hbar} \text{Im } \Sigma_q(\omega_q)$$

Third order anharmonic self-energy

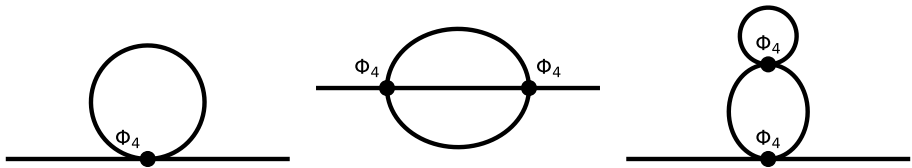


$$\Sigma_q^{TP} = -\frac{1}{\hbar} \sum_{q',j} V(-q; q; \mathbf{0}j) V(\mathbf{0}j; q'; q') \frac{2n+1}{\omega_{\mathbf{0}j}} ; \quad V(q_1; \dots; q_n) = \left(\frac{\hbar}{2}\right)^{n/2} \frac{\Phi(q_1; \dots; q_n)}{\sqrt{\omega_{q_1} \dots \omega_{q_n}}}$$

Phonon linewidth:

$$\Gamma_{qj}^{\text{anh}}(\omega) = \frac{\pi}{2\hbar^2} \sum_{q_1, q_2} \sum_{j_1, j_2} |V_{-qj, q_1 j_1, q_2 j_2}^{(3)}|^2 \times [(n_1 + n_2 + 1)(\delta(\omega - \omega_1 - \omega_2) - \delta(\omega + \omega_1 + \omega_2)) \\ (n_1 - n_2)(\delta(\omega + \omega_1 - \omega_2) - \delta(\omega - \omega_1 + \omega_2))]$$

Fourth order anharmonic self-energy



$$\Sigma_q^{\text{loop}} = - \sum_{q'} V(q; -q; q'; -q') \frac{2n+1}{2}$$

Lattice thermal conductivity

The lattice thermal conductivity tensor $\kappa_{\text{ph}}^{\mu\nu}(T)$

$$\kappa_{\text{ph}}^{\mu\nu}(T) = \frac{1}{VN_q} \sum_{q,j} c_{qj}(T) v_{qj}^{\mu} v_{qj}^{\nu} \tau_{qj}(T),$$

where V is the unit cell volume, $c_{qj} = \hbar\omega_{qj} \partial n_{qj} / \partial T$, and $\tau_{qj}(T)$ is the phonon lifetime. The phonon lifetime is estimated using the Matthiessen's rule as:

$$\tau_{qj}^{-1}(T) = 2(\Gamma_{qj}^{\text{anh}}(T) + \Gamma_{qj}^{\text{iso}}).$$

Bulk thermal conductivity:

$$\kappa_{\text{ph}}^{\mu\mu} = \frac{1}{VN_q} \int_0^{\infty} \sum_{q,j} c_{qj} v_{qj}^{\mu} v_{qj}^{\mu} \tau_{qj} \delta(\omega - \omega_{qj}) d\omega.$$

Anharmonic force constants

- non-linear force-displacement relationship
- large number of independent parameters
- non-linear fitting required (LASSO, NL-LS, genetic algorithms)
- effective implementations exist (ALAMODE, TDEP)
- Expensive post-processing
- Access to multiple experimental parameters:
 - Frequency shifts
 - Phonon lifetimes
 - Line profiles
 - Spectral function
 - Lattice thermal conductivity