Ab initio methods in solid state physics

X. Lattice dynamics - anharmonicity

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Anharmonic lattice dynamics[1][2]

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

[1]A. A. Maradudin, *Theory of Lattice Dynamics in the Harmonic Approximation* (New York :, 1963.)
[2]M. 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 (Dirac 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!

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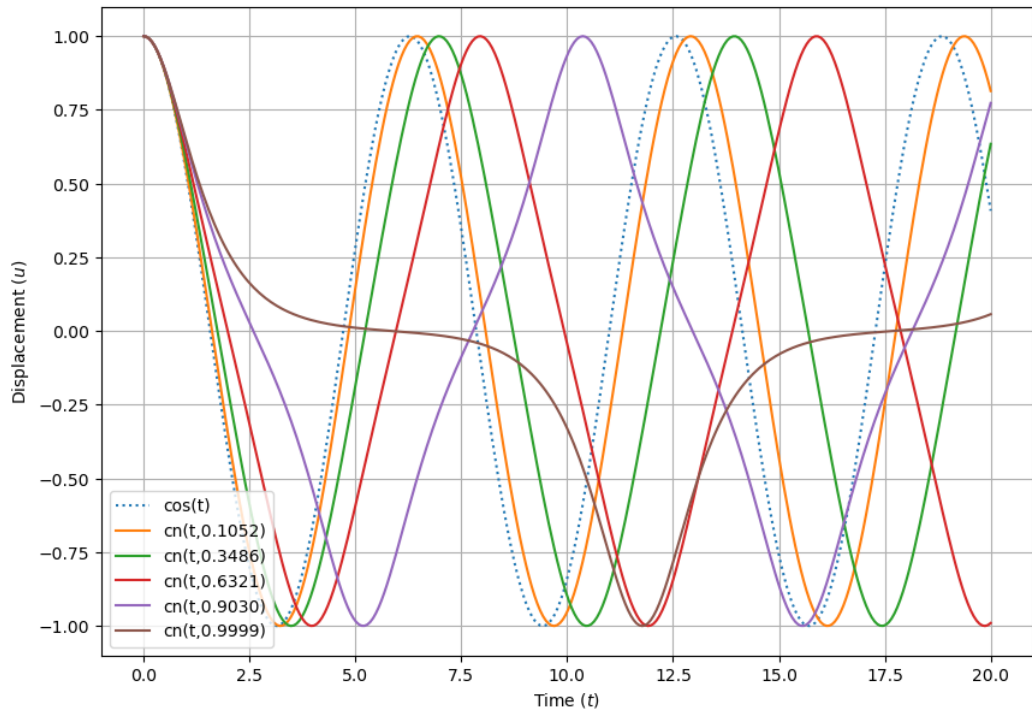
$$V(u) = \frac{m\omega^2}{2}u^2 + \frac{\lambda}{4}u^4,$$

which leads to the equation of motion:

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

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

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

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

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 $U(s) = V(s) - V_0$:

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

Anharmonic perturbation theory

If U_3, U_4 are small compared to U_2, the 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:

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

where $\Sigma_q(\omega)$ 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:

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

Third order anharmonic self-energy
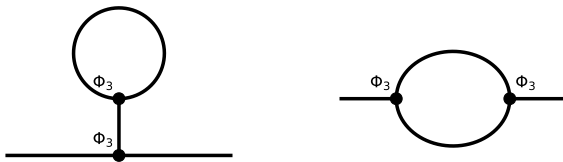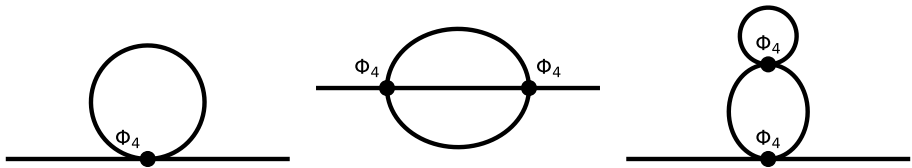

$$\Sigma_q^{TP} = -\frac{1}{\hbar} \sum_{q',j} V(-q;q;\mathbf{0}j)V(\mathbf{0}j;q';q')\frac{2n+1}{\omega_{\mathbf{0}j}} \ ; \quad V(q_1;...;q_n) = \left(\frac{\hbar}{2}\right)^{n/2} \frac{\Phi(q_1;...;q_n)}{\sqrt{\omega_{q_1}\cdots\omega_{q_n}}}$$

Phonon linewidth:

$$\Gamma_{qj}^{\text{anh}}(\omega) = \frac{\pi}{2\hbar^2} \sum_{q_1,q_2} \sum_{j_1,j_2} |V_{-qj,q_1j_1,q_2j_2}^{(3)}|^2 \times [(n_1+n_2+1)(\delta(\omega-\omega_1-\omega_2)-\delta(\omega+\omega_1+\omega_2))$$

$$(n_1-n_2)(\delta(\omega+\omega_1-\omega_2)-\delta(\omega-\omega_1+\omega_2))]$$

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

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:

$$\kappa_{\text{ph}}^{\mu\mu} = \frac{1}{VN_q} \int\limits_{0}^{\infty} \sum_{q,j} c_{qj} v_{qj}^{\mu} v_{qj}^{\mu} \tau_{qj} \delta(\omega - \omega_{qj}) d\omega.$$

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