First-principle phonon calculation

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1 Feynman diagrams for phonons

1.1 Single-phonon Green function

The general definition of the Green function for a real bosonic field is

$$D(\boldsymbol{q}, t-t') = -\mathrm{i}\left\langle \mathcal{T}\, A_{\boldsymbol{q}}(t) A_{\boldsymbol{q}}(t')\right\rangle, \tag{1}$$

where

$$A_{\boldsymbol{q}} = a_{\boldsymbol{q}} + a^{\dagger}_{-\boldsymbol{q}}. \tag{2}$$

In the non-interactive case, we have

$$\begin{aligned} D^{(0)}(\boldsymbol{q}, t-t') &= -\mathrm{i}\left\langle \mathcal{T}(a_{\boldsymbol{q}}\mathrm{e}^{-\mathrm{i}\omega_{\boldsymbol{q}}t} + \mathrm{h.c.})(a_{\boldsymbol{q}}\mathrm{e}^{-\mathrm{i}\omega_{\boldsymbol{q}}t'} + \mathrm{h.c.})\right\rangle \\ &= -\mathrm{i}(\theta(t-t')\mathrm{e}^{-\mathrm{i}\omega_{\boldsymbol{q}}(t-t')} + \theta(t'-t)\mathrm{e}^{\mathrm{i}\omega_{\boldsymbol{q}}(t-t')}). \end{aligned} \tag{3}$$

Then we can evaluate the Fourier transform of it and get

$$D^{(0)}(\boldsymbol{q}, \omega) = \int_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}\omega(t-t')} D^{(0)}(\boldsymbol{q}, t-t') = \frac{1}{\omega - \omega_{\boldsymbol{q}} + \mathrm{i}0^+} - \frac{1}{\omega - \omega_{\boldsymbol{q}} - \mathrm{i}0^+} = \frac{2\omega_{\boldsymbol{q}}}{\omega^2 - \omega_{\boldsymbol{q}}^2 + \mathrm{i}0^+}. \tag{4}$$

This also works for phonons. Note the fact that even when we have zero phonon in the ground state, we still have two terms in the propagator: it comes from the fact that $A_{\boldsymbol{q}}$ always contains both annihilation and creation operators and thus $D^{(0)}$ is always non-zero regardless of the sign of $t-t'$. Also note the minus sign between $1/(\omega \pm \omega_{\boldsymbol{q}})$: it comes from the fact that we are dealing with bosons and not fermions. For phonons, $A_{\boldsymbol{q}}$ is proportional to $X_{\boldsymbol{q}}$; this enables us to link phonon Green function with displacement correlation function.

Just like the case for electrons, we can do self-energy correction to the phonon propagator. Suppose we have already done a Dyson resummation and find

$$D^{-1}(\boldsymbol{q}, \omega) = (D^{(0)}(\boldsymbol{q}, \omega))^{-1} - \Pi(\boldsymbol{q}, \omega). \tag{5}$$

We have

$$D(\boldsymbol{q}, \omega) = \left(\frac{\omega^2 - \omega_{\boldsymbol{q}}^2 - 2\omega_{\boldsymbol{q}}\Pi + \mathrm{i}0^+}{2\omega_{\boldsymbol{q}}}\right)^{-1} = \tag{6}$$

2 The molecular dynamics approach

See [1]. The idea is rather simple: the phonon spectrum just illustrates the vibration modes of atoms, so if we just let atoms move (with an average kinetic energy that agrees with the temperature T in question), then the Fourier transform of the orbitals of the atoms gains high intensity on the dispersion relations. This seems to be the most *ab initio* method I've ever learned about.

A more efficient way is the so-called temperature-dependent effective potential, which is obtained by curve-fitting of the atomic force fields in MD.

References

[1] Xiaohan Zhang et al. "Finite-temperature phonon dispersion and vibrational dynamics of BaTiO 3 from first-principles molecular dynamics". In: *Physical Review B* 105.1 (2022), p. 014304.