Introduction to the Theory of Lattice Vibrations and their Ab Initio Calculation

Lecture 6: Measuring phonons and the problems of the harmonic approximation

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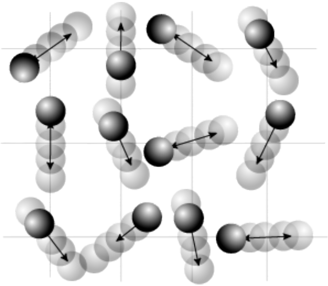

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Outline

1. Experimental techniques to measure phononic excitations
   - Inelastic diffraction experiments
   - IR and Raman techniques
2. Raman and IR spectroscopy selection rules
3. The scattering cross section observed experimentally
   - The scattering cross section in diffraction experiments
   - The scattering cross section in Raman experiments
   - The dielectric function in the infrared
   - Experimental probes in the harmonic approximation
   - Failure of the harmonic approximation in describing the experimental results
4. Other failures of the harmonic approximation
   - Temperature dependence of phonons
   - Stabilization of structure
   - Lattice thermal conductivity
5. Perturbative corrections to the harmonic approximation
   - The interaction self energy and Dyson's equation
   - The anharmonic self-energy in the perturbative limit
   - The electron-phonon self-energy in the perturbative limit
   - The quasiharmonic approximation
6. Exercises

Experimental techniques to measure phonons

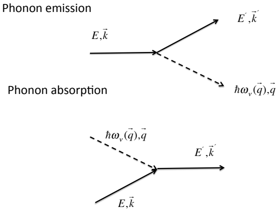
- Spectroscopic techniques valid to obtain phonons at Γ:
    - Infrared spectroscopy
    - Raman spectroscopy
- Diffraction techniques valid to obtain phonons at any $\boldsymbol{q}$ point:
    - Inelastic x-ray diffraction
    - Inelastic neutron diffraction

Inelastic diffraction experiments

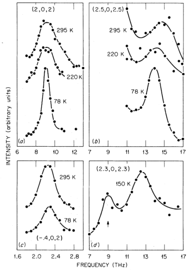
- Inelastic X-ray or neutron scattering experiments provide the the way to measure full phonon dispersions
- The incident beam with energy E and momentum $\mathbf{k}$ can emit or absorb a phonon so that its energy and momentum shift to E' and $\mathbf{k}'$ according to energy and crystal momentum conservation

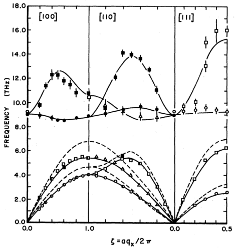
$$\begin{aligned} E' &= E \pm \hbar\omega_\nu(\mathbf{q}) \\ \mathbf{k}' &= \mathbf{k} \pm \mathbf{q} + \mathbf{G}, \end{aligned}$$

- Phonons appear as peaks in the number of counts
- The choice of the measurement momentum $\mathbf{k}'$ determines the $\mathbf{q}$ of the experimentally accessible phonons


Phonon emission

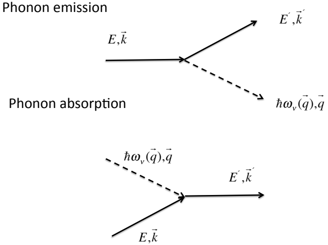
Phonon absorption





Inelastic scattering experiments

- Technically difficult
- It usually requires performing experiments in large facilities like syncrotrons



Phonon emission

$E,\vec{k}$

$E',\vec{k}'$

$\hbar\omega_{\nu}(\vec{q}),\vec{q}$

Phonon absorption

$\hbar\omega_{\nu}(\vec{q}),\vec{q}$

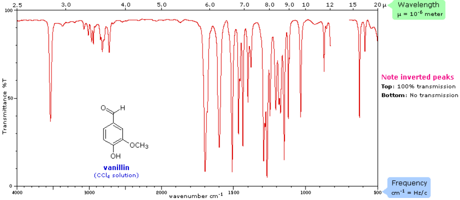
$E',\vec{k}'$

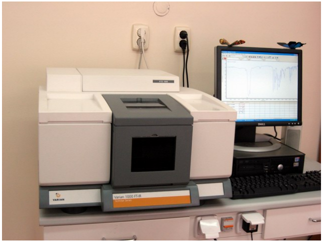
$E,\vec{k}$

Infrared (IR) spectroscopy

Infrared spectroscopy

- The energy of phonons, of order of $\sim$ 10 meV, is in the infrared range
- IR light is passed through the sample and recorded on transmission
- Also phonons can be detected on reflection, as the reflectivity ia also affected by phonons
- IR light is absorbed if the incident light energy matches a phonon frequency at Γ
- The peaks in the absorption represent phonon energies
- Only Γ point phonons can be detected because the wave number of incident light is very small compared to the size of the BZ





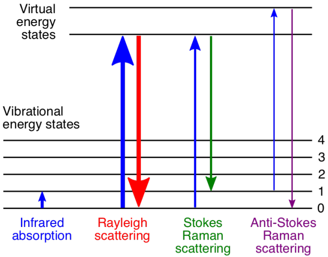
Raman spectroscopy

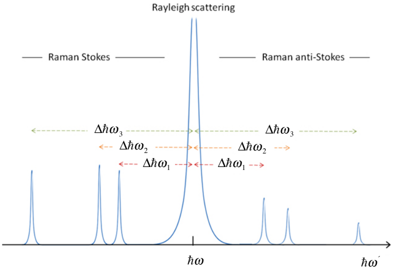
Raman scattering

- Visible light scattered inelastically by a crystal
- Light $(\hbar\omega, \mathbf{k})$ is absorbed by an electron, which emits or absorbs a phonon, and decay inelastically with $(\hbar\omega', \mathbf{k}')$

$$\begin{aligned} \hbar\omega' &= \hbar\omega \pm \hbar\omega_\nu(\mathbf{q}) \\ \mathbf{k}' &= \mathbf{k} \pm \mathbf{q} + \mathbf{G}, \end{aligned}$$

- Stokes scattering when the excited electron decays emitting light with less energy and a phonon
- Anti-Stokes scattering when the excited electron absorbs a phonon and decays into light with larger energy
- $\mathbf{k}$ and $\mathbf{k}'$ so small that $\mathbf{q} \sim 0$ (Γ point)





Raman and IR spectroscopy selection rules

Not all phonon modes at Γ are observable in Raman and IR techniques

$$\langle \Psi_f^{ion} | H_{int} | \Psi_i^{ion} \rangle \neq 0$$

Infrared spectroscopy

- If the incident IR light has an electric field $\mathbf{E}$, the interaction term between the light and the solid is

  $$H_{int} = -\mathbf{E} \cdot \mathbf{d},$$

  where $\mathbf{d}$ is the dipole moment
- Since H_{int} transforms as a vector, only modes that transform as a vector are observable with IR

Raman scattering

- A second-order process (IR first-order)
- The electric dipole in Raman scattering is determined by the polarizability tensor Λ

  $$\mathbf{d} = \Lambda \mathbf{E}$$

  Thus the interaction Hamiltonian is

  $$H_{int} = -\mathbf{E} \Lambda \mathbf{E},$$
- Since H_{int} transforms as a second rank symmetric tensor, only modes that transform as a second rank symmetric tensor are observable

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Gross selection rules

- IR active modes change $\mathbf{d}$
- Raman active modes change Λ

Raman scattering

- A second-order process (IR first-order)
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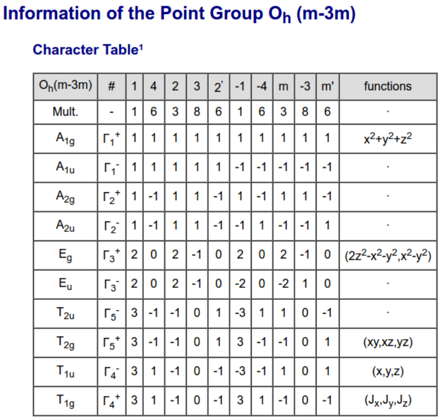
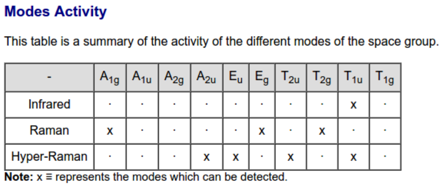
Raman and IR spectroscopy selection rules



Information of the Point Group O_h (m-3m)

Character Table¹

O_h(m-3m)	#	1	4	2	3	2'	-1	-4	m	-3	m'	functions
Mult.	-	1	6	3	8	6	1	6	3	8	6	.
A_{1g}	Γ_1^+	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{1u}	Γ_1^-	1	1	1	1	1	-1	-1	-1	-1	-1	.
A_{2g}	Γ_2^+	1	-1	1	1	-1	1	-1	1	1	-1	.
A_{2u}	Γ_2^-	1	-1	1	1	-1	-1	1	-1	-1	1	.
E_g	Γ_3^+	2	0	2	-1	0	2	0	2	-1	0	$(2z^2-x^2-y^2,x^2-y^2)$
E_u	Γ_3^-	2	0	2	-1	0	-2	0	-2	1	0	.
T_{2u}	Γ_5^-	3	-1	-1	0	1	-3	1	1	0	-1	.
T_{2g}	Γ_5^+	3	-1	-1	0	1	3	-1	-1	0	1	(xy,xz,yz)
T_{1u}	Γ_4^-	3	1	-1	0	-1	-3	-1	1	0	1	(x,y,z)
T_{1g}	Γ_4^+	3	1	-1	0	-1	3	1	-1	0	-1	(J_x,J_y,J_z)



Modes Activity

This table is a summary of the activity of the different modes of the space group.

-	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_u	E_g	T_{2u}	T_{2g}	T_{1u}	T_{1g}
Infrared	.	.	.	.	.	.	.	.	x	.
Raman	x	.	.	.	.	x	.	x	.	.
Hyper-Raman	.	.	.	x	x	.	x	.	x	.

Note: x ≡ represents the modes which can be detected.

Gross selection rules

- IR active modes change **d**
- Raman active modes change Λ

Important rule of thumb

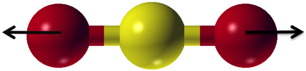
If inversion symmetry is present IR active modes are not Raman active, and Raman active modes are not IR active

Raman and IR spectroscopy selection rules

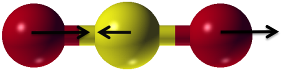
An example:

Vibrational modes in CO_2 molecule

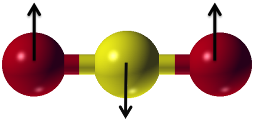
Symmetric stretch



Asymmetric stretch



Bending



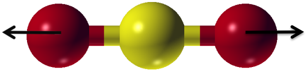
Raman and IR spectroscopy selection rules

An example:

Vibrational modes in CO_2 molecule

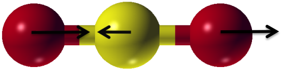
Symmetric stretch

no IR active
Raman active



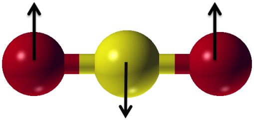
Asymmetric stretch

IR active
no Raman active



Bending

IR active
no Raman active



Cross section in inelastic diffraction experiments

- The cross section in an inelastic diffraction experiment is proportional to the dynamical structure factor $S(\boldsymbol{q},\omega)$, where the momentum transfer to the system is $\hbar\omega$ and the momentum transfer $\hbar\boldsymbol{q}$
- The dynamical structure factor is given by (Cowley, "Anharmonic Crystals", 1968; Ashcroft & Mermin)

$$S(\boldsymbol{q},\omega) = \sum_{ab} e^{-i\boldsymbol{q}\cdot(\boldsymbol{R}_{0a}-\boldsymbol{R}_{0a})} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle e^{i\boldsymbol{q}\boldsymbol{u}_a(0)} e^{i\boldsymbol{q}\boldsymbol{u}_b(t)} \rangle_{\rho_H}$$

- At lowest order, keeping the first order in the exponential, it can be shown that

$$S(\boldsymbol{q},\omega) \propto \sigma(\boldsymbol{q},\omega) = -\frac{\omega}{\pi} \sum_{ab} \mathrm{Im}\left[G_{ab}(\boldsymbol{q},\omega+i\eta)\right]$$

where $G_{ab}(\boldsymbol{q},\omega+i\eta)$ is the analytic continuation ($i\omega_n \to \omega + i\eta$) of the Fourier transform of the displacement correlation function $G_{ab}(i\omega_n)$

Cross section in Raman experiments

- The cross section in a Raman experiment is very similar to the inelastic diffraction experiment
- Again the cross section is proportional to (Elliot et al. RMP 1974) the imaginary part of the displacement correlation function

  $$S(0,\omega) \propto \sum_{ab} C_a C_b \mathrm{Im}\left[G_{ab}(0,\omega+i\eta)\right]$$

  where C_a is the effective Raman polarizability
- Raman scatterin occurs at wave numbers so small that are considere at Γ

Phonon contribution to the dielectric function in the infrared

- The polarization of a material when an electric field (electronmagnetic wave) is applied is

  $$P^{\alpha} = \langle \sum_{b} Z_b^{*\alpha} u_b \rangle_{\rho_H}$$

  The response function (polarizability) is calculated consequently as

  $$\chi^{\alpha\beta}(\omega) = -\frac{N}{\Omega} e^2 \sum_{ab} \frac{Z_a^{*\alpha} Z_b^{*\beta}}{\sqrt{M_a M_b}} G_{ab}(0, \omega + i\eta)$$

  where we have the Fourier transform of the displacement correlation function at Γ
- The dielectric function is then

  $$\epsilon^{\alpha\beta}(\omega) = \epsilon_{\infty}^{\alpha\beta} + 4\pi\chi^{\alpha\beta}(\omega)$$

  where $\boldsymbol{\epsilon}_{\infty}$ is the electronic contribution, or, in other words, the high-frequency limit of the phonon contribution to the dielectric function
- The optical properties are determined in the infrared again by the correlation function

Phonon contribution to the dielectric function in the infrared

- The dielectric function allows to calculate optical properties of solids
- The refraction index $n_\alpha(\omega)$ and the extinction coefficient $\kappa_\alpha(\omega)$ along direction α are easily obtained from

$$\begin{aligned}\mathrm{Re}\left[\epsilon^{\alpha\alpha}(\omega)\right] &= n_\alpha^2(\omega) - \kappa_\alpha^2(\omega) \\ \mathrm{Im}\left[\epsilon^{\alpha\alpha}(\omega)\right] &= 2n_\alpha(\omega)\kappa_\alpha(\omega)\end{aligned}$$

- The reflectivity along direction α is then

$$R_\alpha(\omega) = \frac{(n_\alpha(\omega) - 1)^2 + \kappa_\alpha^2(\omega)}{(n_\alpha(\omega) + 1)^2 + \kappa_\alpha^2(\omega)}$$

The inelastic diffraction and Raman cross sections in the harmonic approximation

- Both the inelastic diffraction and Raman cross sections are proportional to

$$\sigma(\boldsymbol{q},\omega) = -\frac{\omega}{\pi}\sum_{ab}\mathrm{Im}\left[G_{ab}(\boldsymbol{q},\omega+i\eta)\right]$$

- In the harmonic approximation

$$\begin{aligned}
\sigma(\boldsymbol{q},\omega) &= -\frac{\omega}{\pi}\sum_{ab}\sum_{\mu}\mathrm{Im}\left[\frac{e^a_\mu(-\boldsymbol{q})e^b_\mu(\boldsymbol{q})}{(\omega+i\eta)^2-\omega^2_\mu(\boldsymbol{q})}\right] \\
&= -\omega\sum_{ab}\sum_{\mu}\mathrm{Im}\left[\frac{e^a_\mu(-\boldsymbol{q})e^b_\mu(\boldsymbol{q})}{2\omega_\mu(\boldsymbol{q})}\left(\frac{1}{\omega-\omega_\mu(\boldsymbol{q})+i\eta}-\frac{1}{\omega+\omega_\mu(\boldsymbol{q})+i\eta}\right)\right] \\
&= \omega\sum_{ab}\sum_{\mu}\frac{1}{2\omega_\mu(\boldsymbol{q})}e^a_\mu(-\boldsymbol{q})e^b_\mu(\boldsymbol{q})\left[\delta(\omega-\omega_\mu(\boldsymbol{q}))-\delta(\omega+\omega_\mu(\boldsymbol{q}))\right]
\end{aligned}$$

- The cross section is a collection of peaks centered at the harmonic phonon frequencies

The infrared dielectric function in the harmonic approximation

- The calculation can also be performed for the dielectric function analytically

$$\epsilon^{\alpha\beta}(\omega) = \epsilon_{\infty}^{\alpha\beta} + 4\pi\chi^{\alpha\beta}(\omega)$$

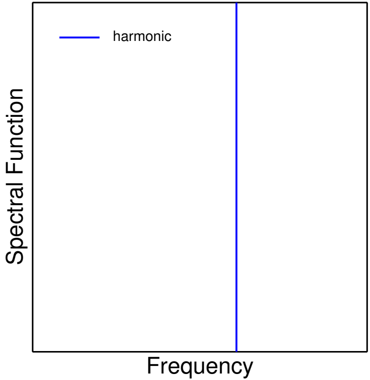
- The response function is anlytical

$$\begin{aligned}
\chi^{\alpha\beta}(\omega) &= -\frac{N}{\Omega}e^2\sum_{ab}\frac{Z_a^{*\alpha}Z_b^{*\beta}}{\sqrt{M_aM_b}}G_{ab}(0,\omega+i\eta) \\
&= -\frac{N}{\Omega}e^2\sum_{ab}\sum_{\mu}\frac{Z_a^{*\alpha}e_\mu^a(0)Z_b^{*\beta}e_\mu^b(0)}{\sqrt{M_aM_b}} \\
&\times \frac{1}{2\omega_\mu(0)}\left(\frac{1}{\omega-\omega_\mu(0)+i\eta}-\frac{1}{\omega+\omega_\mu(0)+i\eta}\right)
\end{aligned}$$

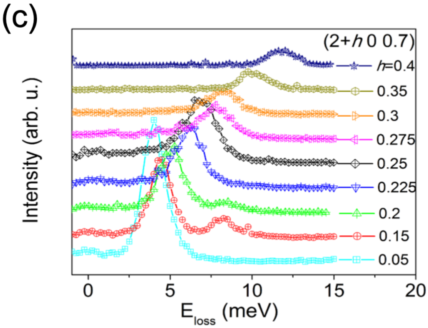
- This also implies that the imaginary part of the dielectric function is a collection of Delta peaks in the harmonic approximation

Experimental diffraction cross sections

The harmonic approximation fails describing the experimental cross sections, they are not Delta peaks



Harmonic theory



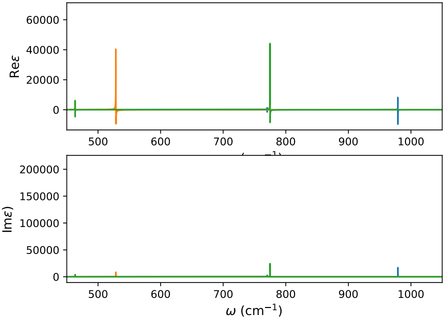
Experiment

Diego et al., Nat Commun. 12, 598 (2021)

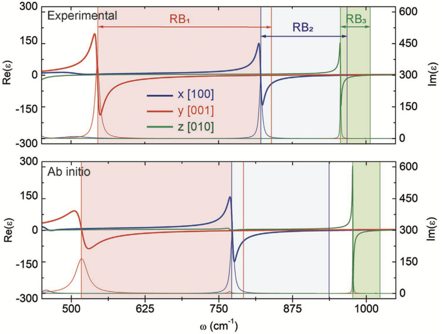
Experimental dielectric function in the infrared

The harmonic approximation fails describing the experimental cross sections, they are not Delta peaks

MoO$_3$:



Harmonic theory



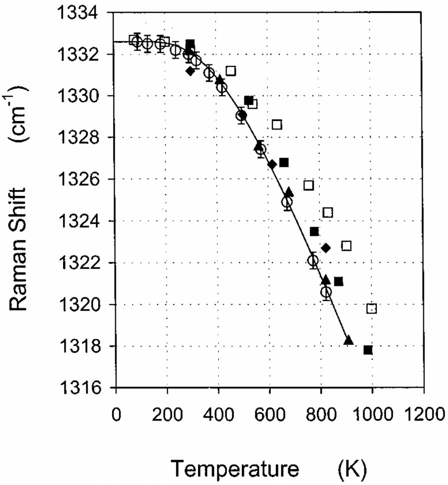
Experiment

Alvarez-Perez et al., Adv. Mater. 32, 1908176 (2020)

Why the harmonic approximation fails in the description of experimental signatures of phonons?

Temperature dependence of phonon frequencies

- Phonon frequencies in the harmonic approximation are obtained diagonalizing the dynamical matrix $\phi^{(2)}_{ab}/\sqrt{M_a M_b}$
- As $V(\boldsymbol{R})$ does not depend on temperature, force constants do not depend on temperature and harmonic phonons are temperature independent
- Experimentally phonons do depend on temperature
- A big failure of the harmonic theory



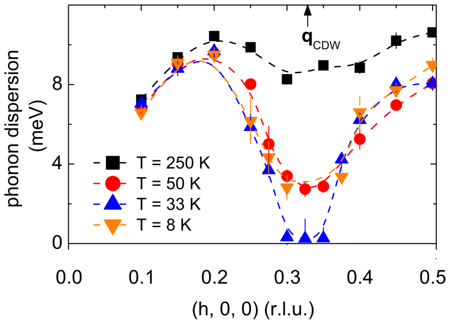
Diamond optical mode at Γ

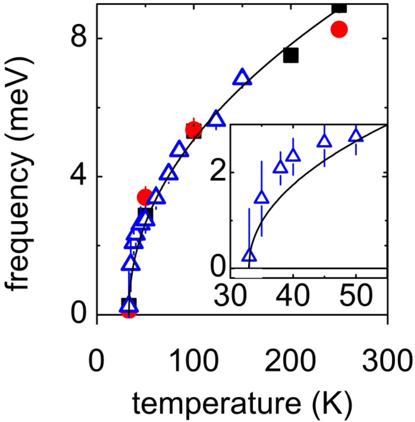
Liu et al., PRB 61, 3391 (2000)

Temperature dependence of phonon frequencies

- The temperature dependence is particularly critical close to a 2nd-order displacive phase transition (CDW, ferroelectric transition)

NbSe$_2$

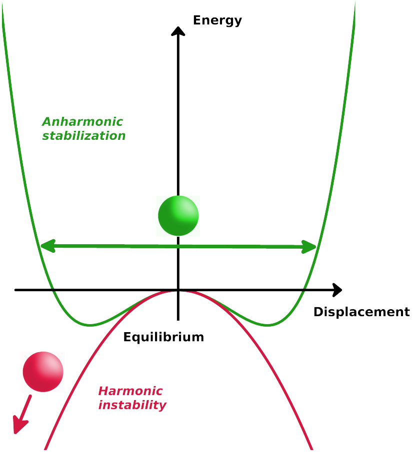




Weber et al., PRL 107, 107403 (2011)

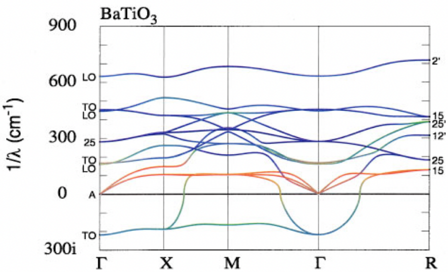
Quantum or thermal stabilization of structures

- There are structures that have imaginary harmonic phonon frequencies, negative ω_μ^2 eigenvalues of $\overset{(2)}{\phi}_{ab}/\sqrt{M_a M_b}$
- This means that the $\boldsymbol{R}_0$ structure is not at a minimum of $V(\boldsymbol{R})$, but a local maximum (at least) along $\boldsymbol{e}_\mu$
- The structure is unstable in this cases within the harmonic approximation, it is not the minimum energy structure of $V(\boldsymbol{R})$
- But the structure may be stable and observed experimentally thanks to quantum or thermal fluctuations
- High-temperature symmetric structures that undergo CDW of ferroelectric transitions are an exmaple



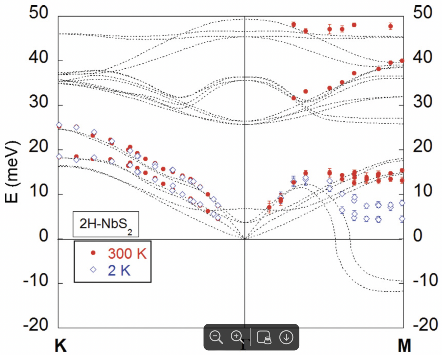
Quantum or thermal stabilization of structures

$BaTiO_3$ paraelectric phase



Ghosez et al., PRB 60, 836 (1999)

NbS_2 2H phase



Leroux et al., PRB 86, 155125 (2012)

If a structure is observed experimentally at zero Kelvin it must be the lowest energy structure.

How is it possible that this may not be the structure which is the minimum of $V(R)$?

If a structure is observed experimentally at zero Kelvin it must be the lowest energy structure.

How is it possible that this may not be the structure which is the minimum of $V(R)$?

$$E(R) \neq V(R)$$

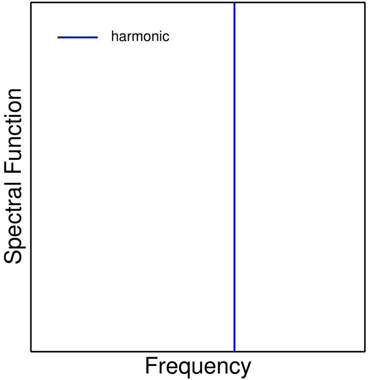
Infinite lattice thermal conductivity of the harmonic crystal

- Phonons carry heat in solids
- In the single mode relaxation time approximation, the lattice thermal conductivity is

$$\kappa = \frac{1}{\Omega k_B T^2} \sum_{\mu \boldsymbol{q}} v_\mu^2(\boldsymbol{q}) \omega_\mu^2(\boldsymbol{q}) \tau_\mu(\boldsymbol{q}) n_B(\omega_\mu(\boldsymbol{q}))[n_B(\omega_\mu(\boldsymbol{q})) + 1]$$

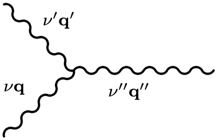
  where $v_\mu(\boldsymbol{q})$ is the phonon velocity and $\tau_\mu(\boldsymbol{q})$ is the lifetime of a phonon

- As phonons are quasiparticle that do not decay in the harmonic approximation, their lifetime is infinite, and the lattice thermal conductivity is infinite
- Obviously all materials have a finite thermal conductivity
- This is a big breakdown of the harmonic approximation

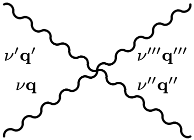


Anharmonicity

- Phonons in reality are not well-defined quasiparticles, they are not eigenvalues of the (full) ionic Hamiltonian
- The full ionic Hamiltonian, with $V(\boldsymbol{R}) = V_2(\boldsymbol{R}) + V_3(\boldsymbol{R}) + V_4(\boldsymbol{R}) + \cdots$, cannot be diagonalized exactly and does not define infinitely lived quasiparticles



3rd-order vertex



4th-order vertex

- Orders in the Taylor expansion beyond the second-order impose phonon-phonon interaction. This is what we call anharmonicity
- Since

$$V_n(\boldsymbol{R}) = \frac{1}{n!} \sum_{a_1 \cdots a_n} \overset{(n)}{\phi}_{a_1 \cdots a_n} (R_{a_1} - R_{a_1 0}) \cdots (R_{a_n} - R_{a_n 0})$$

a term of order n imposes the interaction between n phonons and the $\overset{(n)}{\phi}_{a_1 \cdots a_n}$ force-constants will appear in each vertex

Electron-phonon interaction

- The terms neglected in the BO approximation,

$$\Delta H_{\alpha\alpha'} = \sum_I \frac{1}{M_I} \langle \Psi^e_{\alpha'}(\boldsymbol{R}) | \boldsymbol{P}_I | \Psi^e_{\alpha}(\boldsymbol{R}) \rangle \boldsymbol{P}_I + \sum_I \langle \Psi^e_{\alpha'}(\boldsymbol{R}) | \frac{\boldsymbol{P}_I^2}{2M_I} | \Psi^e_{\alpha}(\boldsymbol{R}) \rangle,$$

  imply derivatives of the electronic state with respect to the ionic positions

- At lowest order, this contribution can be written as a Frölich Hamiltonian:

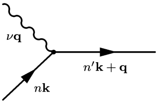
$$H_{e-ph} = \frac{1}{\sqrt{N}} \sum_{\mu \boldsymbol{q}} \sum_{nm\boldsymbol{k}} g^{\mu}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} \hat{c}^{\dagger}_{m\mathbf{k}+\mathbf{q}} \hat{c}_{n\mathbf{k}} \left(\hat{b}_{\mu\mathbf{q}} + \hat{b}^{\dagger}_{\mu-\mathbf{q}} \right)$$

  where $\hat{c}^{\dagger}_{n\mathbf{k}}$ and $\hat{c}_{n\mathbf{k}}$ are the electron creation and annihilation operators

- The electron-phonon matrix elements are

$$g^{\mu}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}} = \sum_a \frac{\epsilon^a_{\mu}(\mathbf{q})}{\sqrt{2M_a \omega_{\mu}(\mathbf{q})}} \langle \psi_{m\mathbf{k}+\mathbf{q}} | \left[\frac{\partial V_{KS}}{\partial u_a(\boldsymbol{q})} \right]_{\boldsymbol{u}=0} | \psi_{n\mathbf{k}} \rangle$$

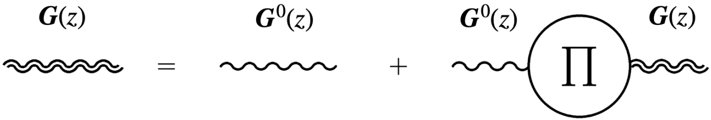
- Each interacting vertex involves one phonon and two electrons
- Each vertex will include the factor $g^{\mu}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}}$



electron-phonon interaction

Self-energy and the Dyson equation

- The effect of anharmonicity and the electron-phonon interaction can be included within many-body perturbation theory in the displacement correlation function or Green's function
$$G_{ab}(z) = -\sqrt{M_a M_b}\langle T_z u_a(z) u_b(0)\rangle_{\rho_H}$$
where now H includes anharmonic and/or electron-phonon interactions
- All the interactions affecting the phonons define the phonon self energy $\boldsymbol{\Pi}$
- The interacting Green function can be calculated through Dyson's equation
$$\boldsymbol{G}(z) = \boldsymbol{G}^0(z) + \boldsymbol{G}^0(z)\boldsymbol{\Pi}(z)\boldsymbol{G}(z)$$
- The non-interacting Green's function is calculated with the harmonic H_0
$$\begin{aligned} G^0_{ab}(z) &= -\sqrt{M_a M_b}\langle T_z u_a(z) u_b(0)\rangle_{\rho_{H_0}} \\ &= -\sum_{\mu} e^a_\mu e^b_\mu \frac{\hbar}{2\omega_\mu}\left[(n_B(\omega_\mu)+1)e^{-z\omega_\mu} + n_B(\omega_\mu)e^{z\omega_\mu}\right] \end{aligned}$$



The interacting spectral function

- The spectral function can be written as

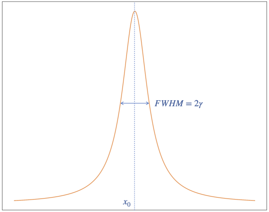
$$\sigma(\boldsymbol{q},\omega) = \frac{1}{2\pi}\sum_{\mu}\left[\frac{-\mathrm{Im}[\mathcal{Z}_{\mu}(\boldsymbol{q},\omega)]}{(\omega-\mathrm{Re}[\mathcal{Z}_{\mu}(\boldsymbol{q},\omega)])^2+\mathrm{Im}[\mathcal{Z}_{\mu}(\boldsymbol{q},\omega)]^2}\right.$$
$$+\left.\frac{\mathrm{Im}[\mathcal{Z}_{\mu}(\boldsymbol{q},\omega)]}{(\omega+\mathrm{Re}[\mathcal{Z}_{\mu}(\boldsymbol{q},\omega)])^2+\mathrm{Im}[\mathcal{Z}_{\mu}(\boldsymbol{q},\omega)]^2}\right]$$

where

$$\mathcal{Z}_{\mu}(\boldsymbol{q},\omega)=\sqrt{\omega_{\mu}^{2}(\boldsymbol{q})+\Pi_{\mu}(\boldsymbol{q},\omega+i\eta)}$$

- This function would be a Lorentzian if Π_{μ} did not depend on ω

$$f(x)=\frac{1}{\pi}\frac{\gamma}{(x-x_0)^2+\gamma^2}$$



The spectral function in the perturbative limit

- In this limit we can assume that the spectral function decays very fast close to the peak and we can assume that the self-energy is frequency independent

$$\Pi_\mu(\boldsymbol{q}, \omega + i\eta) \sim \Pi_\mu(\boldsymbol{q}, \omega_\mu(\boldsymbol{q}) + i\eta)$$

- The spectral function becomes a sum of Lorentzian functions with

$$\begin{aligned} \mathrm{Re}[\mathcal{Z}_\mu(\boldsymbol{q}, \omega_\mu(\boldsymbol{q}) + i\eta)] &\sim \omega_\mu(\boldsymbol{q}) + \frac{\mathrm{Re}[\Pi_\mu(\boldsymbol{q}, \omega_\mu(\boldsymbol{q}) + i\eta)]}{2\omega_\mu(\boldsymbol{q})} \\ \mathrm{Im}[\mathcal{Z}_\mu(\boldsymbol{q}, \omega_\mu(\boldsymbol{q}) + i\eta)] &\sim \frac{\mathrm{Im}[\Pi_\mu(\boldsymbol{q}, \omega_\mu(\boldsymbol{q}) + i\eta)]}{2\omega_\mu(\boldsymbol{q})} \end{aligned}$$

  which has peaks at $\mathrm{Re}[\mathcal{Z}_\mu(\boldsymbol{q}, \omega_\mu(\boldsymbol{q}) + i\eta)]$ and the half-width at half maximum (HWHM) is $-\mathrm{Im}[\mathcal{Z}_\mu(\boldsymbol{q}, \omega_\mu(\boldsymbol{q}) + i\eta)]$ for positive frequencies

The anharmonic self-energy in the perturbative limit

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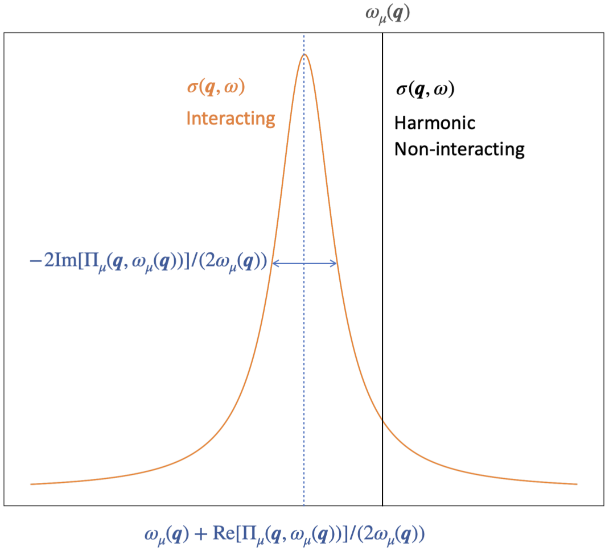
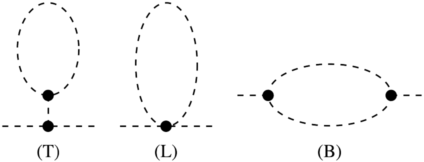
The spectral function in the perturbative limit



The anharmonic self-energy in the perturbative limit

- At the perturbative lowest order there are 3 diagrams that contribute to the phonon self-energy: tadpole (T), loop (L), and bubble (B)
- The self-energy diagrams need to be constructed with Feyman diagram rules and have to be calculated with Matsubara summation techniques (see Mahan book)



- These are the self-energy terms

$$
\begin{aligned}
\overset{(T)}{\Pi}_{\mu}(\boldsymbol{q}) &= \frac{2-\omega_\mu(\boldsymbol{q})}{N}\sum_{\nu\nu'\boldsymbol{q}'}\overset{(3)}{\phi}_{\nu\nu\nu'}(-\boldsymbol{q}',\boldsymbol{q},0)\overset{(3)}{\phi}_{\nu'\mu\mu}(0,\boldsymbol{q},-\boldsymbol{q})\frac{2n_B(\omega_\nu(\boldsymbol{q}'))+1}{\omega_{\nu'}(0)} \\
\overset{(L)}{\Pi}_{\mu}(\boldsymbol{q}) &= \frac{\omega_\mu(\boldsymbol{q})}{N}\sum_{\nu\boldsymbol{q}'}\overset{(4)}{\phi}_{\mu\mu\nu\nu}(\boldsymbol{q},-\boldsymbol{q},\boldsymbol{q}',-\boldsymbol{q}')(2n_B(\omega_\nu(\boldsymbol{q}'))+1) \\
\overset{(B)}{\Pi}_{\mu}(\boldsymbol{q},\omega+i\eta) &= \frac{-\omega_\mu(\boldsymbol{q})}{N}\sum_{\nu\nu'\boldsymbol{q}'}|\overset{(3)}{\phi}_{\mu\nu\nu'}(\boldsymbol{q},\boldsymbol{q}',-\boldsymbol{q}-\boldsymbol{q}')|^2 F(\omega+i\eta,\omega_\nu(\boldsymbol{q}'),\omega_{\nu'}(-\boldsymbol{q}-\boldsymbol{q}'))
\end{aligned}
$$

The anharmonic self-energy in the perturbative limit

- In the equation above

$$\begin{aligned}
\overset{(n)}{\phi}_{\mu_1\cdots\mu_n}(\boldsymbol{q}_1,\cdots,\boldsymbol{q}_n) &= \sum_{a_1\cdots a_n} \frac{\overset{(n)}{\phi}_{a_1\cdots a_n}(\boldsymbol{q},\cdots,\boldsymbol{q}_n)}{\sqrt{M_{a_1}\cdots M_{a_n}}} \frac{e^{a_1}_{\mu_1}(-\boldsymbol{q}_1)\cdots e^{a_n}_{\mu_n}(-\boldsymbol{q}_n)}{\sqrt{2^n\omega_{\mu_1}(\boldsymbol{q}_1)\cdots\omega_{\mu_n}(\boldsymbol{q}_n)}} \\
F(\omega+i\eta,\omega_1,\omega_2) &= \frac{2(\omega_1+\omega_2)(1+n_B(\omega_1)+n_B(\omega_2))}{(\omega_1+\omega_2)^2-(\omega+i\eta)^2} \\
&+ \frac{2(\omega_1-\omega_2)(n_B(\omega_2)-n_B(\omega_1))}{(\omega_1-\omega_2)^2-(\omega+i\eta)^2}
\end{aligned}$$

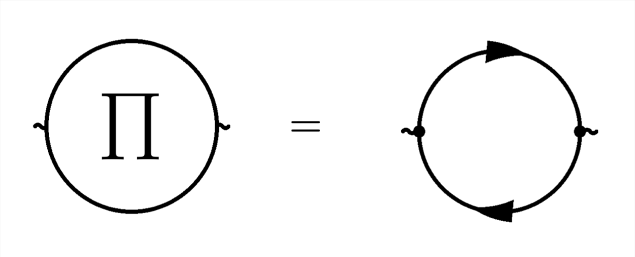
Maradudin and Fein, Phys. Rev. 128, 2589 (1962)

Rousseau and Bergara, PRB 82, 104504 (2010)

The electron-phonon self-energy in the perturbative limit

- At lowest order in the electron-phonon interaction the self-energy is given by the Migdal diagram
- In the diagram we have internal electron lines
- The self-energy is given by

$$\overset{(e-ph)}{\Pi}_{\mu}(\boldsymbol{q}, \omega + i\eta) = \frac{2\omega_{\mu}(\boldsymbol{q})}{N} \sum_{nm\boldsymbol{k}} |g^{\mu}_{m\mathbf{k}+\mathbf{q},n\mathbf{k}}|^2 \frac{f_{n\boldsymbol{k}} - f_{m\boldsymbol{k}+\boldsymbol{q}}}{E_{n\boldsymbol{k}} - E_{m\boldsymbol{k}+\boldsymbol{q}} + \omega + i\eta}$$



Allen and Mitrovic, "Theory of Superconducting Tc"

Grimvall, "The Electron-phonon Interaction in Metals"

Features of perturbation theory

- Phonons acquire a finite lifetime due to the interaction with electrons and other phonons (anharmonicity)
- Experimental cross sections and optical measurements in the infrared can be explained thanks to the interactions
- The lattice thermal conductivity becomes finite
- Phonon linewidths and frequencies are temperature dependent due to anharmonic effects, not the electron-phonon interaction
- The tadpole anharmonic diagram gives thermal expansion and the temperature dependence of the internal degrees of freedom in the Wyckoff positions

The quasiharmonic approximation

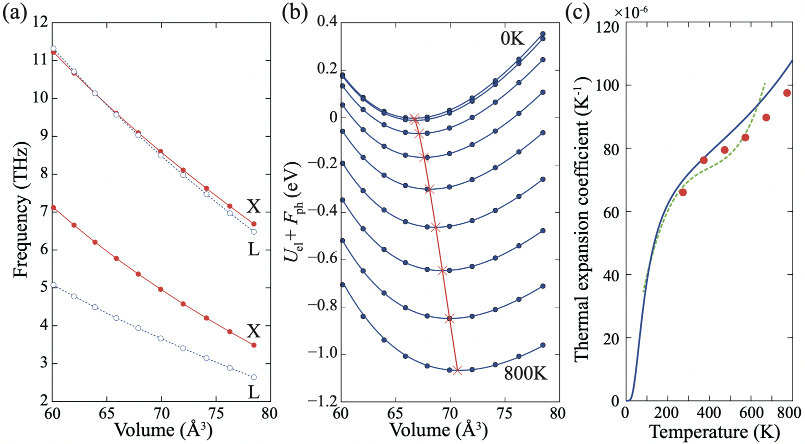
- The quasiharmonic approximation can give an easy, but aproximate, way to at least estimate thermal expansion in the crystal and part of the temperature dependence of phonon frequencies
- Let's assume the free parameters in a crystal are the lattice degrees of freedom $\boldsymbol{A} = \{a, b, c, \alpha, \beta, \gamma\}$ and some free parameters in the Wyckoff positions $\boldsymbol{W} = \{w_1, w_2, \cdots\}$
- In the quasiharmonic approximation the harmonic free energy is calculated as a function of these free parameters

$$F(T, \boldsymbol{A}, \boldsymbol{W}) = \sum_{\mu} \left[\frac{1}{2} \hbar \omega_{\mu}(\boldsymbol{A}, \boldsymbol{W}) - \frac{1}{\beta} \ln(1 + n_B(\omega_{\mu}(\boldsymbol{A}, \boldsymbol{W}))) \right]$$

- By minimizing the free energy at a given temperature T in the parameter space defined by $\boldsymbol{A}$ and $\boldsymbol{W}$, the evolution with temperature of the free parameters in the structure can be approximated
- This is only practically useful if the free parameters are just a few due to symmetry

The quasiharmonic approximation

FCC Al: Only *a* the free degree of freedom in the structure



Togo et al., Scripta Materialia 108, 1 (2015)

Exercises

1. Show that in the harmonic approximation

$$\sigma(\boldsymbol{q},\omega) = \omega \sum_{ab} \sum_{\mu} \frac{1}{2\omega_\mu(\boldsymbol{q})} e^a_\mu(-\boldsymbol{q}) e^b_\mu(\boldsymbol{q}) \left[\delta(\omega - \omega_\mu(\boldsymbol{q})) - \delta(\omega + \omega_\mu(\boldsymbol{q}))\right]$$

2. assuming that in the spectral function $\sigma(\boldsymbol{q},\omega)$ only diagonal terms contribute ($a = b$), calculate the integral

$$\int_{-\infty}^{\infty} d\omega \sigma(\boldsymbol{q},\omega)$$