Advanced Topics in Condensed Matter

Lecture 6: Phonons – Anharmonicity Effects

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What to remember (from last week)

- Elastic scattering is sensitive to the time-averaged structure
- Inelastic scattering is sensitive to the dynamics

$$G(\vec{r},t) = \frac{1}{N} \left\{ \sum_{n,m=1}^{N} \delta\left(r - \left(\left(\vec{r}_{n}(t) - \vec{r}_{m}(0)\right)\right)\right) \right\}$$
$$S_{coh}(\vec{q},\omega) = \frac{1}{2\pi\hbar} \int G(\vec{r},t) e^{-i\vec{q}\vec{r}} e^{i\omega t} d\vec{r} dt$$

 Inelastic neutron scattering is the best tool to measure phonon dispersion over entire range of ω and k

- Raman scattering involves optical phonons (near k=0)
- Brillouin scattering involves acoustic phonons (near k=0)



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Effects related to anharmonicity

V (r) = a
$$(r-r_e)^2$$
 – b $(r-r_e)^3$ + - ...



Effects related to anharmonicity

V (r) = a
$$(r-r_e)^2 - b (r-r_e)^3 + - ...$$

- the blue color of water
- thermal expansion $\boldsymbol{\alpha}$ of the lattice
- elasticity parameters $C_{(...)}$ or B and G are T-dependent
- heat capacity is not strictly constant at high *T*; deviation from Dulong-Petit rule $c = 3Nk_{\rm B}$ since equipartition theorem demands Hamiltonian ~ p^2 and ~ x^2
- interaction of phonons with each other (phonon collisions)
- finite lifetime of phonons

wave solutions with linear superposition not stable with nonlinear terms $\mathcal{O}(u^2)$, *i.e.* $\partial_t \partial_t u = C \partial_x \partial_x u + \mathcal{O}(u^2)$

- heat conduction by phonons
- Grüneisen parameter connects α with c(T) etc



First:

A nice example of the effect of anharmonicity



The color of water

... note that it is not elastic scattering (as for blue sky)



WHY IS THE EARTH CALLED THE BLUE PLANET?



www.lsbu.ac.uk/water

<u>Water</u>





Vater

3 fundamental vibrational excitations

Harmoni Energy Internuclear Separation (r)

Selection rules for the harmonic oscillator $\Delta v = +-1$

What happens for the anharmonic oscillator?

Selection rules for the anharmonic oscillator $\Delta v = +-1, +-2, \dots \parallel \parallel$

This allows for overtones and combination bands, i.e. higher transition energies !!!



 v_1 =3657 cm⁻¹ (2.734 µm)

 $v_2 = 1595 \text{ cm}^{-1}$ (6.269 µm)

 $v_3 = 3756 \text{ cm}^{-1} (2.662 \text{ }\mu\text{m})$

Some notes on the (an)harmonic oscillator

Anharmonicity

→ energy
$$E_v = (v + 1/2) \hbar \omega_e - (v + 1/2)^2 \hbar \omega_e x_e$$
 + higher terms
→ with anharmonicity parameter x_e (usually << 1)
→ in lowest correction we find $\Delta v = +-1, +-2$
→ if higher orders are considered, intensity scales approximately as
→ 1 : x_e : x_e^2 : x_e^3 ...
Anharmonicity changes what we are used to
→ selection rules ... modified ... higher harmonics, e.g. (3* $\hbar \omega_3$)

→ eigenmodes ... coupled ... combination bands, e.g. ($\hbar\omega_1 + \hbar\omega_3$)

Specific example for H2O

- \rightarrow 698 nm absorption from ($\hbar\omega_1$ + 3* $\hbar\omega_3$), but many other combinations contribute
- → this takes vibrational excitations into the visible !!!

Liquid water vs gas phase H2O

- \rightarrow broadening of lines
- \rightarrow librations in addition to vibrations

www.lsbu.ac.uk/water https://en.wikipedia.org/wiki/Color_of_water

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Some notes on the (an)harmonic oscillator

Anharmonicity changes what we are used to

- \rightarrow selection rules ... modified ... higher harmonics,
- \rightarrow eigenmodes ... coupled ... combination bands,

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www.lsbu.ac.uk/water Hertel / Schulz // Tennyson https://en.wikipedia.org/wiki/Color_of_water



e.g. (3* ħω₃) e.g. $(\hbar\omega_1 + \hbar\omega_3)$ $W(v_1, v_2, v_3) / \text{cm}^{-1}$ (111)(210)(031)8000 (050) (002)(200)130 (101)(021)120)(040)6000 (110) (011) (030)(001)4000 020 (010)2000 (000)

Some notes on the (an)harmonic oscillator

Important test via isotope effects in H2O vs D2O

- $\begin{array}{c|c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$
- \rightarrow note that for D2O the vibrational frequencies are *lower* (by ~ $\sqrt{2}$, but not quite; rather 1.36)
- ightarrow thus the effect on the absorption in the visible is *weaker*
- \rightarrow thus D2O is "less blue" than H2O (supporting the notion of vibrations being responsible)
- → looking at the λ^{10} decrease in the spectrum, we have $(1.36)^{10} \sim 20$ x less absorption in the visible

NS -	$ u_1/{ m cm}^{-1}$	$ u_2/\mathrm{cm}^{-1}$	$ u_3/\mathrm{cm}^{-1}$
$\mathrm{H_2}{}^{16}\mathrm{O}$	3657.053	1594.746	3 755.929
HD ¹⁶ O	2 723.68	1 403.48	3707.47
$D_2 {}^{16}O$	2669.40	1178.38	2787.92

Anharmonicity

- \rightarrow H2O in gas phase is already anharmonic, but condensed phase amplifies anharmonicity
- → the anharmonicity is (largely) due to the H-bonds, where moving H away from O leads to increasing attraction by the neighboring O, and thus flattening of the potential at larger distance

www.lsbu.ac.uk/water https://en.wikipedia.org/wiki/Color_of_water

Anharmonicity x_e for diatomic molecules

	LPISSOCIUM	n Lner	8y
Energy	Harmonic v=6 v=5 v=4 v=3 v=2 v=1 v=0	De	
Iz ^a	r _e Internuclear Separation	(<i>r</i>)	

Molekül	$\omega_e/\mathrm{cm}^{-1}$	$\omega_e x_e/\mathrm{cm}^{-1}$	B_e/MHz	$lpha_e/\mathrm{MHz}$	${\cal D}_e/{ m kHz}^{ m a}$
H_2^+	2321.7	66.2	905 400	50 370	
H_2	4 401.21	121.33	1824330	91 800	
D_2	3115.50	61.82	912 660	32 336	
LiH	1405.65	23.20	225258	6 4 9 1	
HC1	2990.946	52.8186	317582	9 209	
N_2	2358.57	14.324	59 906	519	
O ₂	1580.19	11.98	43 100	477	
CO	2169.756	13.288	57 908	524.8	184
NO	1904.2	14.075	50121	534	34
Na ₂	159.124	0.7254	4638.0	26.19	
NaCl ^b	364.684	1.776	6537.37	48.709	9.3506
Cl_2	559.7	2.67	7 319.5	45.5	

Soweit nicht anders vermerkt nach Huber und Herzberg (1979); Lovas et al. (2005). ^anicht zu verwechseln mit der Minimumssenergie D_e .

 $^{\rm b}{\rm f\ddot{u}r}$ das Isotopolog $^{23}{\rm Na}^{35}{\rm Cl}$ nach Ram et al. (1997).

→ energy $E_v = (v + 1/2)\hbar\omega_e - (v + 1/2)^2\hbar\omega_e x_e$ + higher terms

- \rightarrow with anharmonicity parameter x_e ... relates to D and to b in the potential V(r)
- \rightarrow x_e for diatomics typically (only) on the (few) % level (or even below)

Second:

Effect of anharmonicity

<u>Thermal expansion</u> $\alpha = d(\ell / \ell_0) / dT$



Side note:

thermal expansion α has very similar *T* dependence as specific heat c(T); explanation by Grüneisen based on thermodynamics (later)

Second:

Effect of anharmonicity

<u>Thermal expansion</u> $\alpha = d(\ell / \ell_0) / dT$







Fundamental effects

of anharmonicity on phonons



Before we discuss anharmonicity effects

on phonons,



first a recap of structural dynamics

in the harmonic approximation

Phonons

Harmonic approximation



Restoring force on atom n from atom n+1 (Hooke's law):

$$F_n = C(u_{n+1} - u_n)$$

Considering interactions only with next neighbors n+1 and n-1 gives resulting force on atom n:

$$F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n)$$

which leads to the equations of motion

$$M\frac{d^{2}u_{n}}{dt^{2}} \equiv M\ddot{u}_{n} = C \cdot (u_{n+1} + u_{n-1} - 2u_{n})$$

This is solved by the usual plane wave ansatz, which then gives the dispersion relation $\omega(k)$

$$\omega = \sqrt{\frac{4C}{M}} |\sin\frac{ka}{2}|$$

See BM KoMa

Phonons

Harmonic approximation

Real dispersion of silicon theoretically and experimentally (Nach P. Giannozzi et al., Phys. Rev. B 43, 7231 (1991)).

(see Hunklinger, Fig.6.20)

The calculation of simple systemen can be considered understood, i.e. also the interatomic potentials V(r)



Phonons

Harmonic approximation

Integral over all phonon excitations gives internal energy *U*

Debye model of the specific heat c = dU/dTworks very well with only one material-specific parameter, the Debye temperature θ (see Hunklinger, Fig.6.30)





Fundamental effects



of anharmonicity on phonons

Phonons calculated from the harmonic approximation

are no longer clean eigenstates when anharmonic terms are considered. This leads to

- Phonon phonon interactions
- 3 phonon processes for 3rd order term
- 4 phonon processes for 4th order term





Fundamental effects



of anharmonicity on phonons



Finite lifetime of phonons, around nanosec., picosec., ... broad range depending on system

Third:

Fundamental effects



of anharmonicity on phonons



- Heat conduction λ by phonons (only in crystal, not in glass)
- Consider "phonon gas" in analogy to classical gas with
 - c = specific heat
 - v = sound velocity
 - Λ = mean free path



Fourth:

Thermodynamic implications

of anharmonicity



Violation of the Dulong-Petit law,
 i.e. heat capacity is *not* constant
 (and above 3Nk_B) for high *T*



Fourth:

Thermodynamic implications

of anharmonicity



thermal expansion α has very similar *T* dependence as specific heat *c*(*T*); explanation by Grüneisen based on thermodynamics

$$\gamma = (\alpha B) / (c \rho)$$



Structural Dynamics

Internship at ILL in Grenoble



What to remember

- Harmonic approximation and structural dynamics
- inelastic neutron scattering still best tool to measure $\omega(k)$
- phonon dispersion $\omega(k)$ can be calculated well

Anharmonicity leads to many relevant additional effects

- the blue color of water
- thermal expansion α of the lattice
- elasticity parameters $C_{(...)}$ or B and G are f(T)
- heat capacity is not strictly constant at high *T*; deviation from Dulong-Petit rule $c = 3Nk_{\rm B}$
- interaction of phonons with each other (phonon collisions)
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wave solutions with linear superposition not stable with nonlinear terms $\mathcal{O}(u^2)$, *i.e.* $\partial_t \partial_t u = C \partial_x \partial_x u + \mathcal{O}(u^2)$

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