Advanced Topics in Condensed Matter

Lecture 7: Phonons – Anharmonicity Effects (part II)

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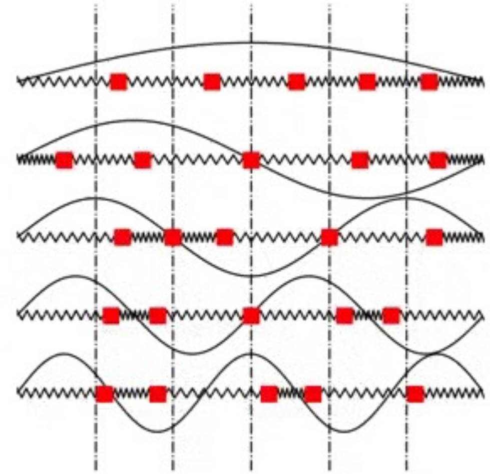
What to remember (from last week)

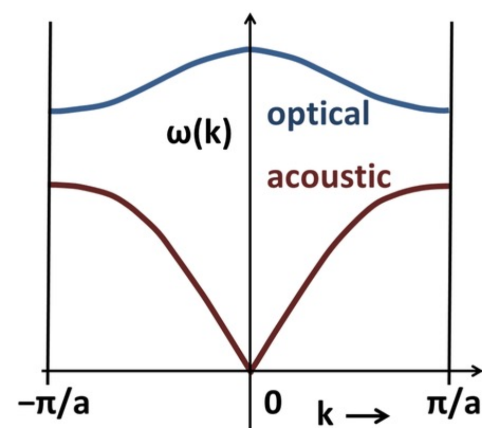
- Elastic scattering is sensitive to the time-averaged structure
- Inelastic scattering is sensitive to the dynamics

$$G(\vec{r},t) = \frac{1}{N}\left\langle \sum_{n,m=1}^{N} \delta\left(r - \left(\left(\vec{r}_n(t) - \vec{r}_m(0)\right)\right)\right)\right\rangle$$

$$S_{coh}(\vec{q},\omega) = \frac{1}{2\pi\hbar}\int G(\vec{r},t)e^{-i\vec{q}\vec{r}}e^{i\omega t}d\vec{r}\,dt$$



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

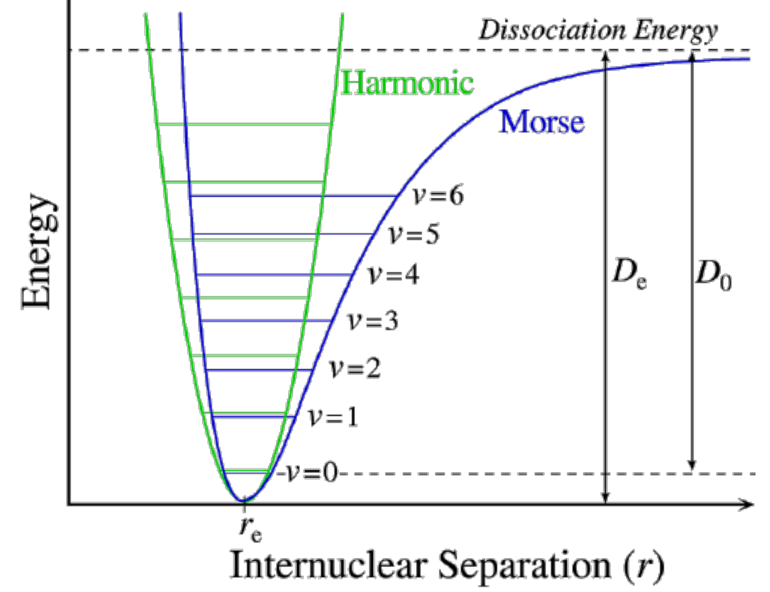


- Raman scattering involves optical phonons (near k=0)

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

Effects related to anharmonicity

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



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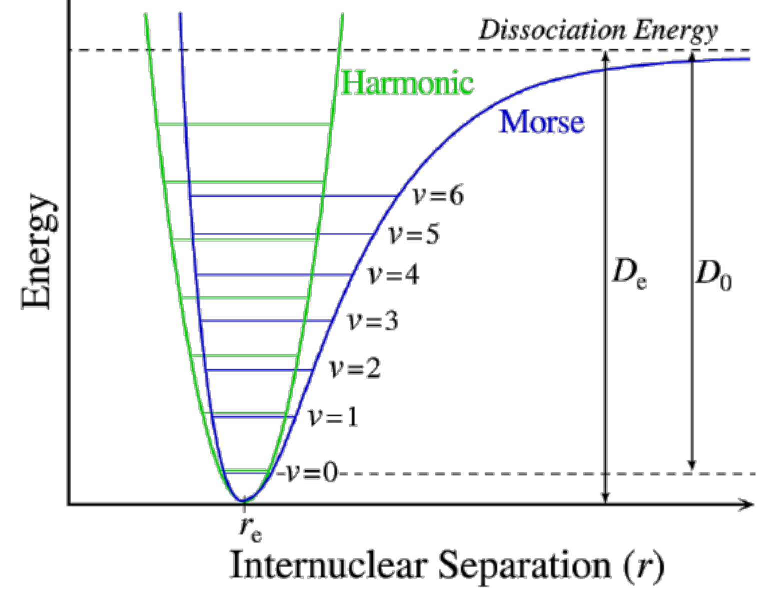
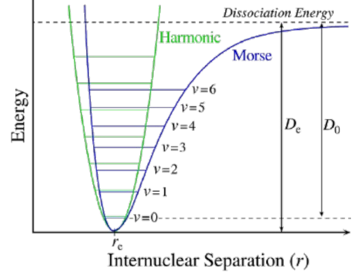
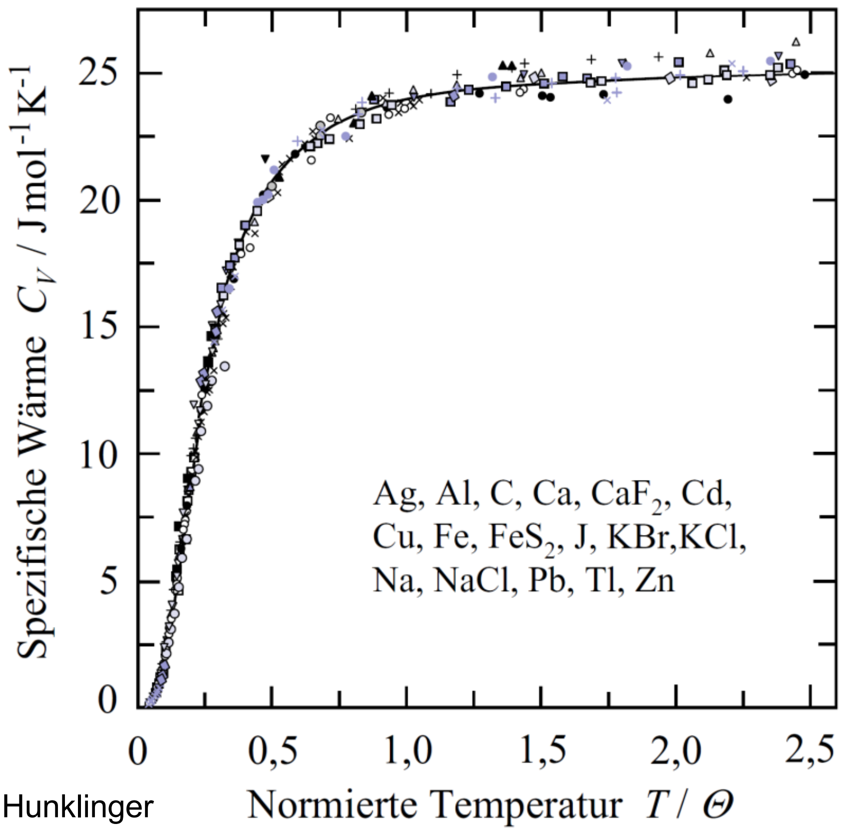


- the blue color of water
- thermal expansion α of the lattice
- elasticity parameters $C_{(\ldots)}$ or B and G are T-dependent
- heat capacity is not strictly constant at high T;
  deviation from Dulong-Petit rule $c = 3Nk_B$
  since equipartition theorem demands Hamiltonian ~ p^2 and ~ x^2
- interaction 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

Fourth: Thermodynamic implications of anharmonicity

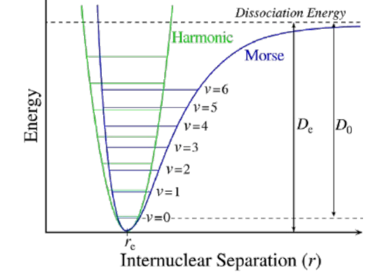


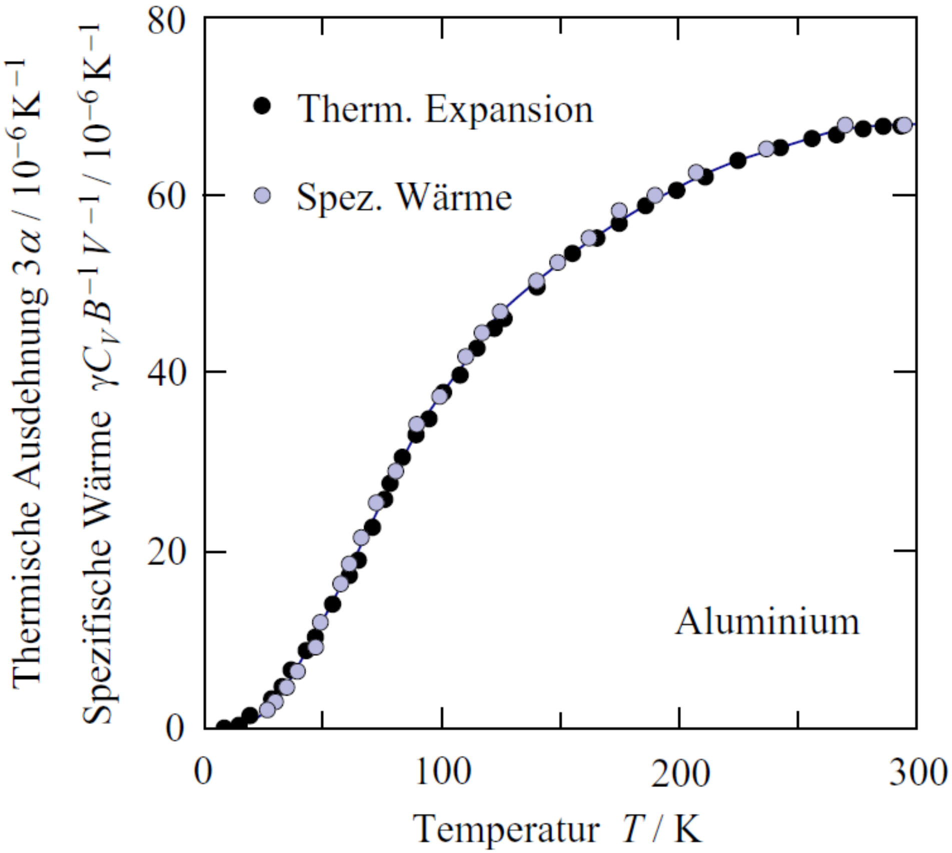


Hunklinger

- 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

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

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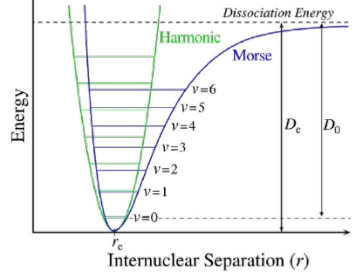


Fourth:

Thermodynamic implications of anharmonicity

Note the numerous versions of the Grüneisen parameter (and the miracles of thermodynamics)

In condensed matter, **Grüneisen parameter** γ is a dimensionless thermodynamic parameter named after German physicist Eduard Grüneisen, whose original definition was formulated in terms of the phonon nonlinearities.[1]

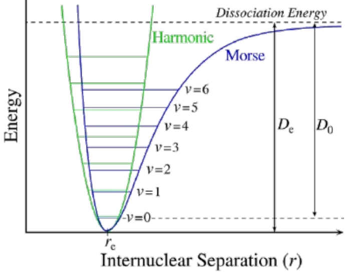
Because of the equivalences of many properties and derivatives within thermodynamics (e.g. see Maxwell relations), there are many formulations of the Grüneisen parameter which are equally valid, leading to numerous interpretations of its meaning. Some formulations for the Grüneisen parameter include:

$$\gamma = V\left(\frac{dP}{dE}\right)_V = \frac{\alpha K_T}{C_V \rho} = \frac{\alpha K_S}{C_P \rho} = \frac{\alpha v_s^2}{C_P} = -\left(\frac{\partial \ln T}{\partial \ln V}\right)_S$$

where V is volume, C_P and C_V are the principal (i.e. per-mass) heat capacities at constant pressure and volume, E is energy, S is entropy, α is the volume thermal expansion coefficient, K_S and K_T are the adiabatic and isothermal bulk moduli, v_s is the speed of sound in the medium, and ρ is density. The Grüneisen parameter is dimensionless.

Wikipedia

Fourth: Thermodynamic implications of anharmonicity



The Grüneisen parameter γ can be related to the anharmonicity.

A proper description of γ is a stringent test for any type of interaction potential.

Lattice	Dimensionality (d)	Lennard-Jones potential	Mie Potential	Morse potential
Chain	1	$10\frac{1}{2}$	$\frac{m+n+3}{2}$	$\frac{3\alpha a}{2}$
Triangular lattice	2	5	$\frac{m+n+2}{4}$	$\frac{3\alpha a-1}{4}$
FCC, BCC	3	$\frac{19}{6}$	$\frac{n+m+1}{6}$	$\frac{3\alpha a-2}{6}$
"Hyperlattice"	∞	$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$
General formula	d	$\frac{11}{d}-\frac{1}{2}$	$\frac{m+n+4}{2d}-\frac{1}{2}$	$\frac{3\alpha a+1}{2d}-\frac{1}{2}$

Note that analytical calculcations are possible for model potentials

Wikipedia

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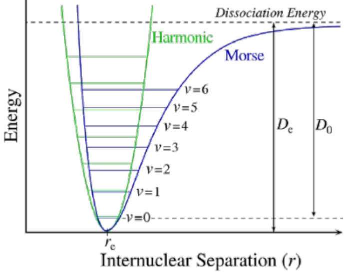

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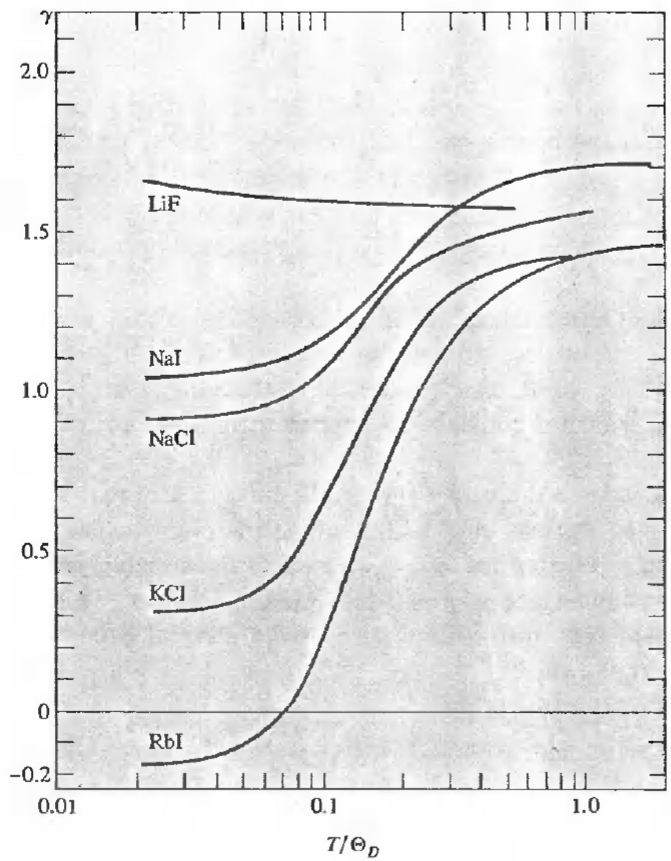


Figure 25.1
Grüneisen parameter vs. T/Θ_D for some alkali halide crystals. (From G. K. White, *Proc. Roy Soc. London* **A286**, 204 (1965).)

Ashcroft / Mermin

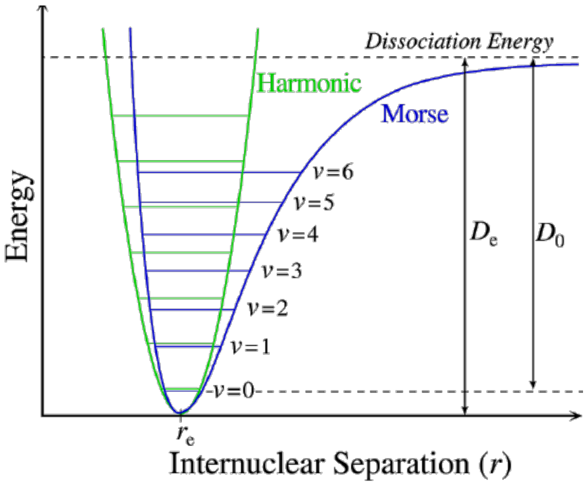
Structural Dynamics

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 $C_{(\ldots)}$ or B and G are f(T)
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  deviation from Dulong-Petit rule $c = 3Nk_B$
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