Study of Grüneisen Parameter as Anharmonic Metric

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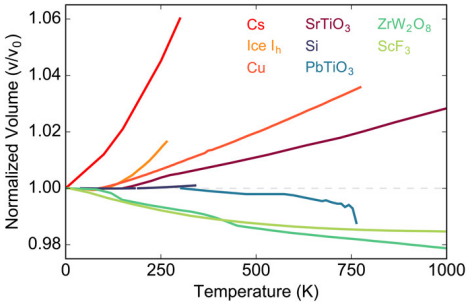
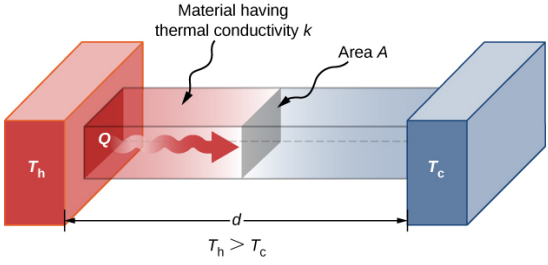
June 28, 2021

Thermal Expansion and Thermal Conductivity

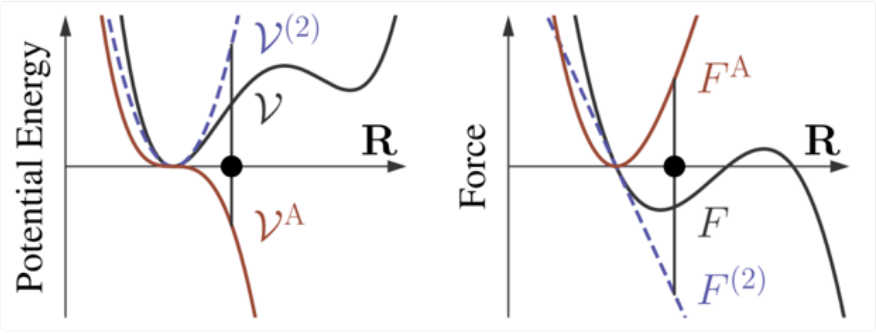




These macroscopic, observable effects are often used as a measure for anharmonicity.

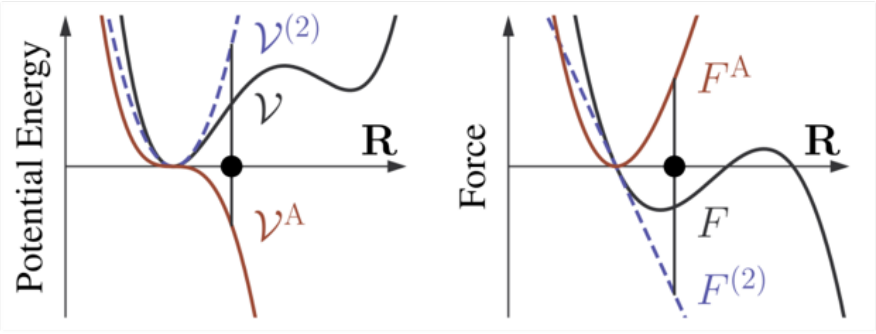
Journal of Applied Physics 126, 171102 (2019)
https://opentextbc.ca/universityphysicsv2openstax/chapter/mechanisms-of-heat-transfer/

Microscopic Anharmonic Metric



Knoop et al. anharmonicity metric.

Microscopic Anharmonic Metric



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Is Grüneisen parameter a reliable anharmonic metric?

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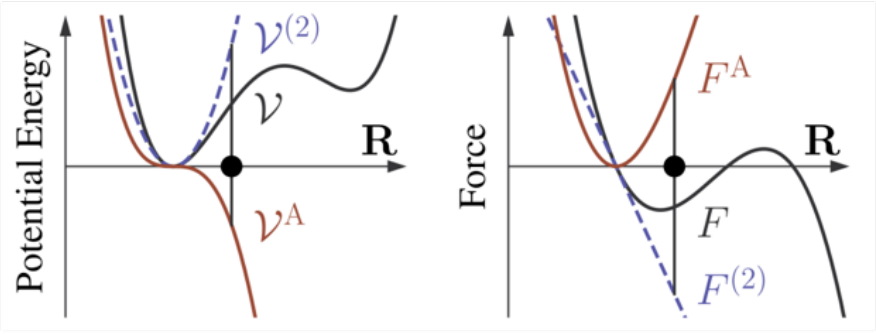


Knoop et al. anharmonicity metric.

Is Grüneisen parameter a reliable anharmonic metric?
Let's check with thermal conductivity!

Calculation of lattice thermal conductivity

Thermal current density

$$U_j = -\sum_i \kappa_{ji} \frac{\partial T}{\partial x_i}$$

Boltzmann Transport Equation

$$-\boldsymbol{v}_{qj} \cdot \nabla T \frac{\partial n_{qj}}{\partial T} + \frac{\partial n_{qj}}{\partial t}|_{scatt} = 0 \; n_{qj}\text{: phonon distribution}$$

Relaxation Time Approximation

$$\frac{\partial n_{qj}}{\partial t} = \frac{n^0_{qj} - n_{qj}}{\tau_{qj}} \Rightarrow n_{qj} - n^0_{qj} = -C_{qj} \boldsymbol{v}^2_{qj} \nabla T \tau_{qj}$$

Lattice Thermal Conductivity per mode

$$\kappa_{qj} = \frac{1}{\Omega_{qj}} C_{qj} \boldsymbol{v}^2_{qj} \tau_{qj} \Rightarrow \kappa_L = \frac{1}{V} \sum_{qj} C_{qj} \boldsymbol{v}^2_{qj} \tau_{qj}$$

Ward, Alistair, et al. Physical Review B 80.12 (2009): 125203.
Amelia Carolina Sparavigna. Mechanics, Materials Science Engineering Journal, Magnolithe, 2016, 2016 (3), pp.57-66.

Calculation of Grüneisen Parameter

mode Grüneisen parameter

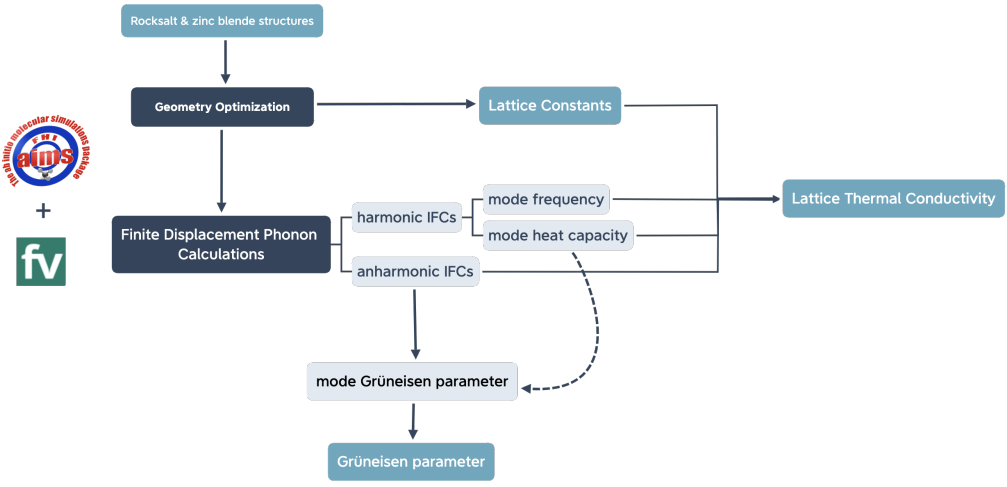
$$\gamma_\lambda = -\frac{V}{\omega_\lambda}\frac{\partial \omega_\lambda}{\partial V} = -\frac{(e_\lambda)^T \delta D(k) e_\lambda}{6M\omega_\lambda^2}$$

average Grüneisen parameter

$$\gamma = \frac{\sum C_\lambda \gamma_\lambda}{\sum C_\lambda}$$

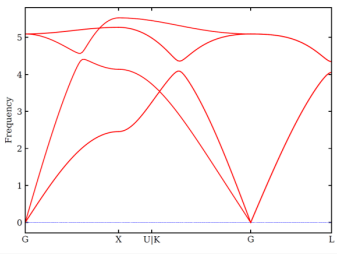
- $\delta D(k)$: change in dynamical matrix due to volume change δV

How they can be fulfilled by ab initio calculations

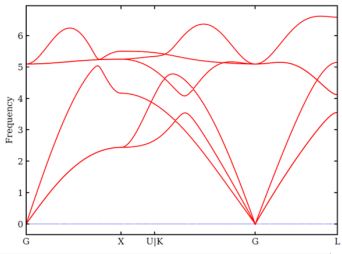


Calculations of NaCl

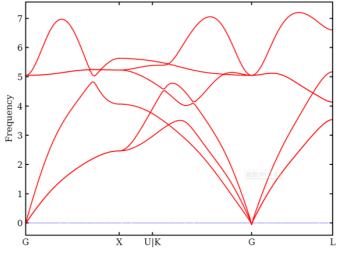
Phonon bandstructures of NaCl



8-atom supercell, 6×6×6 k-grid, light basis sets, PBEsol



64-atom supercell, 3×3×3 k-grid, light basis sets, PBEsol



216-atom supercell, 2×2×2 k-grid, light basis sets, PBEsol

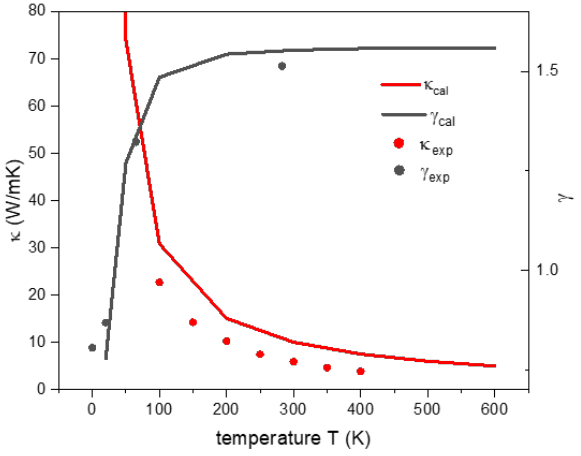
Supercell with 64 or 216 atoms seems appropriate.

Convergence test for 3-phonon calculations

Table: Results of NaCl at 300 K with different supercell sizes and cutoff pair distances

Atom/supercell	**cutoff pair distance (Å)**	κ_L **(W/mK)**	γ
64	5	8.266	1.585
64	7.5	8.243	1.586
64	10	8.225	1.592
64	100	8.225	1.592
216	5	9.155	1.527
216	7.5	9.185	1.547
216	10	9.098	1.569
216	100	9.167	1.606

Temperature dependent thermal conductivity and Gruneisen parameter of NaCl



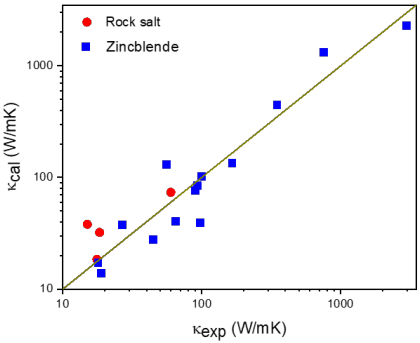
Ashcroft, Neil W., and N. David Mermin. "Solid state physics." (1976).
B. Håkansson, and P. Andersson. Journal of Physics and Chemistry of Solids 47.4 (1986)

A High-throughput Computation

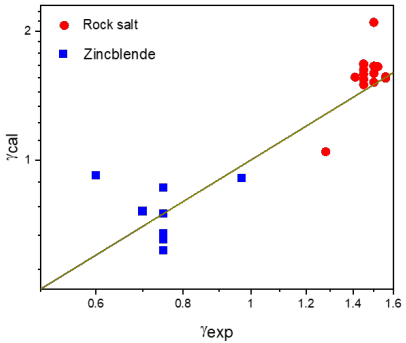
A High(Low)-throughput Computation

- 15 rock salt and 14 zincblende materials
- Convergence tests of supercell size and cutoff pair distance
  - 216-atom supercell and cutoff 100 $\AA$ (all displacements included)
- Other calculation parameters
  - PBEsol as xc functional
  - light basis sets
  - $2\times2\times2$ k-grid
  - displacement $= 0.03$ $\AA$
  - $21\times21\times21$ q-mesh

Results - thermal conductivity and Grüneisen parameter



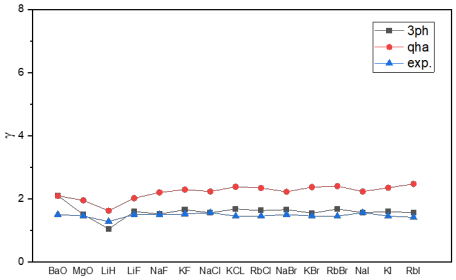
(c) Thermal conductivity at 300 K

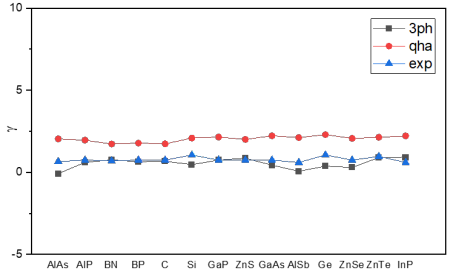


(d) Grüneisen parameter at 300 K

D. T. Morelli and G. A. Slack, Springer, New York, 2006.

Comparison with other computational results of Grüneisen parameter

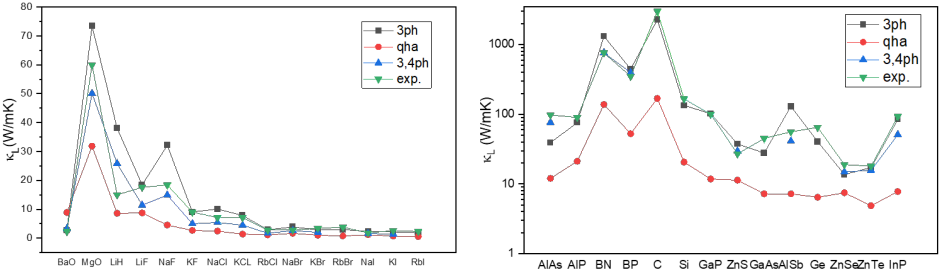




3ph: calculated in this study
qha: calculated by quasiharmonic Debye model
3,4ph: self-consistent phonon approximation + 3,4 ph

C. Toher, et al. Phys. Rev. B 90, 174107 (2014)
Y. Xia, et al. Physical Review X 10.4 (2020)
D. T. Morelli and G. A. Slack, Springer, New York, 2006.

Comparison with other computational results of thermal conductivity



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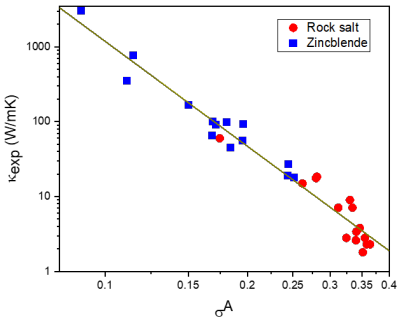
Sigma metric

Sigma metric for measuring the degree of anharmonicity

- Degree of anharmonicity $\sigma^A(T) = \frac{\sigma[F^A]_T}{\sigma[F]_T}$
  - $\sigma[F^A]_T$: standard deviation of the distribution of anharmonic force compnents.
  - $\sigma[F]_T$: standard deviation of the distribution of total force.



F. Knoop, T.A.R. Purcell, M. Scheffler, and C. Carbogno. Phys. Rev. Materials 4, 083809 (2020)

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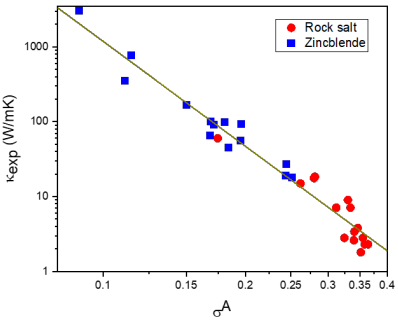

$\log \kappa$ inversely proportional to $\log \sigma^A$

$R^2 = 0.95$

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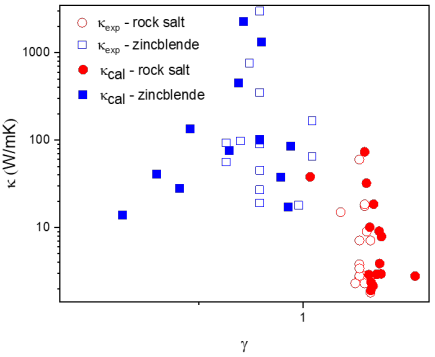
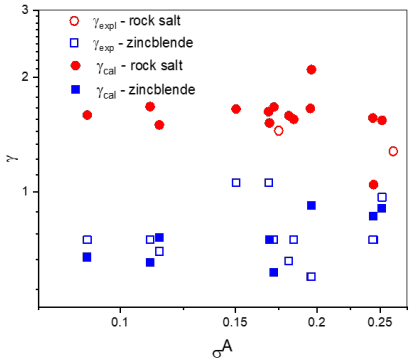
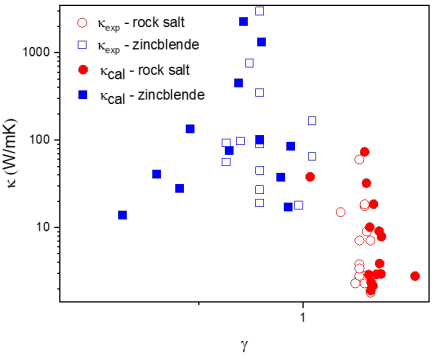
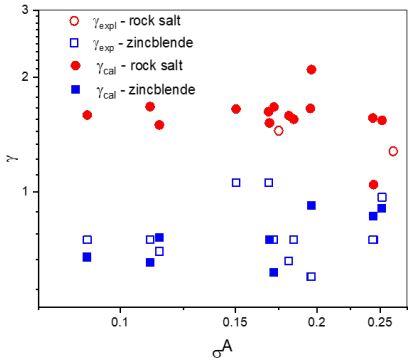
Grüneisen parameter as anharmonic metric





Grüneisen parameter as anharmonic metric





In comparison with σ^A, γ is worse at indicating the anharmonicity.

Conclusion and Outlook

- Systematic investigation of 29 compounds are performed.
- Data reveal that the sigma metric is a more reliable descriptor for anharmonicity – despite the fact that Grüneisen parameters are rooted in observables.
- So far, only very simple materials with relatively low anharmonicity considered.
  $\rightarrow$ More anharmonic materials next!
- So far, only direct, linear correlations were considered.
  $\rightarrow$ What about more complex, Machine-learned models (SISSO)?

Thank You

And many thanks to Thomas Purcell and Christian Carbogno for their supports and suggestions!