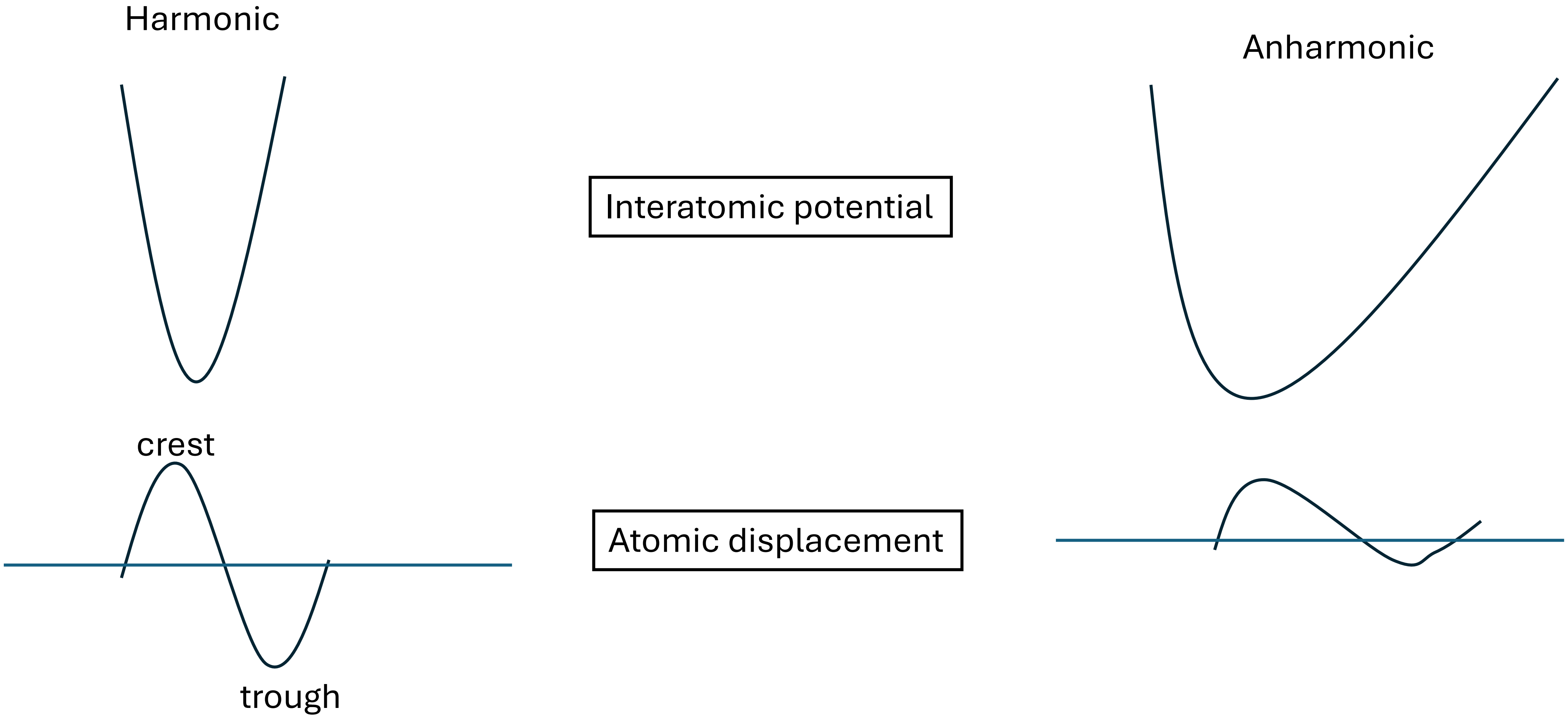
Anharmonicity and third-order elastic constants in silicon

A finite Grüneisen parameter implies asymmetry between atomic displacements at the crest (expansion) and trough (compression) of a longitudinal lattice vibration.

Fundamentally , this is a consequence of the anharmonicity of the interatomic (Lennard-Jones) potential.



One way to quantify anharmonicity is to look at higher order elastic constants

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First-principles calculation of higher-order elastic constants using exact deformation-gradient tensors

S. P. Łepkowski
Institute of High Pressure Physics - Unipress, Polish Academy of Sciences, ul. Sokołowska 29/37, 01-142 Warszawa, Poland

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$$\rho_0 E(\boldsymbol{\eta}) = \rho_0 E(0) + \frac{1}{2!}\sum_{i,j=1}^{6} C_{ij}\eta_i\eta_j + \frac{1}{3!}\sum_{i,j,k=1}^{6} C_{ijk}\eta_i\eta_j\eta_k$$

Mass density

Free energy

Strain tensor

Second-order elastic constants

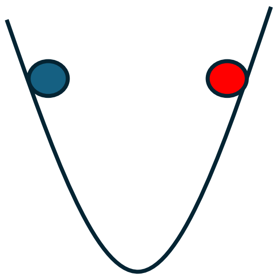
Third-order elastic constants

Harmonic and anharmonic cases

Harmonic

$$\rho_0 \frac{\partial E}{\partial \eta_i} = \frac{1}{2!} \sum_{j=1}^{6} C_{ij} \eta_j$$

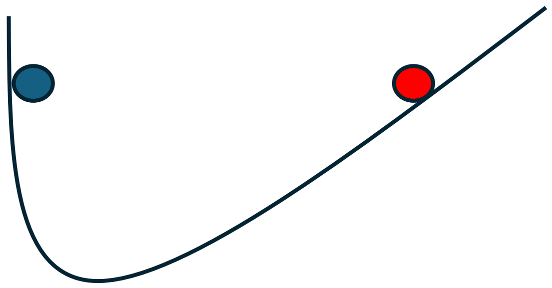
$$\eta_{crest} = \eta_{trough} = \eta_{average}$$



Anharmonic

$$\rho_0 \frac{\partial E}{\partial \eta_i} = \frac{1}{2!} \sum_{j=1}^{6} C_{ij} \eta_j + \frac{1}{3!} \sum_{j,k=1}^{6} C_{ijk} \eta_j \eta_k$$

$$(\eta_{crest} - \eta_{trough})/\eta_{average} \approx \frac{\langle C_{ijK} \rangle}{3\langle C_{ij} \rangle}$$



The ratio of third-order to second-order elastic constants is a measure of anharmonicity!

Elastic constants of silicon in GPa

Second order

Constant	Value (GPa)
C_{11}	165.7
C_{12}	63.9
C_{44}	79.6

Average:103 GPa

Third order

Constant	Value (GPa)	Uncertainty
C_{111}	−760	±20
C_{112}	−430	±20
C_{123}	−90	±20
C_{144}	+20	±10
C_{155}	−690	±20
C_{456}	−80	±10

Average:338 GPa

Sources:

- https://sense.fas.sfu.ca/internal/Si_elastic.pdf
- M. A. Hopcroft J. Micromech. Syst. 19, 229 (2010)
- N. P. Keating, Phys. Rev. 149, 674 (1966)

How anharmonic is silicon?

$$(\eta_{crest}-\eta_{trough})/\eta_{average} \approx \frac{\langle C_{ijK} \rangle}{3\langle C_{ij} \rangle} \approx 1.1$$

How anharmonic is silicon?

Its Grüneisen parameter is of the order of unity!

$$\gamma_i = \frac{\partial ln\omega_i}{lnV} \approx \sim 1$$

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Lattice thermal conductivity of silicon from empirical interatomic potentials

D. A. Broido and A. Ward
Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467, USA

N. Mingo
NASA-Ames Center for Nanotechnology, Moffet Field, California 94035, USA
(Received 26 January 2005; revised manuscript received 3 June 2005; published 29 July 2005)

TABLE I. Mode Grüneisen parameters for the Tersoff EIP calculated using three different parameter sets as described in the text and compared to experimental values from Ref. 36.

	Set B	Set C	Set B*	Experiment
$\gamma_{LTO}(\Gamma)$	1.33	1.32	1.39	0.98±0.06
$\gamma_{TA}(X)$	−6.46	−0.20	−0.91	−1.4±0.3
$\gamma_{TO}(X)$	1.66	1.60	1.71	1.5±0.1
$\gamma_{TA}(L)$	−3.13	−0.31	−1.24	−1.3±0.3
$\gamma_{TO}(L)$	1.48	1.45	1.55	1.3±0.2