Ab-initio lattice thermal conductivity calculations for large libraries of compounds: challenges and strategies

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Lattice thermal conductivity (κ_ℓ)

Practical heat management challenges:

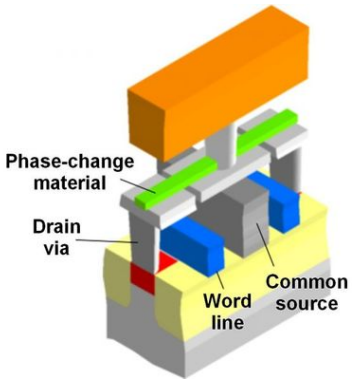
Power electronics: Increase heat dissipation per unit area

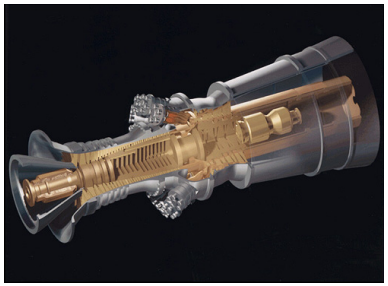
Data storage: Increase thermal efficiency of phase-change memories

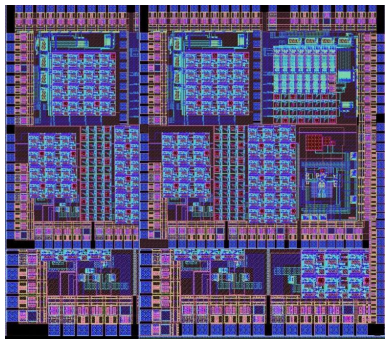
Nanoscale CMOS: Precise design of heat pathway at the nanometer level

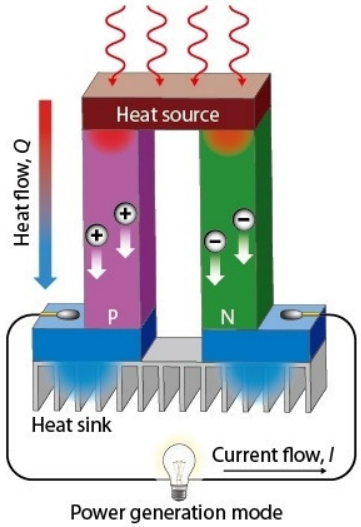
High-temperature turbines: Lower alloy temperature by reducing thermal conductivity of coatings

Thermoelectricity: Decrease κ to increase $ZT = \frac{\sigma S^2}{\kappa} T$









κ_ℓ is the dominant factor in common scenarios

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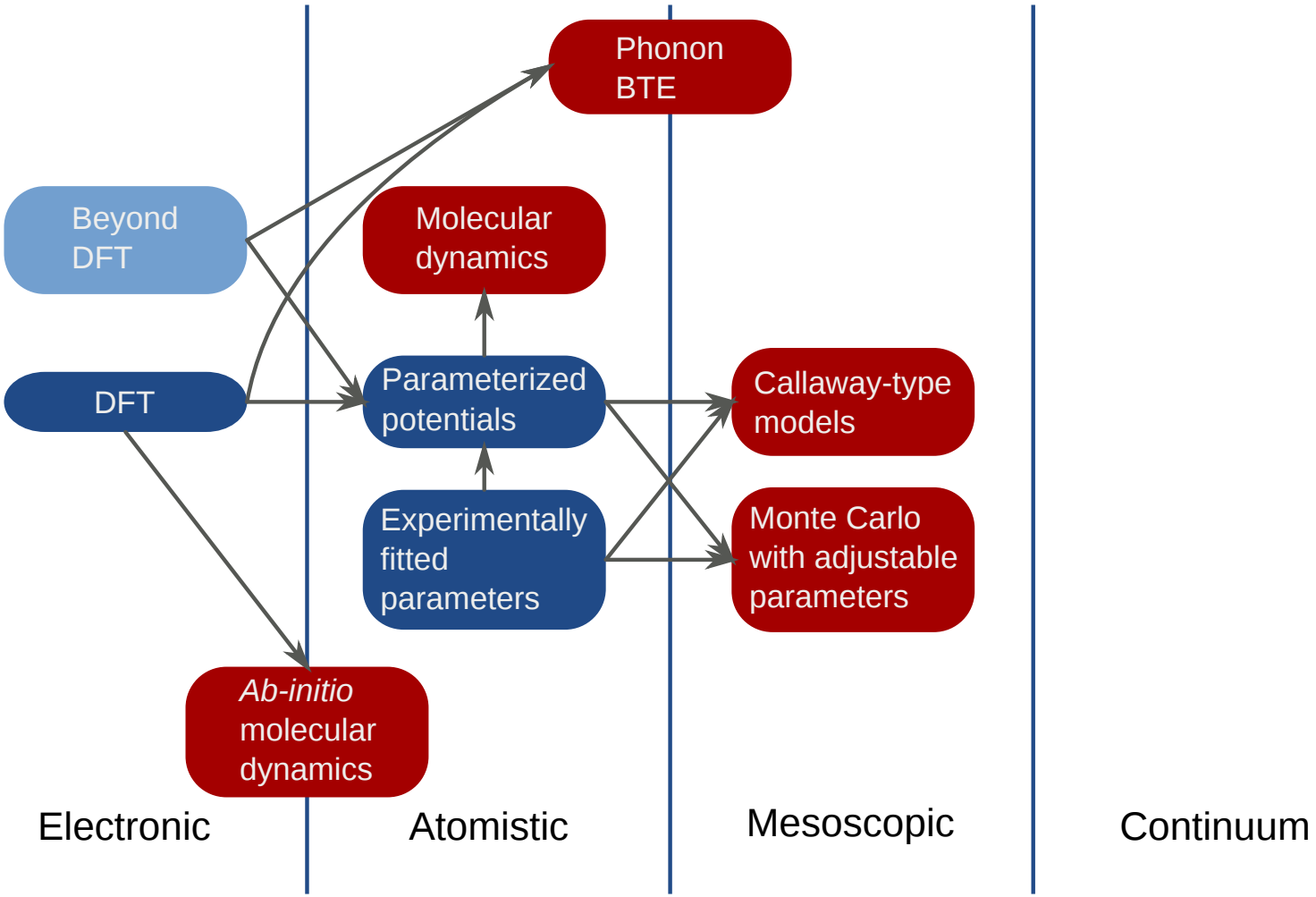
Computing κ_ℓ in crystalline compounds

Many approaches



All paths useful, few predictive, even fewer predictive+practical

The steady-state distribution of phonons

- Phonon-contributed heat current: $\boldsymbol{J} = \sum_\lambda f_\lambda \hbar\omega_\lambda \boldsymbol{v}_\lambda$
- Equilibrium distribution: $f_0(\omega) = \left[e^{\frac{\hbar\omega}{k_B T}} - 1 \right]^{-1}$ (Bose-Einstein)
- When a temperature gradient ∇T is present:
  $\frac{df_\lambda}{dt} = \left.\frac{\partial f_\lambda}{\partial t}\right|_{\text{diffusion}} + \left.\frac{\partial f_\lambda}{\partial t}\right|_{\text{scattering}} = 0$, with $\left.\frac{\partial f_\lambda}{\partial t}\right|_{\text{diffusion}} = -\nabla T \cdot \boldsymbol{v}_\lambda \frac{\partial f_\lambda}{\partial T}$
- Linear regime: $f_\lambda = f_0(\omega_\lambda) + g_\lambda$, with $g_\lambda = -\boldsymbol{F}_\lambda \cdot \nabla T \frac{df_0}{dT}$
- Knowledge of the phonon spectrum and of $\boldsymbol{F}_\lambda$ suffices to solve the problem

Lattice thermal conductivity

$$\kappa_\ell^{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_\lambda f_0 \left(f_0 + 1\right) \left(\hbar\omega_\lambda\right)^2 v_\lambda^\alpha F_\lambda^\beta$$

The Boltzmann transport equation for phonons

The linearized BTE can be reduced to a large linear system:

$$\boldsymbol{F}_\lambda = \tau_\lambda^0(\boldsymbol{v}_\lambda + \boldsymbol{\Delta}_\lambda)$$

Several iterative solution approaches:

- Omini and Sparavigna, *Physica B: Condens. Matter* 212 (1995) 101.
- Mauri and coworkers, *Phys. Rev. B* 88 (2013) 045430.

A bit of history

1929: Peierls-Boltzmann transport equation for phonons

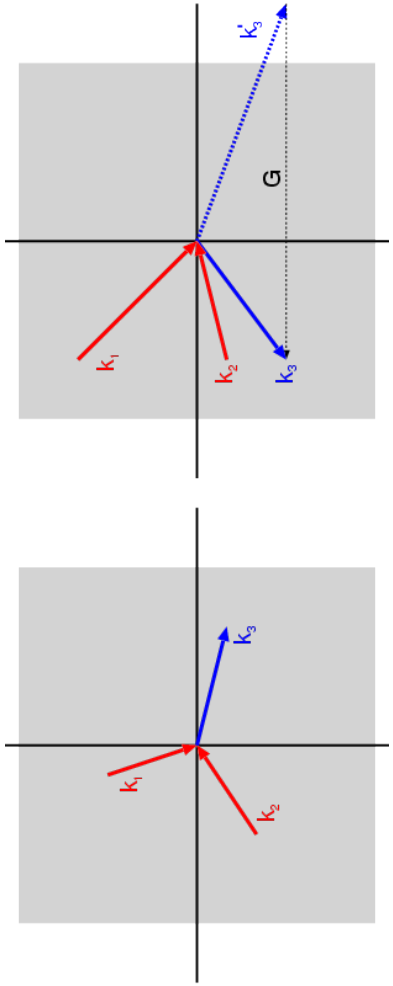
1963: "It is the author's belief that progress towards a more accurate evaluation of the lattice conductivity can only be made along this path for example, by the use of more complicated trial functions. The Boltzmann equation is so exceedingly complex that it seems hopeless to expect to generate a solution from it directly." (J. Ziman, Electrons and Phonons: The Theory of Transport Phenomena in Solids)

1996: First iterative numerical solution (M. Omini & A. Sparavigna, *Phys. Rev. B* 53, 9064).

2007: First ab-initio solution (D. A. Broido, M. Malorny, G. Birner, Natalio Mingo & D. A. Stewart, *Appl. Phys. Lett.* 91, 231922)

The relaxation time approximation (RTA)

- Thee-phonon scattering rates depend on phonon populations
- In $\boldsymbol{F}_\lambda = \tau_\lambda^0(\boldsymbol{v}_\lambda + \boldsymbol{\Delta}_\lambda)$, $\boldsymbol{\Delta}_\lambda$ depends on $\{\boldsymbol{F}_{\lambda'}\}$
- BTE: consistency condition
- 0th-order approximation: $\boldsymbol{\Delta}_\lambda = 0$
- N processes treated as U processes
- $\lesssim 10\%$ error for most materials
- Catastrophic failure for diamond and other high-κ_ℓ compounds
- The full iterative solution is needed for a general approach to the problem



Source: Wikipedia

The ingredients of the BTE

$$\frac{1}{\tau_\lambda^0} = \frac{1}{N}\left(\sum_{\lambda'\lambda''}^{+} \Gamma^{+}_{\lambda\lambda'\lambda''} + \sum_{\lambda'\lambda''}^{-} \frac{1}{2}\Gamma^{-}_{\lambda\lambda'\lambda''} + \sum_{\lambda'} \Gamma_{\lambda\lambda'}\right)$$

$$\begin{aligned}\boldsymbol{\Delta}_\lambda = &\frac{1}{N}\sum_{\lambda'\lambda''}^{+} \Gamma^{+}_{\lambda\lambda'\lambda''}\left(\xi_{\lambda\lambda''}\boldsymbol{F}_{\lambda''} - \xi_{\lambda\lambda'}\boldsymbol{F}_{\lambda'}\right) + \\ &+ \frac{1}{N}\sum_{\lambda'\lambda''}^{-} \frac{1}{2}\Gamma^{-}_{\lambda\lambda'\lambda''}\left(\xi_{\lambda\lambda''}\boldsymbol{F}_{\lambda''} + \xi_{\lambda\lambda'}\boldsymbol{F}_{\lambda'}\right) + \\ &+ \frac{1}{N}\sum_{\lambda'} \Gamma_{\lambda\lambda'}\xi_{\lambda\lambda'}\boldsymbol{F}_{\lambda'}\end{aligned}$$

- $\xi_{\lambda\lambda'} := \omega_{\lambda'}/\omega_\lambda$
- $N := N_1 \times N_2 \times N_3$: Number of $\boldsymbol{q}$ points sampled
- Conservation of momentum: $\boldsymbol{q}'' = \boldsymbol{q} \pm \boldsymbol{q}' + \boldsymbol{Q}$

Two-phonon processes: Isotopic scattering

Tamura's formula:

$$\Gamma_{\lambda\lambda'} = \frac{\pi\omega^2}{2} \sum_{i \in \text{u.c.}} g(i) \left| \boldsymbol{e}^*_\lambda(i) \cdot \boldsymbol{e}_{\lambda'}(i) \right|^2 \delta\left(\omega_\lambda - \omega_{\lambda'}\right)$$

Each atom i replaced by a statistical combination of isotopes

- Masses and relative abundancies: $\left\{ \left(M_s(i), f_s(i) \right) \right\}$
- Average mass: $\overline{M}(i) = \sum_s f_s(i) M_s(i)$
- Pearson deviation coefficient: $g(i) = \sum_s f_s(i) \left[1 - M_s(i) / \overline{M}(i) \right]^2$

Also applicable as a crude description of alloys

Three-phonon processes: Anharmonic scattering

$$\Gamma^{+}_{\lambda\lambda'\lambda''} = \frac{\hbar\pi}{4}\frac{f_0' - f_0''}{\omega_\lambda\omega_{\lambda'}\omega_{\lambda''}}\left|V^{+}_{\lambda\lambda'\lambda''}\right|^2\delta\left(\omega_\lambda + \omega_{\lambda'} - \omega_{\lambda''}\right)$$

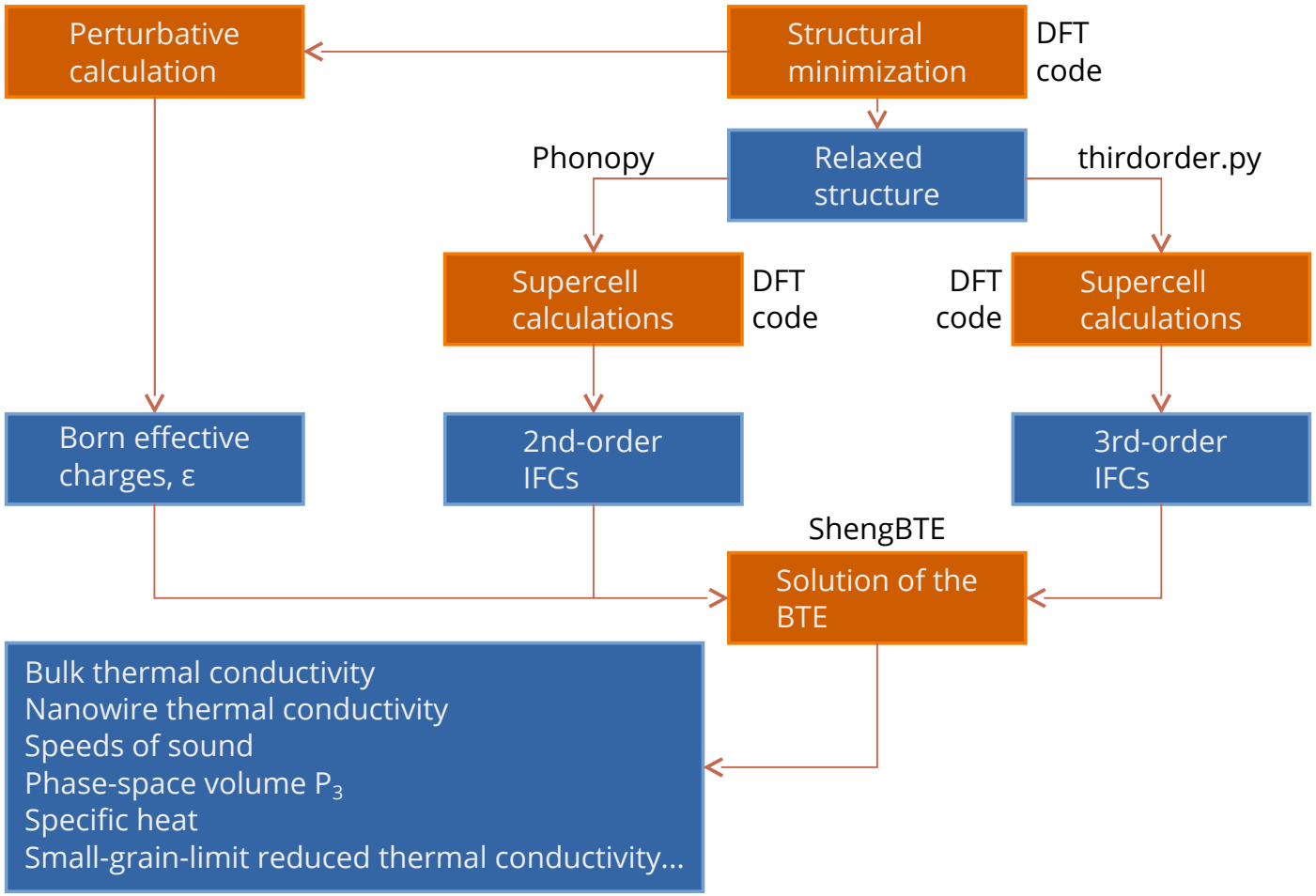
$$\Gamma^{-}_{\lambda\lambda'\lambda''} = \frac{\hbar\pi}{4}\frac{f_0' + f_0'' + 1}{\omega_\lambda\omega_{\lambda'}\omega_{\lambda''}}\left|V^{-}_{\lambda\lambda'\lambda''}\right|^2\delta\left(\omega_\lambda - \omega_{\lambda'} - \omega_{\lambda''}\right)$$

$$V^{\pm}_{\lambda\lambda'\lambda''} = \sum_{i\in\text{u.c.}}\sum_{j,k}\sum_{\alpha\beta\gamma}\Phi^{\alpha\beta\gamma}_{ijk}\frac{e^{\alpha}_{\lambda}(i)\,e^{\beta}_{p',\pm\boldsymbol{q}'}(j)\,e^{\gamma}_{p'',-\boldsymbol{q}''}(k)}{\sqrt{M_i M_j M_k}}$$

$\Phi^{\alpha\beta\gamma}_{ijk} = \frac{\partial^3 E}{\partial r^{\alpha}_i \partial r^{\beta}_j \partial r^{\gamma}_k}$: Third-order interatomic force constants (IFCs)

Our free implementation: ShengBTE

Our workflow



Harmonic calculations

Second-order IFCs: $\Phi_{ij}^{\alpha\beta} = \frac{\partial^2 E}{\partial r_i^\alpha \partial r_j^\beta} = -\frac{\partial f_i^\alpha}{\partial r_j^\beta}$; $f_i^\alpha = -\left\langle \frac{\partial H}{\partial r_i^\alpha} \right\rangle$

Density matrix: $D(q) = \sum_R \Phi_{0,R} e^{-i\vec{q}\cdot\vec{R}}$
Two kinds of approaches:

Real-space: Supercells + finite-difference formula. $\Phi_{ij}^{\alpha\beta} \simeq \frac{f_i^\alpha\left(r_j^\beta=-h\right)-f_i^\alpha\left(r_j^\beta=h\right)}{2h}$

Density-functional perturbation theory: D computed directly at some q + Fourier interpolation

Comparison

- Real-space methods are more straightforward to implement
- DFPT methods can be faster

Both implemented in Quantum Espresso
VASP + Phonopy (`http://phonopy.sourceforge.net/`): Very flexible, complete and user-friendly combination for real-space

Dielectric parameters

When polar bonds are present, a long-range correction to the dynamical matrix is necessary.
Several formulations with common ingredients:

Dielectric tensor / permitivity: ϵ such that $\epsilon \boldsymbol{E} = \epsilon_0 \boldsymbol{E} + \vec{\boldsymbol{P}}$ in the $\omega \to \infty$ limit

Born effective charges: $q_i^{\alpha\beta} = \Omega \frac{\partial P^\alpha}{\partial r_i^\beta}$

Choice of algorithm:

2nd-order constants from supercells: 100% reciprocal space ``Ewald summation'', Gonze *et al.*, *Phys. Rev. B* 50 (1994) 13035

2nd-order constants from DFPT: Mixed-space approach with zero correction at commensurate $\boldsymbol{q}$ points, Want *et al.*, *J. Phys.: Condens. Matter* 22 (2010) 202201

Parameter calculation:

- Finite fields
- DFPT

Third-order force constants

We have implemented a real-space, supercell-based approach

$$\Phi_{ijk}^{\alpha\beta\gamma} \simeq \frac{1}{4h^2}\left[f_k^\gamma\begin{pmatrix} r_i^\alpha = h \\ r_j^\beta = -h\end{pmatrix} + f_k^\gamma\begin{pmatrix} r_i^\alpha = -h \\ r_j^\beta = h\end{pmatrix} - f_k^\gamma\begin{pmatrix} r_i^\alpha = h \\ r_j^\beta = h\end{pmatrix} - f_k^\gamma\begin{pmatrix} r_i^\alpha = -h \\ r_j^\beta = -h\end{pmatrix}\right]$$

- n-atom unit cell, $\mathcal{N}$-atom supercell $\Rightarrow 4 \times 27 n^2 \mathcal{N}$ DFT runs (easily into the thousands)
- Space-group symmetries and equality of mixed partials allow us to reduce this number
- It is necessary to enforce $\sum_k \Phi_{ijk}^{\alpha\beta\gamma} = 0$. ``Raw'' IFCs give wrong order of magnitude
- Lagrange-multiplier approach: Minimize sum of squares of relative corrections to the IFCs while enforcing the sum rules

Conservation of energy and momentum

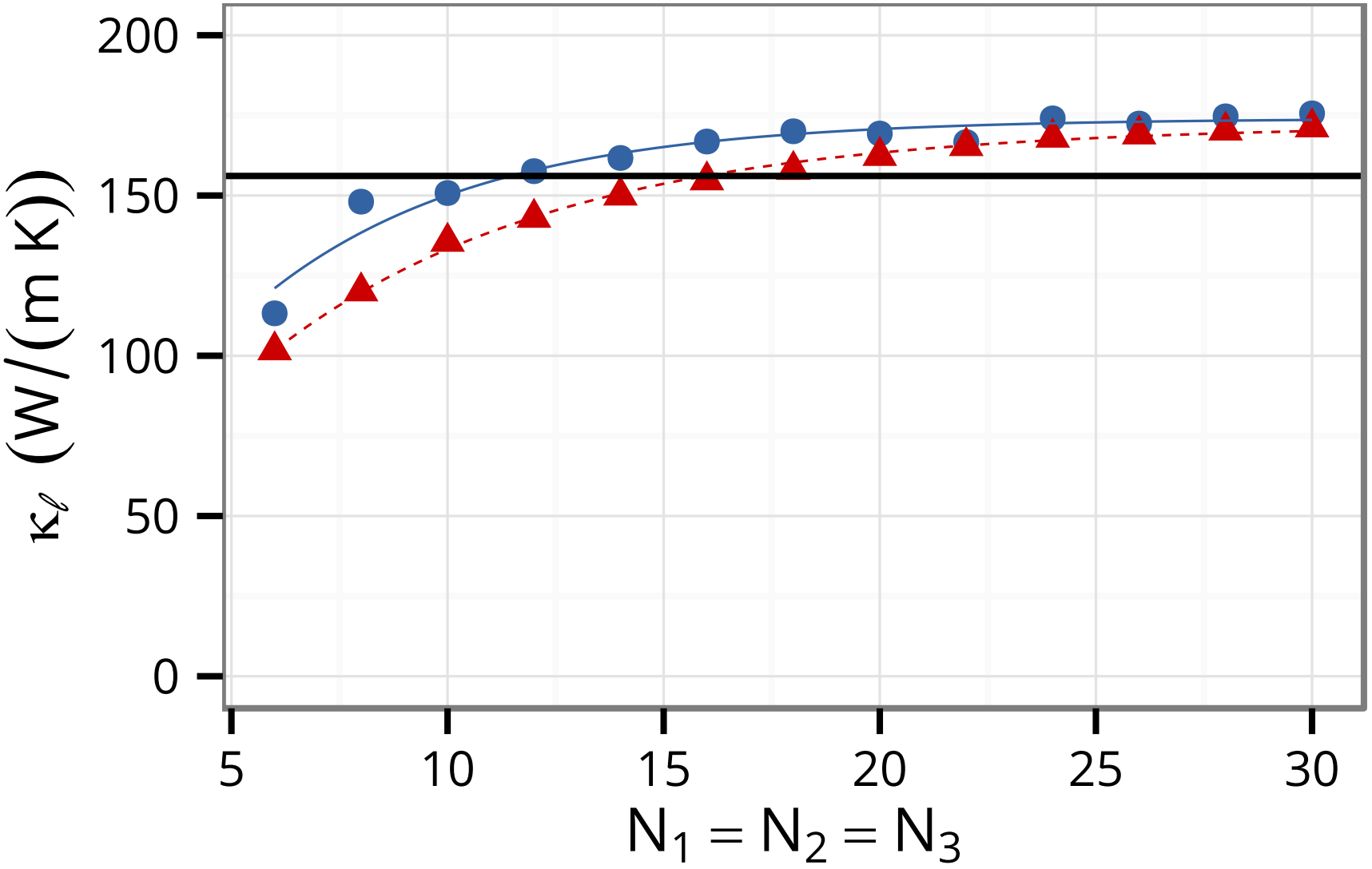
- Allowed three-phonon processes must fulfill $\omega_\lambda - \left(\pm\omega_{\lambda'} + \omega_{\lambda''}\right) = 0$
- Most of the requires λ' and λ'' are not sampled by the $\boldsymbol{q}$-point grid
- Two solutions:
  1. Solve for λ''
  2. Regularize the δ distribution
- Our proposal: Locally adaptive Gaussian smearing

$$g\left(\omega_\lambda - W\right) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{\left(\omega_\lambda - W\right)^2}{2\sigma^2}}$$

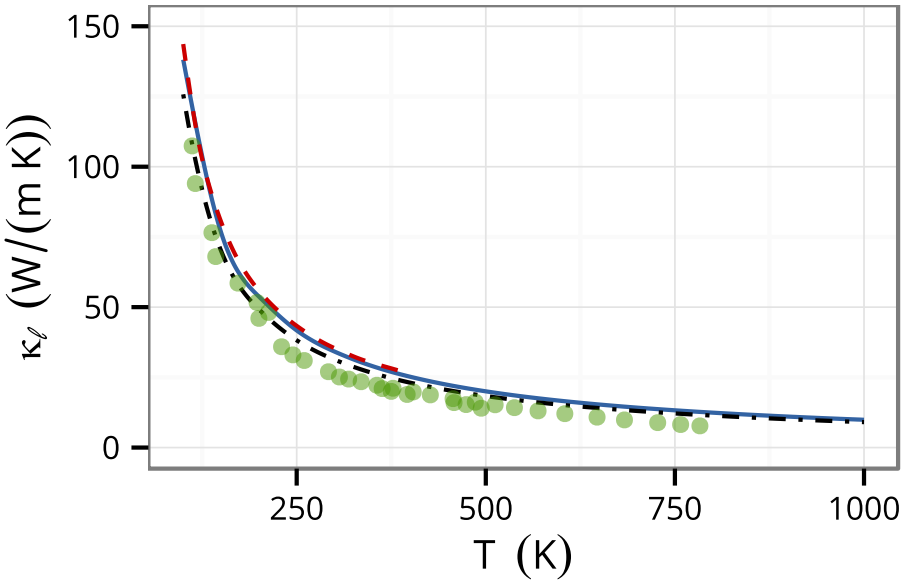
$$W \simeq W\left(\boldsymbol{q}'_0\right) + \sum_\mu \frac{\partial W}{\partial \mathrm{q}'^\mu}\left(\mathrm{q}'^\mu - \mathrm{q}'^\mu_0\right) \Rightarrow \overline{W} \simeq W\left(\boldsymbol{q}'_0\right);\ \sigma^2_W \simeq E\left\{\left[W - W\left(\boldsymbol{q}'_0\right)\right]^2\right\}$$

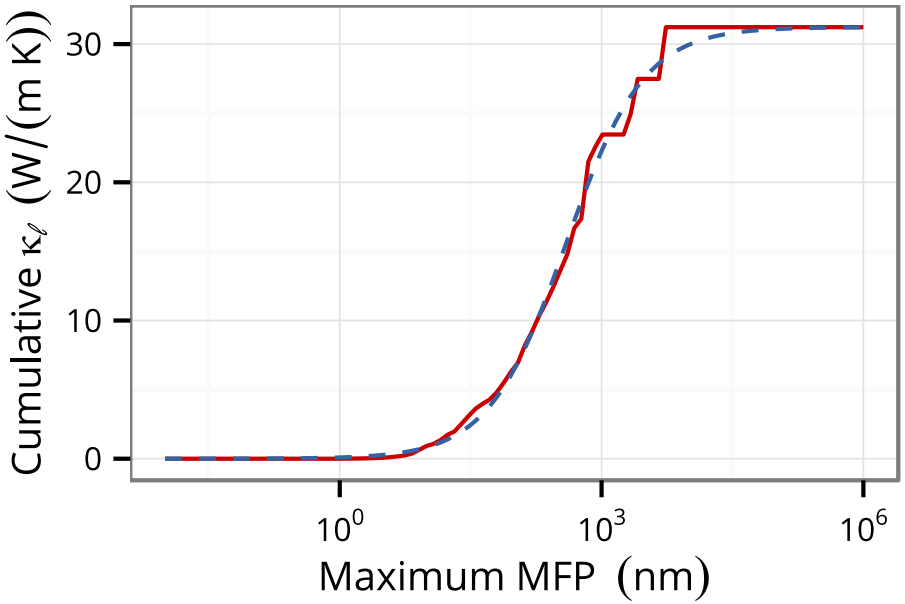
$$\sigma^2_W \simeq \sum_\mu \left(\frac{\partial W}{\partial \mathrm{q}'^\mu}\right)^2 E\left\{\left(\mathrm{q}'^\mu - \mathrm{q}'^\mu_0\right)^2\right\} = \frac{1}{\sqrt{12}} \sqrt{\sum_\mu \left[\sum_\alpha \left(v^\alpha_{\lambda'} - v^\alpha_{\lambda''}\right) \frac{Q^\alpha_\mu}{N_\mu}\right]^2}$$

Some results: Si

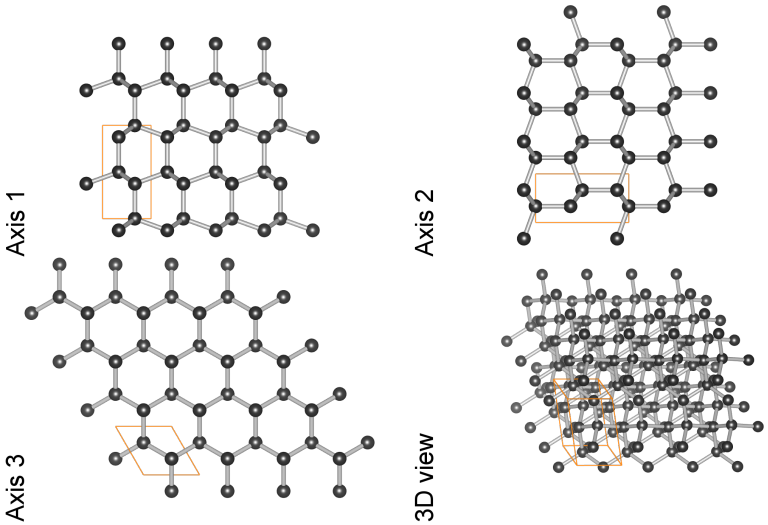


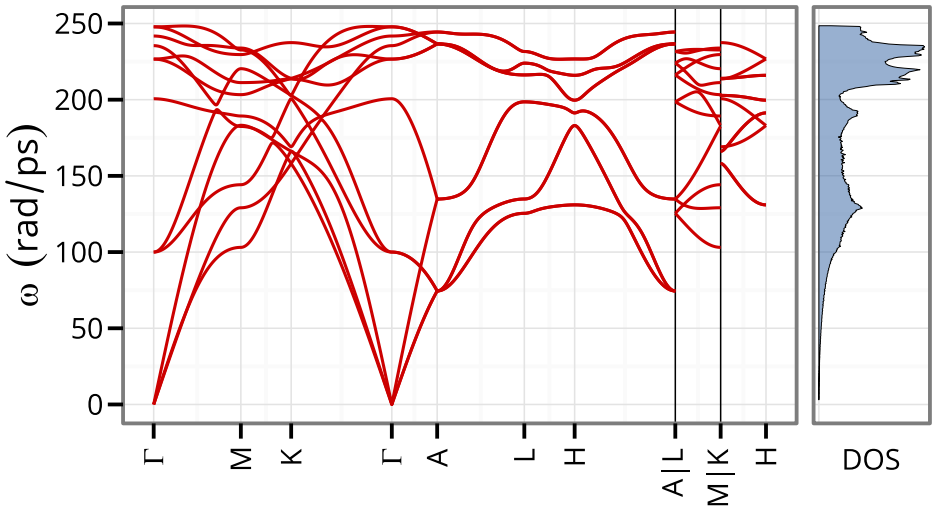
Some results: InAs





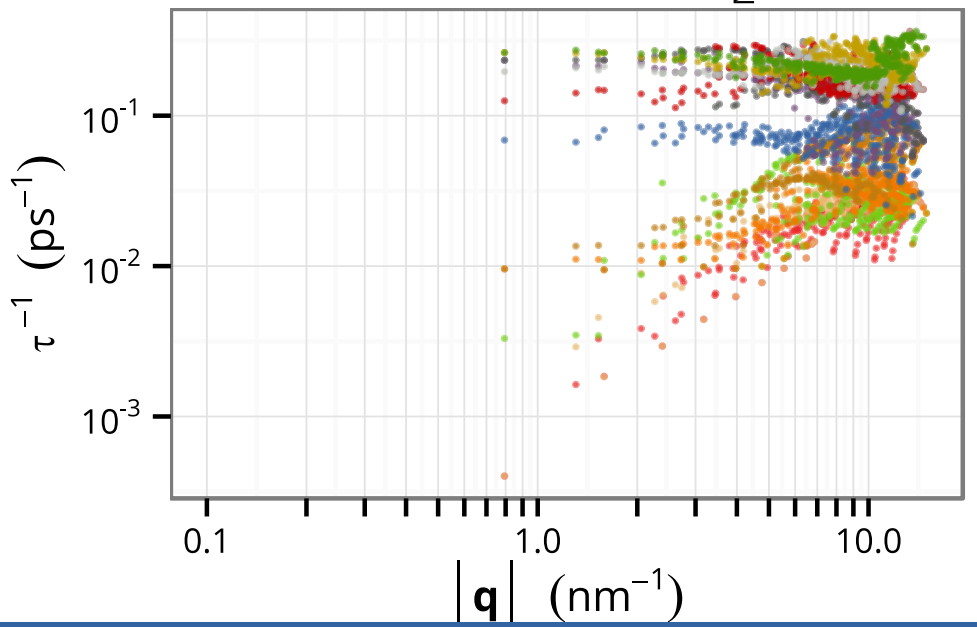
Some results: Lonsdaleite





At 300 K:

- $\kappa_{\parallel} = 1500\,\mathrm{W/(m\,K)}$
- $\kappa_{\perp} = 1270\,\mathrm{W/(m\,K)}$

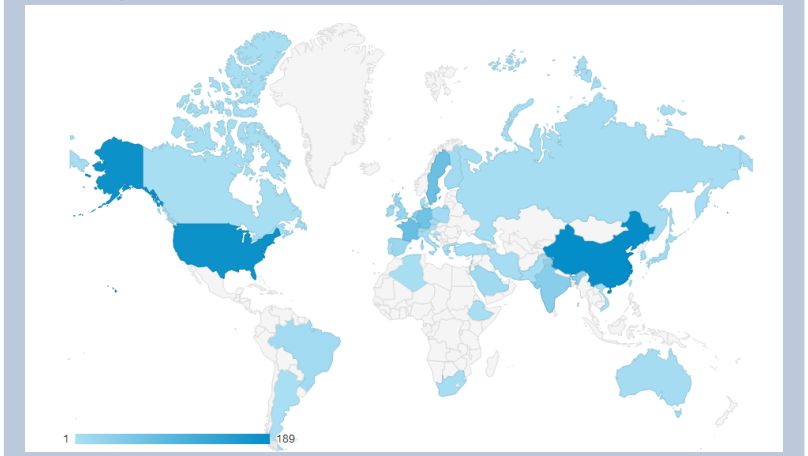


ShengBTE

Our GPL program can:

- Compute κ_ℓ from first principles
- Deal with arbitrary structures
- Yield plenty of additional information: c_v, small-grain conductivity, scattering rates, cumulative κ_ℓ…
- Treat ``thick'' nanowires with diffusive boundaries
- Use harmonic information from VASP or QE

`http://www.shengbte.org`



~ 800 downloads in the first month

Wu Li, J. Carrete, N. A. Katcho & N. Mingo, *Comp. Phys. Comm.* (in press)

A complementary script for third-order calculations is also available for download.

Scaling up: problems and solutions

The problem

The method is very precise but:

- ~ 300 DFT runs needed for a simple unit cell
- 99% of time spent in third-order calculations
- Very conservative estimate:
$$300 \frac{\text{tasks}}{\text{compound}} \times 32 \frac{\text{processors}}{\text{task}} \times 4 \frac{\text{CPU h}}{\text{processor}} \times \frac{\$0.01}{1 \text{ CPU h}} \sim \frac{\$400}{1 \text{ compound}}$$

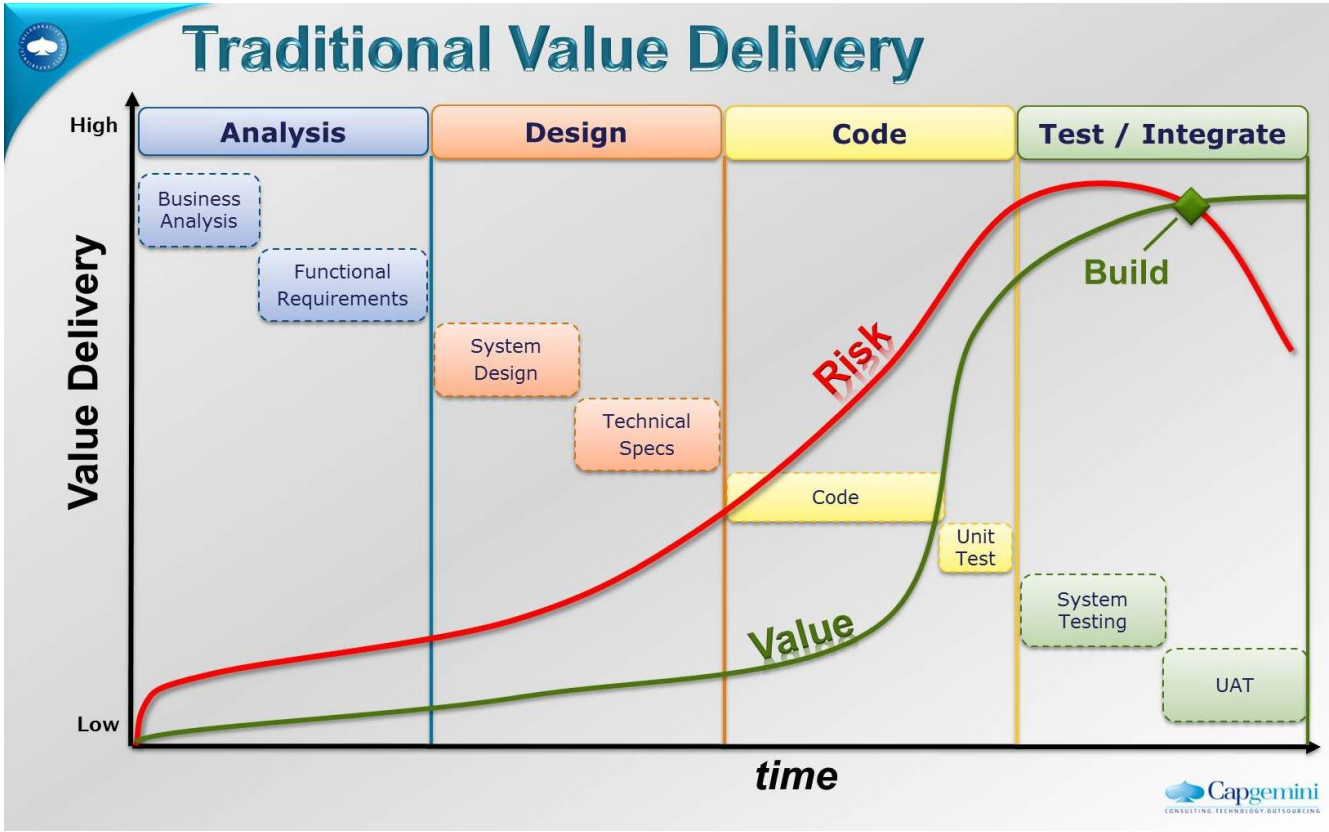
Situations where hundreds of κ_ℓ values are needed are not uncommon:

- High-throughput studies
- Parametric explorations (pressure, strain, defect concentration…)

Added problem: good IFCs are needed for a good value of κ_ℓ; IFCs depend on a good structural minimization, which depends on a good DFT description.

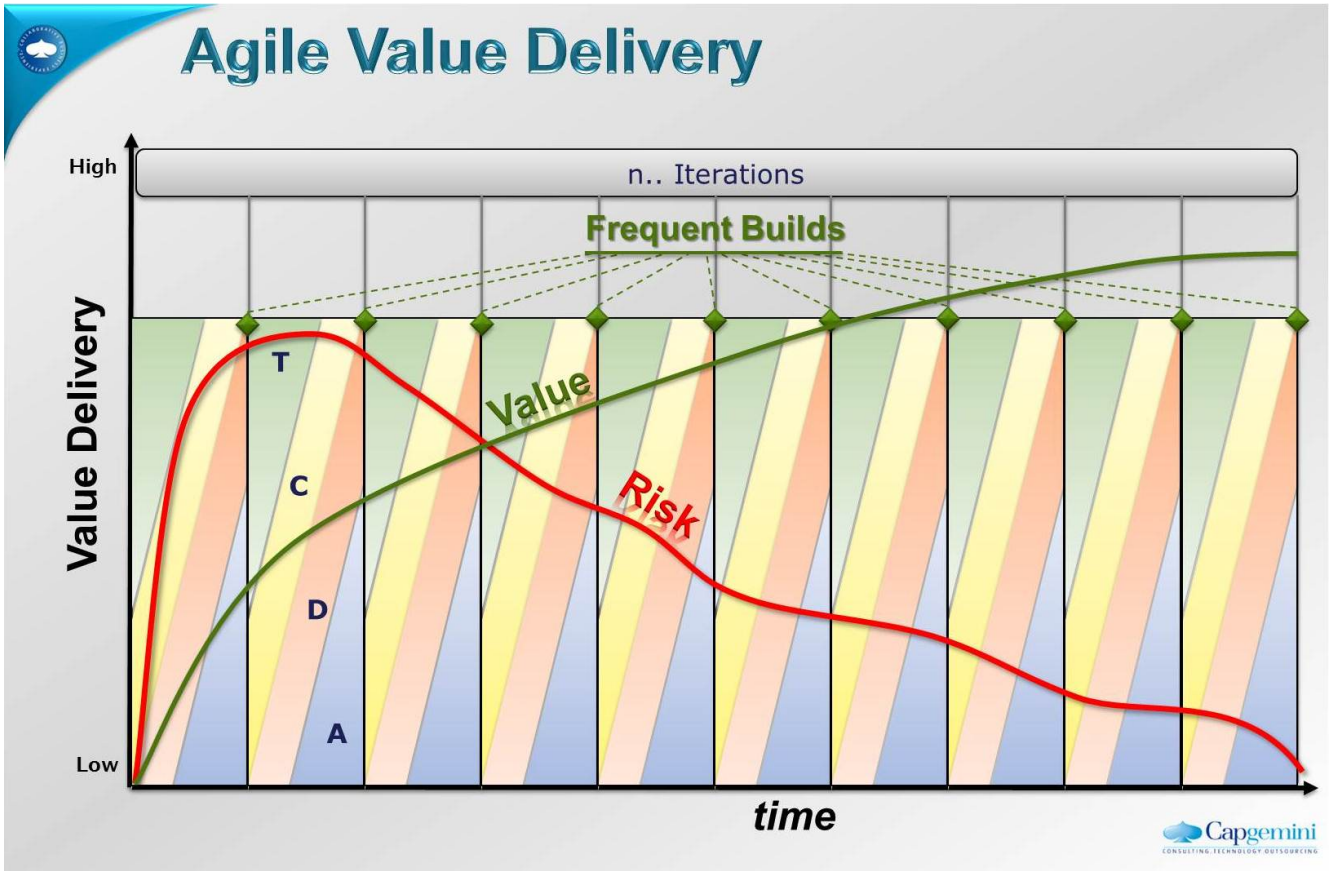
Hints from project management: Waterfall

Simply chaining computation steps and checking κ_ℓ at the end $\Rightarrow$ Setting oneself up for failure



Hints from project management: Agile

Test-driven process ⇒ Incremental growth in scientific value

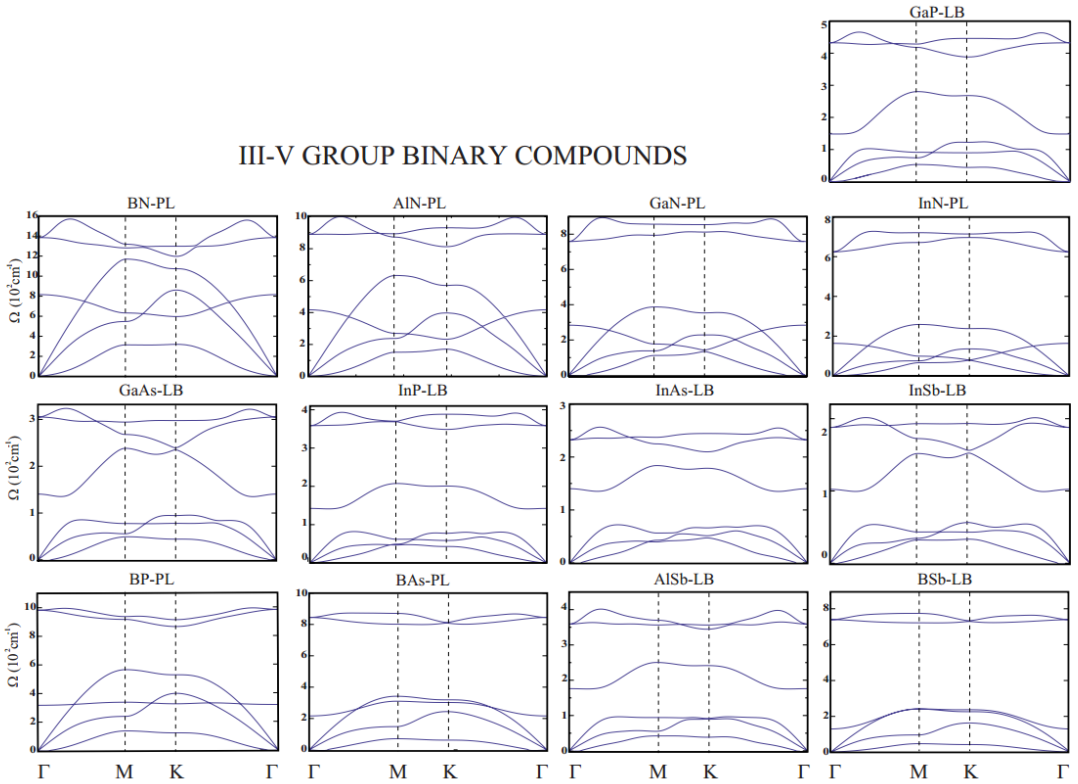


Best points to test: relaxation (very fast), harmonic properties ($< 1\%$ of the cost)

Theoretical uncertainties as an obstacle to testing

A convex acoustic mode close to Γ is usually a sign of trouble in 3D systems. In 2D systems it is the norm.

Unsolved question: Can the convex acoustic mode have a nonzero speed of sound?



Source: Ciraci and coworkers, *Phys. Rev. B* 80 (2009) 155453

Theoretical uncertainties as an obstacle to testing

Arguments for $c = 0$

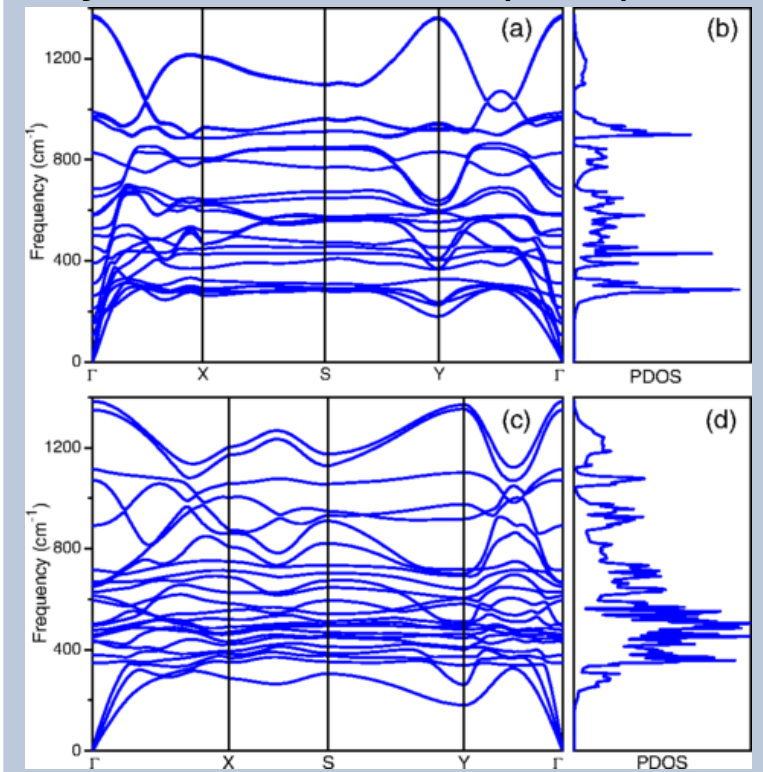
- Easy to prove analytically for graphene
- Simulation data for graphene-like materials
- True in a continuum description: flexural Lamb mode ($v_g \propto \sqrt{\omega}$)

Not available yet

- Theoretical result for atomistic systems
- General implementation of rotational sum rules:
  1. Born-Huang (1954)
  2. Gazis-Wallis (1960)
  3. Wang-Zhang-Wu (2007)

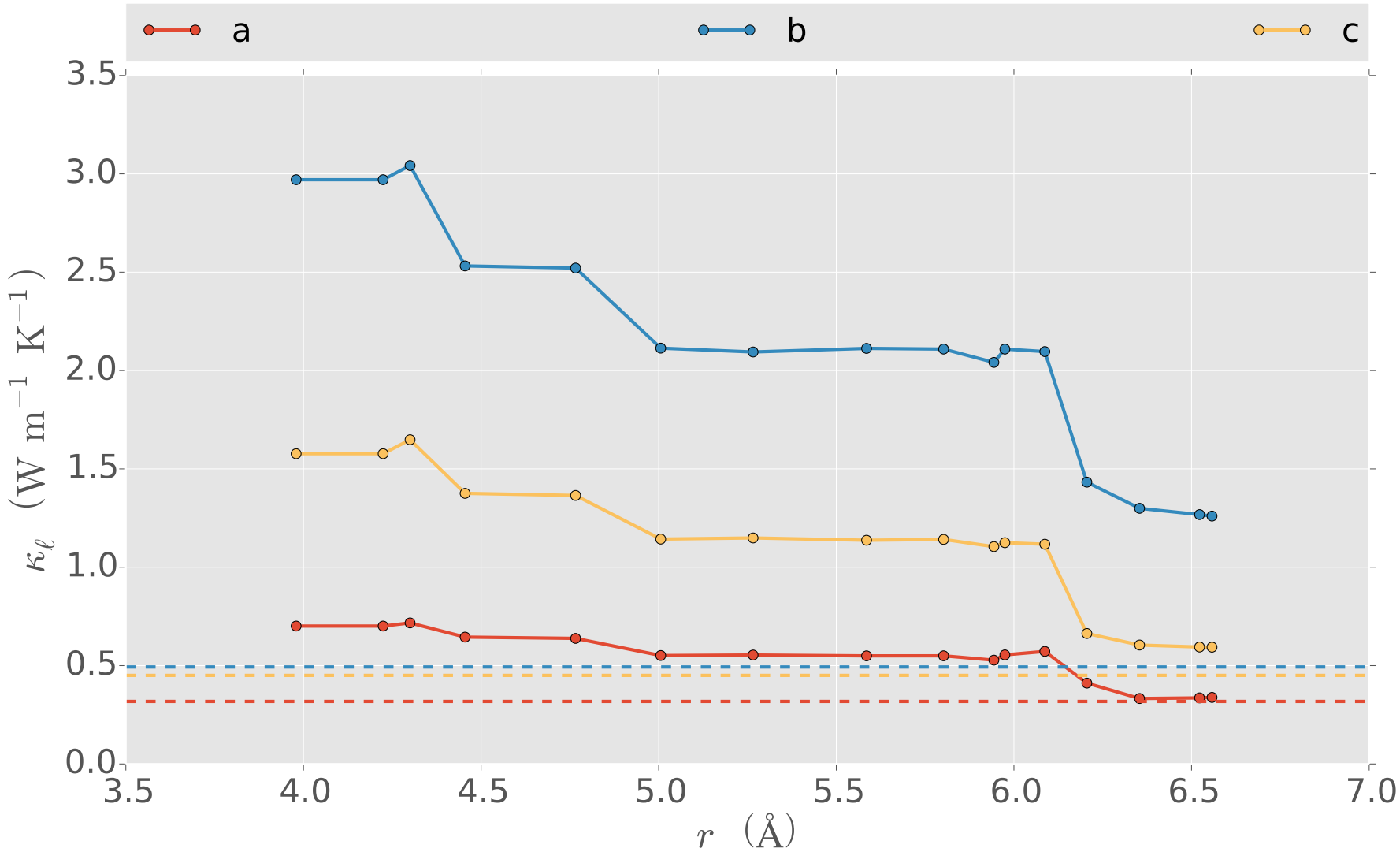
A counterexample

Zhou *et al.*,
Phys. Rev. Lett. 112 (2014) 085502

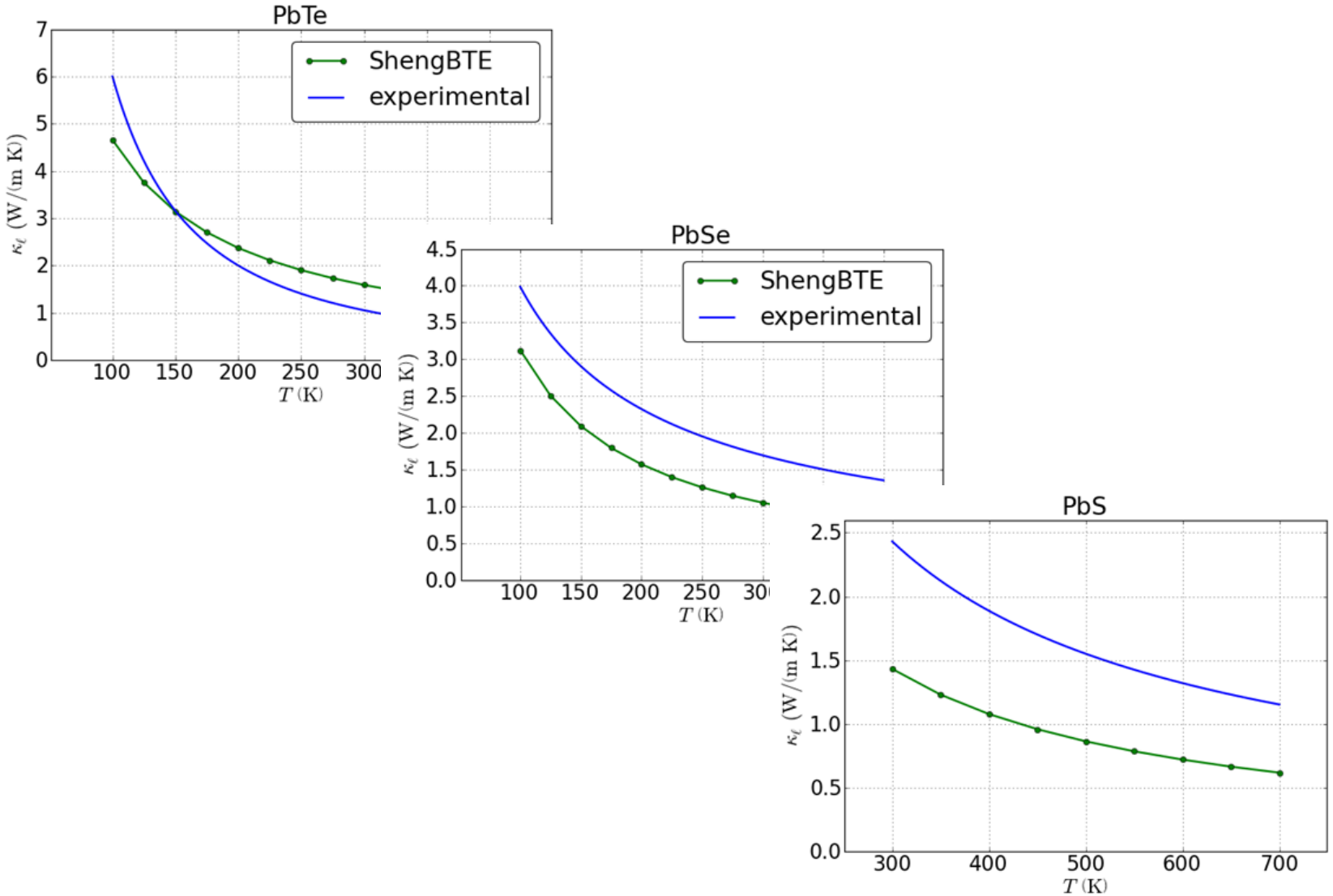


For two finite-thickness 2D phases of boron

Convergence with respect to force cutoff

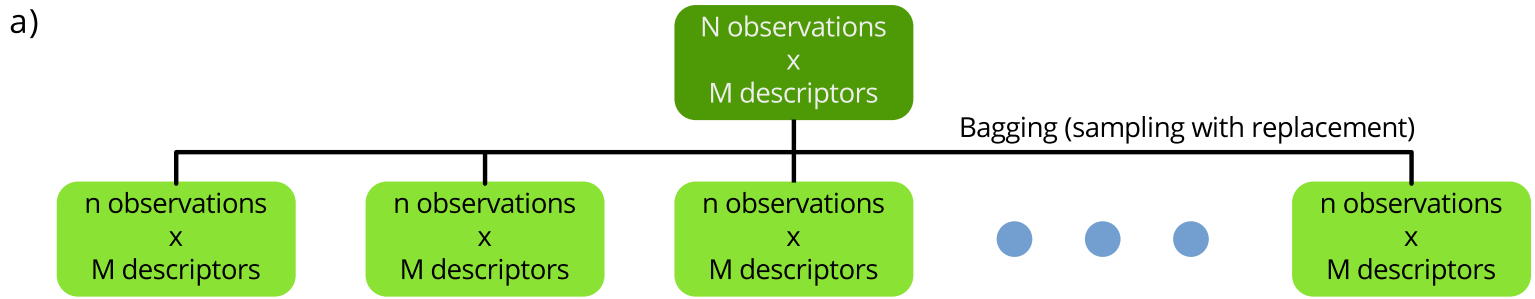


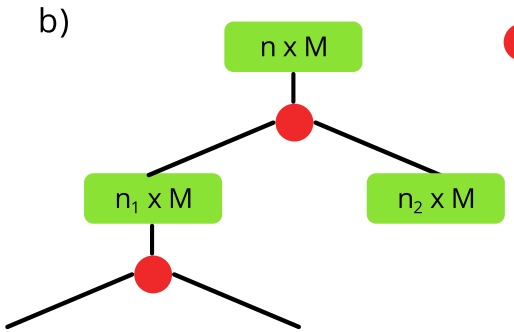
The importance of electronic structure



Solution: spin-orbit coupling [G. Chen and coworkers, *Phys. Rev. B* 85 (2012) 184303]

Avoiding 3rd-order calculations through machine learning: Random forests





= random selection of
m << M descriptors
+
optimal split

c) Run new data down all trees and obtain prediction:
- From majority (classification)
- From average (regression)

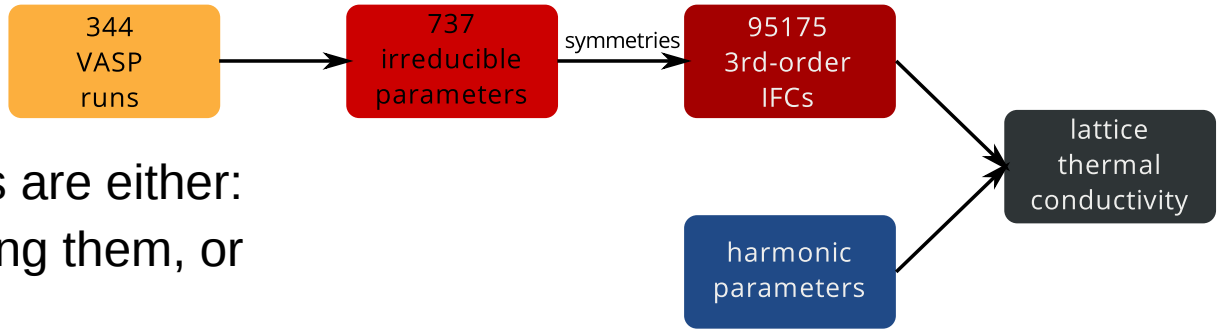
Advantages:

- Resistant to overfitting
- Can handle correlated inputs
- Intrinsic importance metric
- No need for cross-validation

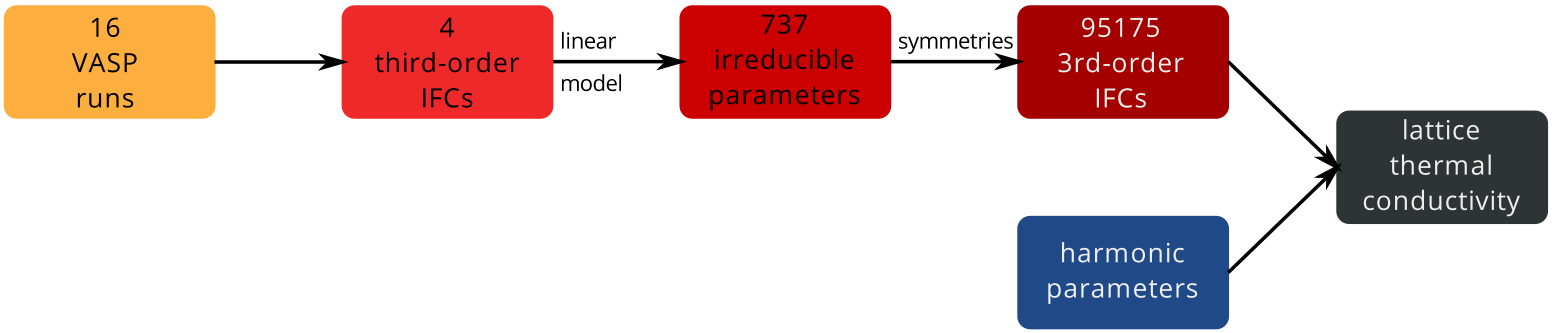
Limitations:

- Prediction bounded by training data
- Centralizing effect

Avoiding 3rd-order calculations through machine learning: κ_ℓ from 4 IFCs in half Heuslers



- Many of the 737 parameters are either:
  - Strongly correlated among them, or
  - Too small to matter
- Analysis of the training set:
  - Principal component analysis: 4 components explain $\sim 99\%$ of the variance
  - Those components can be computed from 4 large, weakly correlated constants
  - Linear regression of the 737 on those 4
  - Net effect: partial least squares regression



Performance of κ_4

	$\kappa_\ell \left(\frac{\mathrm{W}}{\mathrm{m\,K}}\right)$	$\kappa_4 \left(\frac{\mathrm{W}}{\mathrm{m\,K}}\right)$
AgBaSb	0.24	0.17
AgKTe	0.51	0.52
AgNaTe	2.00	1.70
BeNaP	4.10	6.20
BiBaK	2.20	1.20
BiKSr	2.00	2.00
BiLiSr	3.00	2.40
CoAsZr	24.00	28.00
CoBiHf	19.00	22.00
CoSbZr	25.00	24.00
CoScSe	15.00	16.00
CoSiTa	38.00	37.00
FeNbP	110.00	49.00
GeCaZn	2.70	2.80
GeNaY	8.10	8.20
InBaSr	0.58	1.20
InCdY	4.10	4.40
IrPTi	27.00	41.00

	$\kappa_\ell \left(\frac{\mathrm{W}}{\mathrm{m\,K}}\right)$	$\kappa_4 \left(\frac{\mathrm{W}}{\mathrm{m\,K}}\right)$
NiPbTi	110.00	26.00
NiSbSc	20.00	16.00
NiSnTi	18.00	17.00
NiSnZr	20.00	17.00
OsSbTa	27.00	29.00
PdAsY	5.50	4.30
PdSrTe	1.20	0.68
PtGaTa	33.00	32.00
PtGeTi	17.00	27.00
PtInNb	17.00	13.00
RhHfSb	22.00	21.00
RhNbSi	15.00	27.00
RuAsV	24.00	30.00
SbCaK	2.70	2.50
SiCdSr	14.00	3.50
SnBaSr	2.00	1.60
TeAgLi	1.50	1.90
TlLaMg	12.00	10.00

Repeated 2-fold cross-validation shows robustness with respect to the choice of training set

J. Carrete, Wu Li, N. Mingo, S. Wang & S. Curtarolo, *Phys. Rev. X* 4 (2014) 011019.

n-phonon, higher-order processes

Experimental $\kappa_\ell(T)$ curves can be steeper than $1/T$:

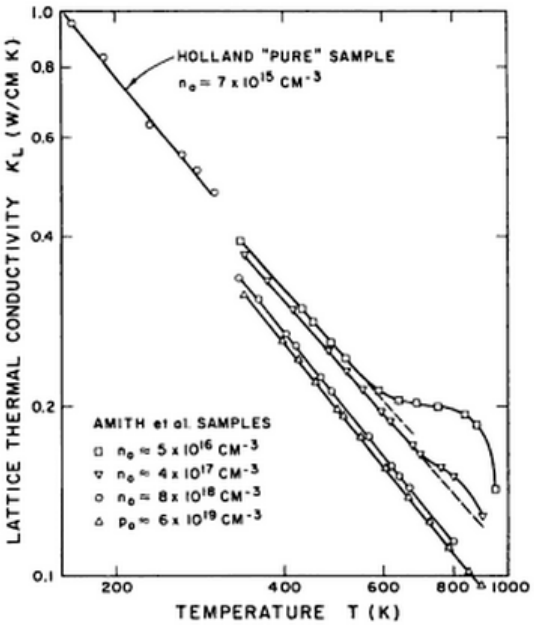


FIG. 17. Lattice conductivity $\kappa_L(T)$ in the range 340–950 K, as measured by Amith *et al.*[106] for three *N*- and one *P*-type GaAs monocrystal sample. Also, at upper left, the higher temperature portion of $\kappa_L(T)$ as measured by Holland[104] for a lightly doped sample.

Source: J. S. Blakemore (ed.), *Gallium Arsenide*, Springer, 1961.

The treatment of anharmonicity in the BTE framework presented here is incomplete:

- Only three-phonon processes
- First-order perturbation theory

Four-phonon processes and second-order three-phonon terms can partially explain the observations [D. J. Ecsedy and P. G. Klemens, *Phys. Rev. B* 15 (1977) 5957].

Ab-initio approaches to these terms involve formidable computational challenges.

Complex unit cells

Sometimes $1/T$ is too steep. High/temperature plateaus have been measured

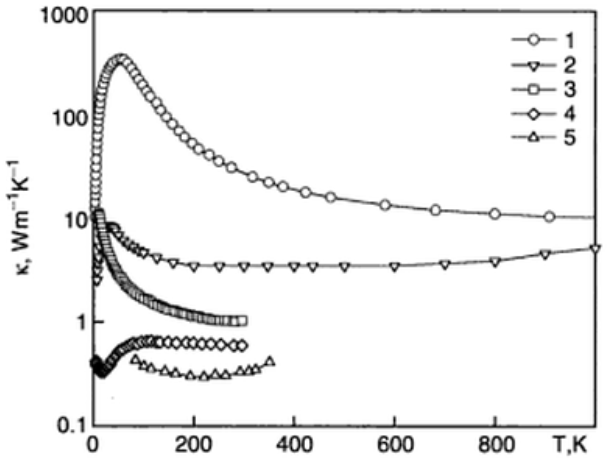


FIGURE 6.1 Temperature dependencies of thermal conductivity of some materials with a complex crystal structure: 1, β-B[1]; 2, $MnSi_{1.7}$[2]; 3, Cs_8Sn_{44}[3]; 4, $Eu_8Ga_{16}Ge_{30}$[3]; 5, Ag_8SnSe_6.[4]

Source: Zaitsev & Fedorov in *Thermoelectrics Handbook: Macro to Nano*, CRC Press, 2005.

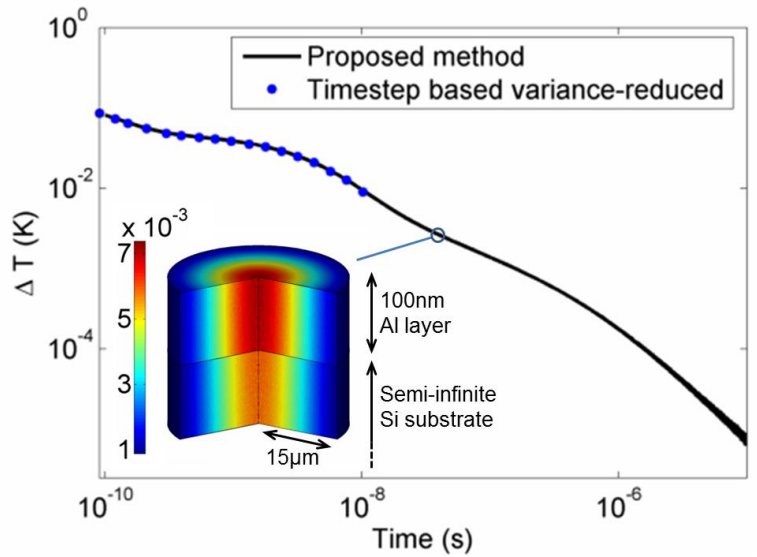
- ``Minimum thermal conductivity'' models (Cahill, Slack) are merely qualitative
- Predictive models for amorphous materials may be needed

Space- or time-dependent problems

Great practical interest:

- Thermo-reflectance experiments
- Nanostructures
- Electronic devices

Space- and time-dependent BTE affected by the ``curse of dimensionality''.
6-dimensional $(\boldsymbol{r}, \boldsymbol{p})$ space.



Source: Hadjiconstantinou group,

`http://web.mit.edu/ngh-group/research2-phonon.html`

Proposed approaches:

- Averaging schemes [Wu Li *et al.*, *Phys. Rev. B* 85 (2012) 195436]
- Sparse bases / wavelet methods (V. Peikert, PhD. thesis, ETH Zurich, 2013)
- Variance-reduced Monte Carlo [J-P. M. Péraud & N. G. Hadjiconstantinou, *Phys. Rev. B* 84 (2011) 205331]

Conclusions

Conclusions

- The thermal conductivity of crystals and alloys can be computed from first principles using a BTE-based approach
- This method offers an attractive cost/predictive power tradeoff
- All the tools needed to complete this workflow are available under open source licenses
- When performing many calculations, checking the result of every intermediate step is crucial to avoid wasting CPU time
- Some important challenges remain open, including:
  - Space- and time-dependent problems
  - Complex unit cells
  - Higher-order anharmonicity
  - Amorphous materials

Ab-initio lattice thermal conductivity calculations for large libraries of compounds: challenges and strategies

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