Thermal Transport Calculations for Crystals and nanostructures based on the Boltzmann Transport Equation

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2023-06-14

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A workflow for the thermal conductivity of bulk crystalline solids

# 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 $ZT = \frac{\sigma S^2}{\kappa} T$
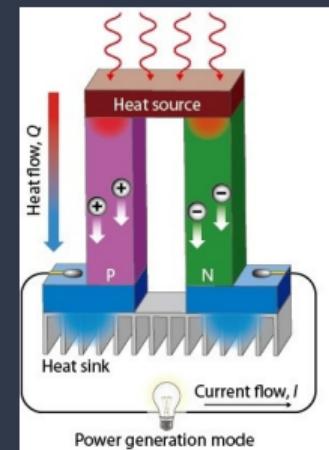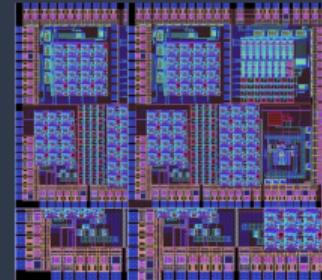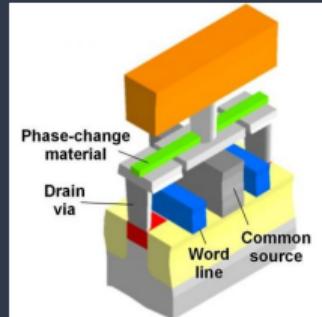
κ_ℓ is the dominant factor in common scenarios

Lattice-dynamical calculations

A truncated power-series potential energy model

$$E_{\text{pot}} = E_0 + \frac{1}{2!} \sum_{\substack{a,b \\ \alpha,\beta}} \phi_{ab}^{(\alpha\beta)} x_a^{(\alpha)} x_b^{(\beta)} + \frac{1}{3!} \sum_{\substack{a,b,c \\ \alpha,\beta,\gamma}} \phi_{abc}^{(\alpha\beta\gamma)} x_a^{(\alpha)} x_b^{(\beta)} x_c^{(\gamma)} + \frac{1}{4!} \sum_{\substack{a,b,c,d \\ \alpha,\beta,\gamma,\delta}} \phi_{abcd}^{(\alpha\beta\gamma\delta)} x_a^{(\alpha)} x_b^{(\beta)} x_c^{(\gamma)} x_d^{(\delta)} + \ldots$$

Symbols:

- $a, b, c, d \ldots$: atom indices
- $\alpha, \beta, \gamma, \delta \ldots$: Cartesian directions
- $x_a^{(\alpha)}$: Atomic displacements from the energy minimum
- $\phi_{a_1 a_2 a_3 \ldots a_k}^{(\alpha_1 \alpha_2 \alpha_3 \ldots \alpha_k)}$: k-th order interatomic force constant (IFC)

Most basic incarnation: $\phi_{a_1 a_2 a_3 \ldots a_k}^{(\alpha_1 \alpha_2 \alpha_3 \ldots \alpha_k)} = \dfrac{\partial^k E_{\text{pot}}}{\partial x_{a_1}^{(\alpha_1)} \partial x_{a_2}^{(\alpha_2)} \partial x_{a_3}^{(\alpha_3)} \ldots \partial x_{a_k}^{(\alpha_k)}}$

The lattice thermal conductivity in ordered, weakly anharmonic semiconductors

- Two ingredients:
  - Phonon band structure (from $\phi_{ab}^{\alpha\beta}$)
 - Phonon scattering (from $\phi_{abc}^{\alpha\beta\gamma}$)

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

- Scattering $\simeq$ anharmonic + isotopic
- F_λ satisfies the linearized Boltzmann transport equation for phonons

$$F_\lambda = \tau_\lambda^0 (v_\lambda + \Delta_\lambda)$$

- Coefficients determined by
  - Allowed 3ph processes
  - Third-order IFCs

Example workflow:
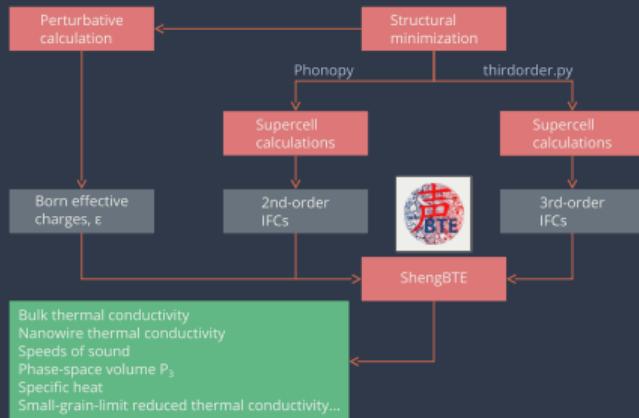


> 99% of time spent on the third-order part

Details: Wu Li, J. Carrete, N. A. Katcho, N. Mingo, Computer Physics Communications **185** (2014) 1747–1758

SiC, 3C phase
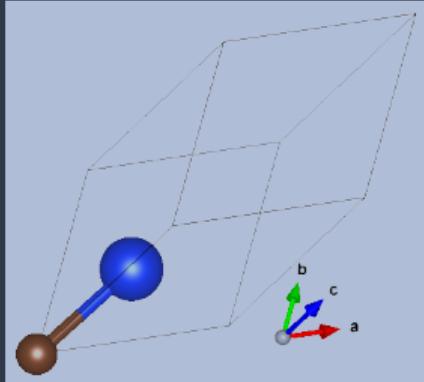
SiC, 6H phase
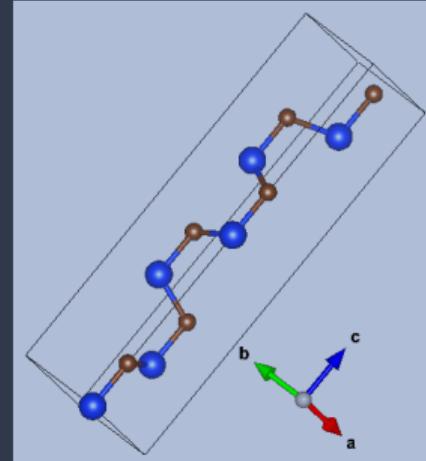

- 216 DFT runs
- 56754 third-order IFCs

- 1644 DFT runs
- 355752 third-order IFCs

Comparison with experiment: InAs
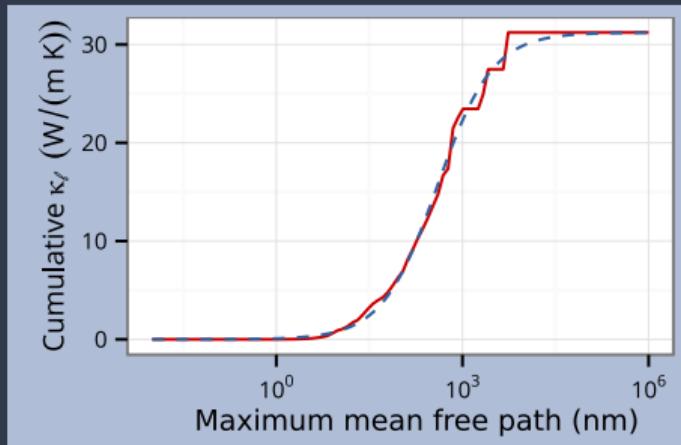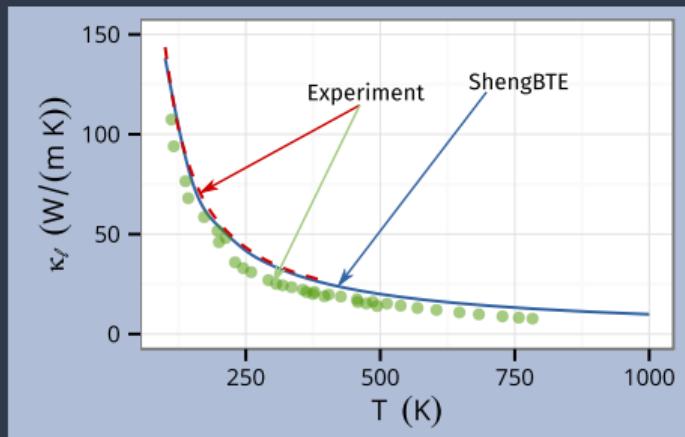
- Typically within $5\% - 10\%$
- Very detailed results
- Predictive for not-yet-measured systems

[W. Li, J. Carrete, N. A. Katcho & N. Mingo, Comput. Phys. Commun. 185 (2014) 1747]

Beyond this model
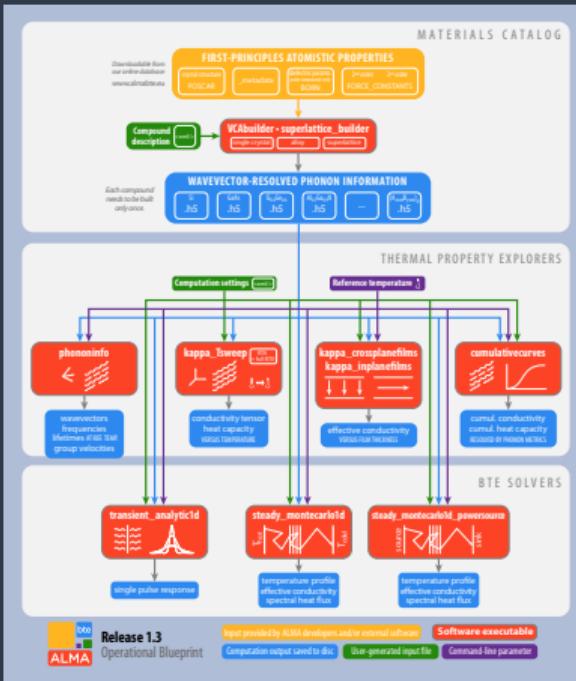
[J. Carrete et al.,
Comput. Phys. Commun. 220 (2017) 351]

Scattering and Green's functions

Bounded defect (vacancy, substitution, insterstitial, antisite...)
$\implies$ broken translation symmetry
$\implies$ elastic phonon scattering rates:

$$\Gamma_{\lambda\lambda'} = \frac{\pi}{\omega_\lambda}\left|\left\langle\phi_\lambda'\left|t^+\right|\phi_\lambda\right\rangle\right|^2\delta\left(\omega_{\lambda'}^2 - \omega_\lambda^2\right)$$

- T matrix: $t^+ = V\left(1 - g^+V\right)^{-1}$
- Perturbation matrix: $V \coloneqq \phi_{2,\text{system}} - \phi_{2,\text{reference}}$
- Causal Green's function: $g^+(\omega) \coloneqq \lim_{\eta \longrightarrow 0^+}\left[\left(\omega^2 + i\eta\right)\mathbf{1} - K\right]^{-1}$
- Fermi's golden rule recovered only when $\left|g^+V\right| \ll 1$
- V requires big supercells, careful relaxation, different charge states...

Comparison with experiments:
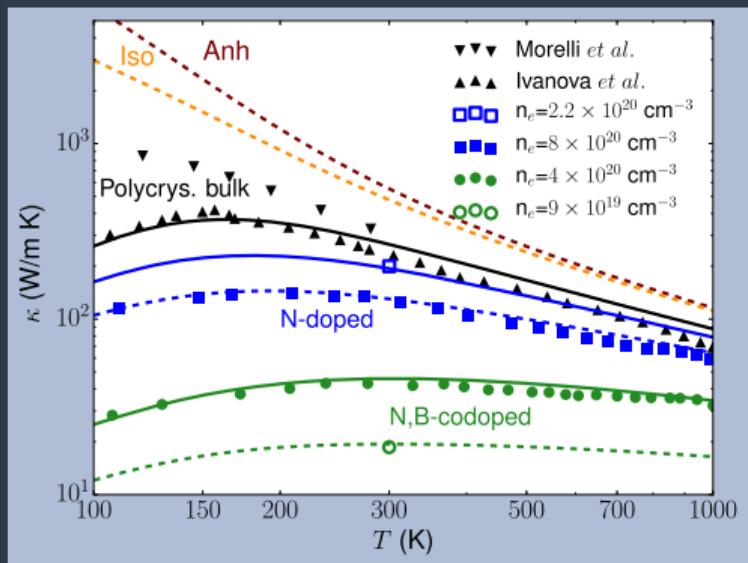
Boron as a superscatterer:
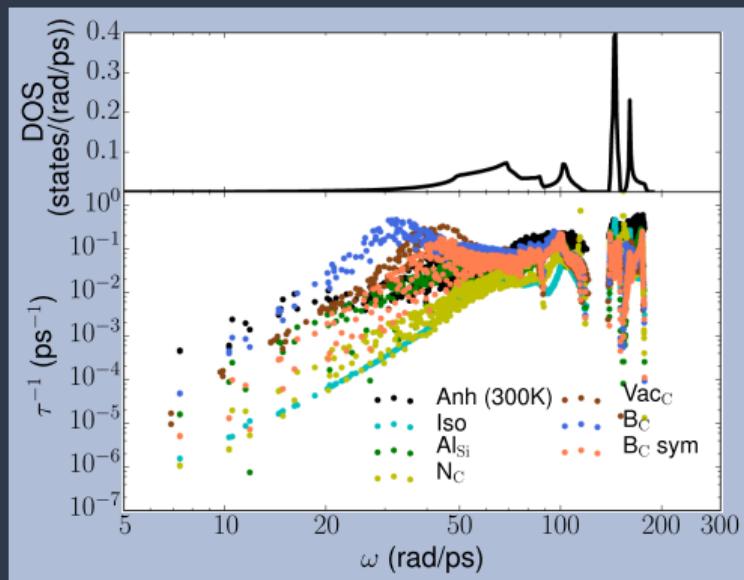
[A. Katre, J. Carrete, B. Dongre, G. K. H. Madsen & N. Mingo, Phys. Rev. Lett. 119 (2017) 075902]
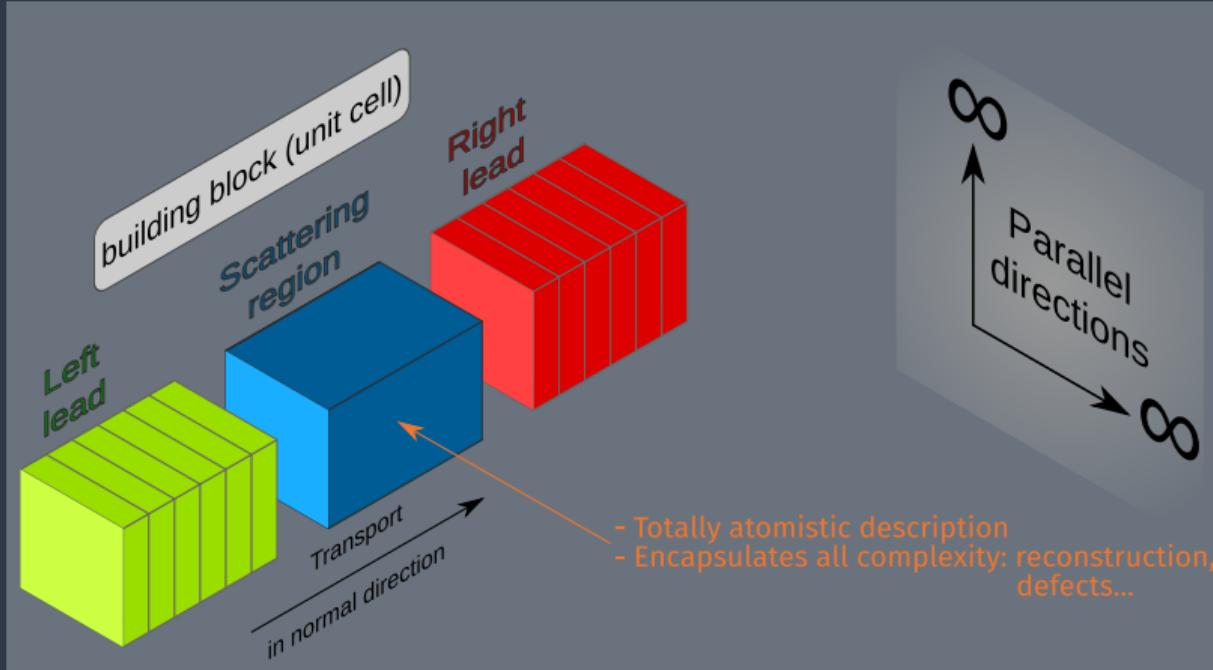
- Requires harmonic IFCs for building blocks of leads + scattering region
- Full details of stable implementation:
  Z.-Y. Ong, J. Appl. Phys., 124 (2018) 151101

"Phase" and "twin" interfaces in GaP
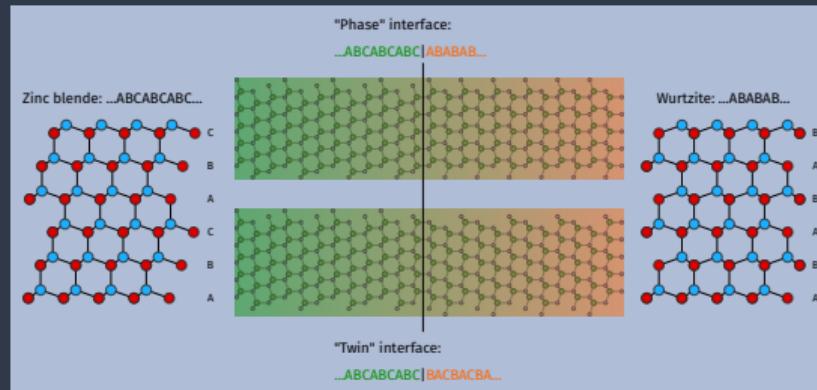
Mode-to-mode transmission as a function of $\omega \left(\text{rad ps}^{-1} \right)$
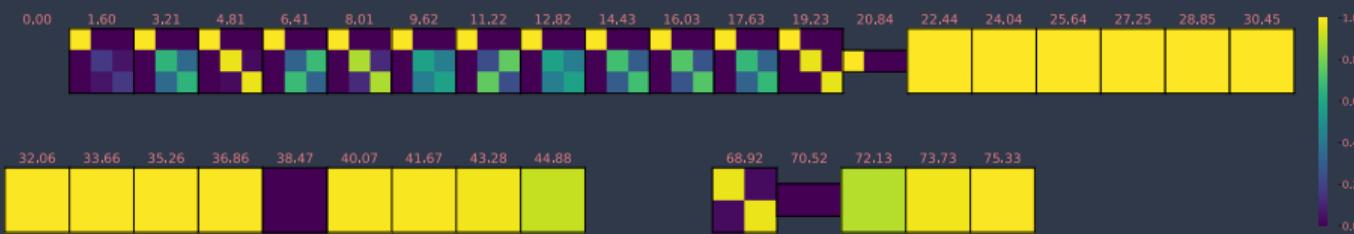
[J. Carrete, M. López-Suárez, M. Raya-Moreno, A. S. Bochkarev, M. Royo, G. K. H. Madsen, X. Cartoixà, N. Mingo & R. Rurali *et al.*, Nanoscale 11 (2019) 16007–16016]

Effective harmonic potentials
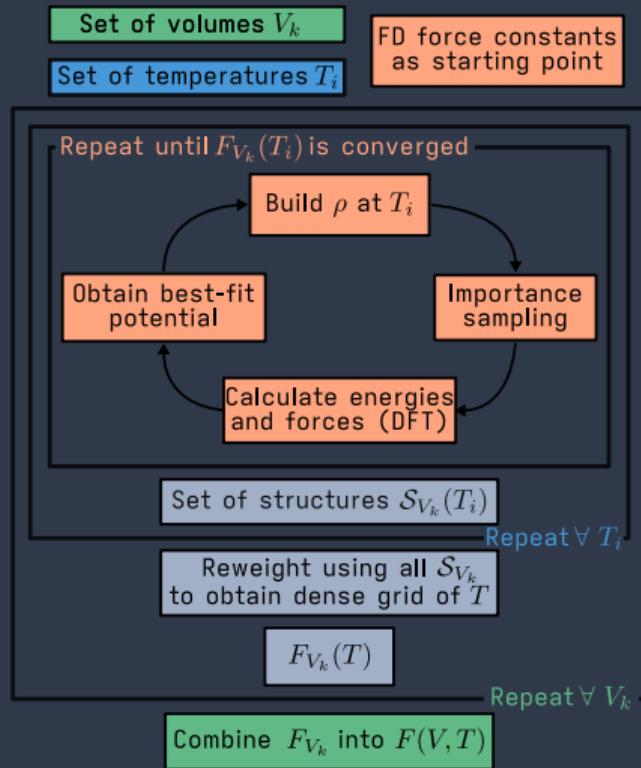
Try to combine:

- Simplicity of harmonic models
- Flexibility of arbitrary IFCs

Common uses:

- Vibrations in finite-T phases [e.g.: cubic perovskites, Phys. Rev. Materials 4 (2020) 113804]
- Strongly T-dependent vibrational frequencies
- Thermodynamic phase stability

Different approaches, like:

- Perturbation theory + fourth-order IFCs
- Minimization of free-energy functional
- Self-consistency between real-space distribution function and forces

Ultrahigh Thermal Conductivity of θ-Phase Tantalum Nitride

Ashis Kundu,[1,2] Xiaolong Yang,[1,2] Jinlong Ma,[1,4] Tianli Feng,[3,6] Jesús Carrete,[5]
Xiulin Ruan,[7] Georg K. H. Madsen,[5] and Wu Li[1,*]

Extracting long-lasting performance from electronic devices and improving their reliability through effective heat management requires good thermal conductors. Taking both three- and four-phonon scattering as well as electron-phonon and isotope scattering into account, we predict that semimetallic θ-phase tantalum nitride (θ-TaN) has an ultrahigh thermal conductivity (κ) of 995 and 820 W m⁻¹ K⁻¹ at room temperature along the *a* and *c* axes, respectively. Phonons are found to be the main heat carriers, and the high κ hinges on a particular combination of factors: weak electron-phonon scattering, low isotopic mass disorder, and a large frequency gap between acoustic and optical phonon modes that, together with acoustic bunching, impedes three-phonon processes. On the other hand, four-phonon scattering is found to be significant. This study provides new insight into heat conduction in semimetallic solids and extends the search for high-κ materials into the realms of semimetals and noncubic crystal structures.
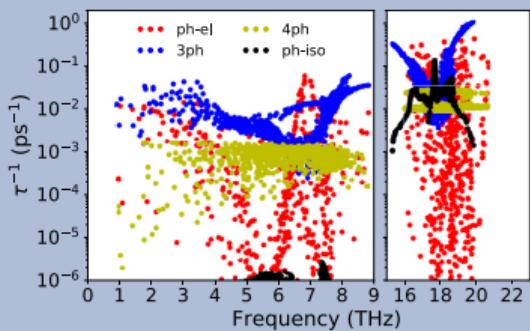
FIG. 3. Calculated three-phonon (3ph), four-phonon (4ph), phonon-isotope (ph-iso), and phonon-electron (ph-el) scattering rates for TaN at 300 K.
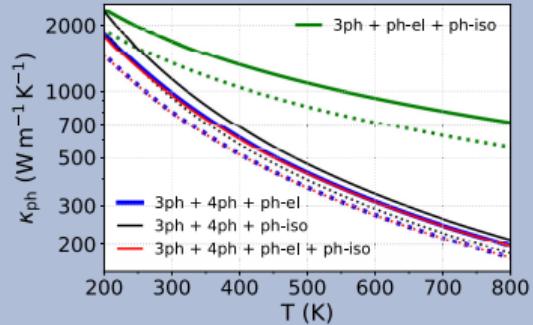

FIG. 4. Temperature dependence of κ_{ph} in TaN when only certain combinations of phonon scattering mechanisms are considered. The solid and dotted lines correspond to the κ_{ph} along the *a* and *c* axes, respectively.

The machine-learning revolution

$$f_a^{(\alpha)} = -\sum_{\substack{b \\ \beta}} \phi_{ab}^{(\alpha\beta)} \underbrace{x_b^{(\beta)}}_{\text{inputs}} - \frac{1}{2!} \sum_{\substack{b,c \\ \beta,\gamma}} \phi_{abc}^{(\alpha\beta\gamma)} \underbrace{x_b^{(\beta)} x_c^{(\gamma)}}_{\text{inputs}} - \frac{1}{3!} \sum_{\substack{b,c,d \\ \beta,\gamma,\delta}} \phi_{bcd}^{(\alpha\beta\gamma\delta)} \underbrace{x_b^{(\beta)} x_c^{(\gamma)} x_d^{(\delta)}}_{\text{inputs}} + \ldots$$

outputs

Accelerated workflow:

1. Randomly sample displacement space
2. Use all forces obtained from DFT for each configuration
3. Solve the underdetermined linear regression problems while promoting sparsity

Early work: F. Zhou et al., Phys. Rev. Lett. 113 (2014) 185501

Open-source implementation
[P. Erhart's group]:
https://hiphive.materialsmodeling.org

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A Differentiable Neural-Network Force Field for Ionic Liquids

Hadrián Montes-Campos, Jesús Carrete, Sebastian Bichelmaier, Luis M. Varela, and Georg K. H. Madsen

Cite This: *J. Chem. Inf. Model.* 2022, 62, 88−101

JCIM JOURNAL OF CHEMICAL INFORMATION AND MODELING
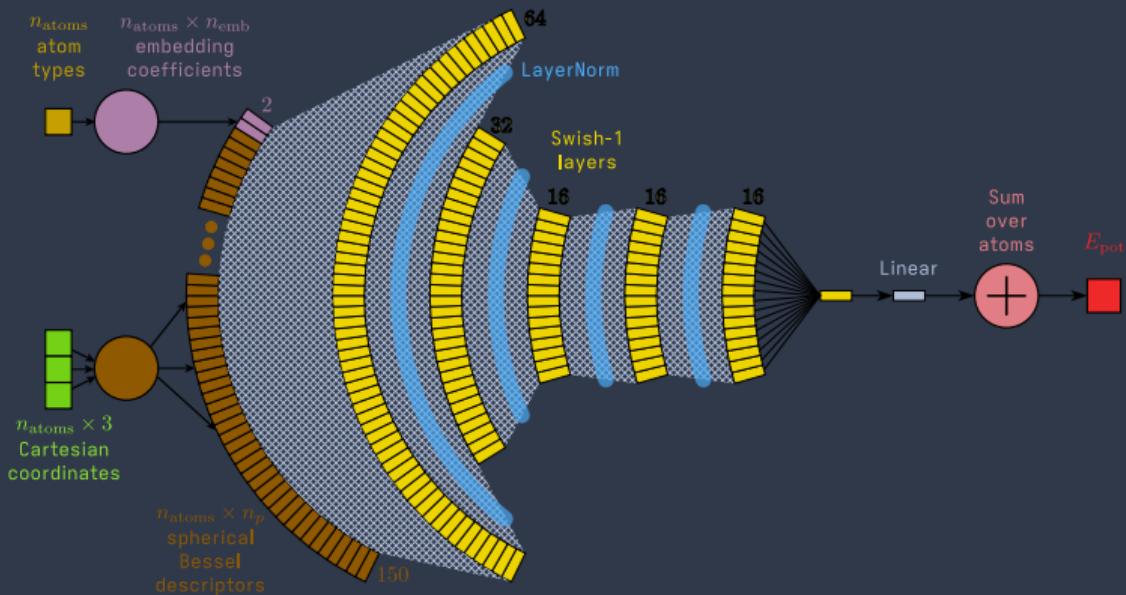
Behler-Parrinello model with some unique features

- End-to-end differentiability
- Orthogonal spherical Bessel descriptors
- 1-cycle learning rate schedule
- Modern activation function
- Normalization to avoid vanishing gradients

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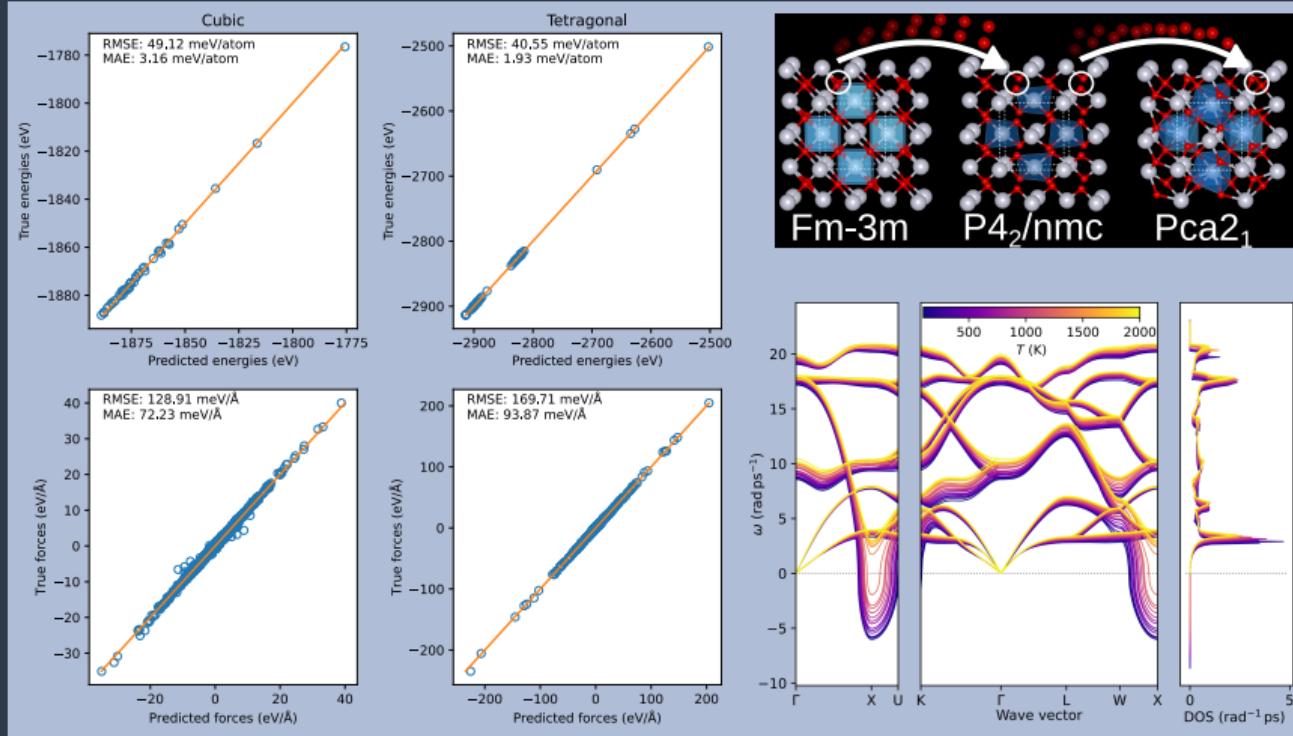
[S. Bichelmaier, J. Carrete, R. Wanzenböck, F. Buchner & G. K. H. Madsen, Phys. Rev. B 107 (2023) 184111]

NeuralIL is implemented on top

of

Features:

- Automatic differentiation
- Just-in-time compiler (fast code)
- Vectorization on CPUs, GPUs and TPUs

Foundation of new Google ML ecosystem: Flax, Optax...

AD implements two differential operators using the chain rule systematically:

$$f : \mathbb{R}^n \longrightarrow \mathbb{R}^m$$

- Jacobian-vector product (forward mode): $\mathrm{JVP}\big(f, x \in \mathbb{R}^n, u \in \mathbb{R}^n\big) \in \mathbb{R}^m$
- Vector-Jacobian product (reverse mode): $\mathrm{VJP}\big(f, x \in \mathbb{R}^n, v \in \mathbb{R}^m\big) \in \mathbb{R}^n$

Accurate like the function itself, almost as fast, easy and natural to use

Force constants from automatic differentiation

Lennard-Jones toy model

```python
#!/usr/bin/env python

import numpy.random as random
import jax
import jax.numpy as np

def lj_potential(positions):
    "Lennard-Jones potential in reduced units."
    # Compute all relative positions between pairs without iterating.
    delta = positions[:, np.newaxis, :] - positions
    # Take only the combinations of two different atoms.
    indices = np.triu_indices(positions.shape[0], k=1)
    delta = delta[indices[0], indices[1], :]
    # Compute the squared distances and evaluate the potential energy.
    r2 = (delta * delta).sum(axis=1)
    rm2 = 1. / r2
    rm6 = rm2 * rm2 * rm2
    rm12 = rm6 * rm6
    return (rm12 - 2. * rm6).sum()

lj_gradient = jax.jit(jax.grad(lj_potential))   # Automatic gradient function
lj_hessian = jax.jit(jax.hessian(lj_potential))  # Automatic Hessian function
lj_potential = jax.jit(lj_potential)  # Compiled potential function
test_positions = 5. * random.random_sample((20, 3))  # Put 20 particles in a cube of side 5.
e_pot = lj_potential(test_positions)
forces = -lj_gradient(test_positions)
hessian = lj_hessian(test_positions)
```

Same procedure regardless of complexity:

- Forces: gradient = single-shot VJP (row of Jacobian)
- Harmonic IFCs: column-by-column Jacobian of gradient (forward mode composed over reverse mode)
- ...

A truncated power series through nested JVPs

$$E_{\text{pot}} = E_0 + \frac{1}{2!} \sum_{\substack{a,b \\ \alpha,\beta}} \phi_{ab}^{(\alpha\beta)} x_a^{(\alpha)} x_b^{(\beta)} + \frac{1}{3!} \sum_{\substack{a,b,c \\ \alpha,\beta,\gamma}} \phi_{abc}^{(\alpha\beta\gamma)} x_a^{(\alpha)} x_b^{(\beta)} x_c^{(\gamma)} + \frac{1}{4!} \sum_{\substack{a,b,c,d \\ \alpha,\beta,\gamma,\delta}} \phi_{abcd}^{(\alpha\beta\gamma\delta)} x_a^{(\alpha)} x_b^{(\beta)} x_c^{(\gamma)} x_d^{(\delta)} + \dots$$

$$E_{\text{pot}} = \sum_{n=0}^{n_{\max}} \mathscr{T}_n(r_0, x), \text{ where } \mathscr{T}_0(r, t) = E_{\text{pot}}(r) \text{ and } \mathscr{T}_n(r, t) = \frac{1}{n} \frac{\partial \mathscr{T}_{n-1}(r, t)}{\partial r} \cdot t$$

- Trivial to implement
- Avoids catastrophic scaling of number of constants with order

Effective vibrational frequencies of LJ-6 cluster
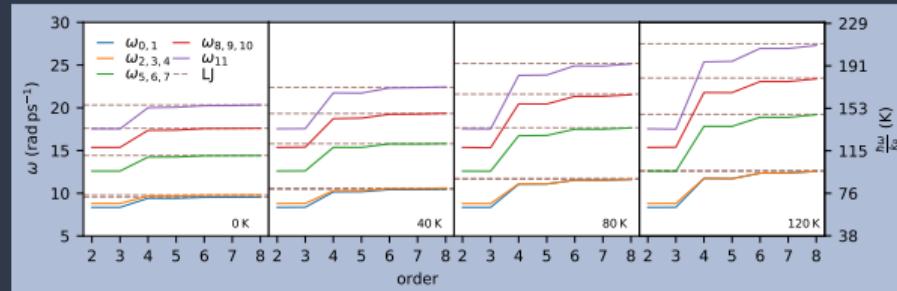
Thermal expansion of the LJ crystal:

[S. Bichelmaier, J. Carrete, G. K. H. Madsen, Int. J. Quantum. Chem. 123 (2023) e27095]

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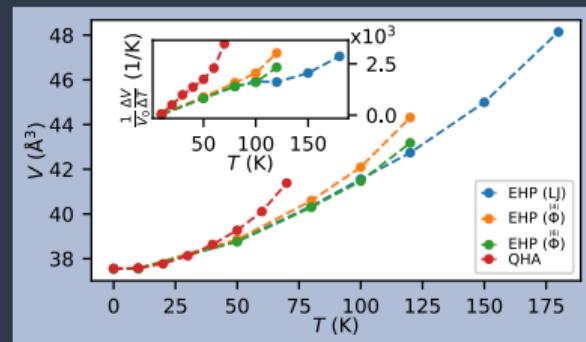
The dynamical matrix

Normal modes in reciprocal space

$$D(q)w_\lambda = \omega_\lambda^2 w_\lambda, \text{ with } D_{a,b}^{(\alpha\beta)}(q) = \frac{1}{\sqrt{m_a m_b}} \sum_{B} \phi_{0,a \atop B,b}^{(\alpha\beta)} e^{-iq \cdot R_B}$$

Each element of D is a vector-Hessian-vector product between:

- $\ell(a, \alpha)$: $\frac{1}{\sqrt{m_a}}$ for atom a and direction α in first unit cell, 0 everywhere else
- $r(q, b, \beta)$: $\frac{1}{\sqrt{m_b}} \exp(-iq \cdot R_B)$ for atom b and direction β in each unit cell B, 0 everywhere else

Implementation: JVP of JVP

```python
def uHv_complex(p, t, c, u, v):
    """Compute a vector-Hessian-vector product.

    Assume real u and complex v.
    """
    function = lambda x: energy_calculator(x, t, c)
    b_function = lambda x: jax.jvp(function, (x, ), (u, ))[1]
    re_braket = jax.jvp(b_function, (p, ), (v.real, ))[1]
    im_braket = jax.jvp(b_function, (p, ), (v.imag, ))[1]
    return re_braket + 1.j * im_braket
```

- Automatic and efficient
- Similar to DFPT
- Can be done irrep by irrep

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Even more derivatives!

A differentiable $D(q)$ provides automatic access to information within and beyond the harmonic approximation:

- Group velocities:

$$v_{g,\lambda}^{(\alpha)} = \frac{\partial \omega_\lambda}{\partial q^{(\alpha)}} = \frac{1}{2\omega_\lambda} w_\lambda^* \cdot \frac{\partial D(q)}{\partial q^{(\alpha)}} w_\lambda$$

- Grüneisen parameters:

$$\gamma_\lambda = -\frac{V}{\omega_\lambda} \frac{\partial \omega_\lambda}{\partial V} = -\frac{V}{2\omega_\lambda^2} w_\lambda^* \cdot \frac{\partial D(q)}{\partial V} w_\lambda$$

Extreme example:
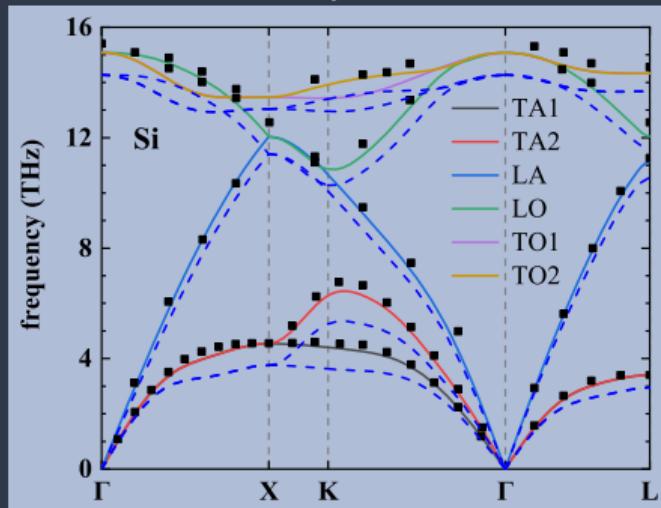
- Solid lines: computed Si spectrum
- Dashed lines: Si spectrum computed with Ge IFCs

Source: G. Guo, X. Yang, J. Carrete and Wu Li, J. Phys.: Condens. Matter 33 (2021) 285702

Regression models can detect regularities in diverse families like the half Heuslers
[J. Carrete, Wu Li, N. Mingo, S. Wang & S. Curtarolo, *Phys. Rev. X* 4 (2014) 011019]

Vibrational Properties of Metastable Polymorph Structures by Machine Learning

Fleur Legrain, Ambroise van Roekeghem, Stefano Curtarolo, Jesús Carrete, Georg K. H. Madsen, and Natalio Mingo
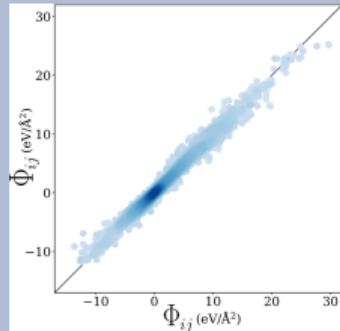
	Pearson coefficient	Spearman coefficient	mean absolute error	root-mean-square error
$\mathrm{tr}(\mathbf{\Phi}_{ij})$	0.99	0.98	0.25 (eV/Å²)	0.38 (eV/Å²)
$\mathrm{tr}(\mathbf{\Phi}_{ij}^2)$	0.98	0.95	0.27 (eV/Å²)	0.41 (eV/Å²)
$\sqrt{\mathrm{tr}(\mathbf{\Phi}_{ij}^2)}$	0.98	0.95	0.28 (eV/Å²)	0.43 (eV/Å²)
$\mathbf{\Phi}_{ij}$	0.99	0.93	0.17 (eV/Å²)	0.32 (eV/Å²)
variance $\sqrt{\langle(\omega - \overline{\omega})^2\rangle}$	0.88	0.87	0.88 (rad/ps)	1.14 (rad/ps)
mean $\overline{\omega}$	0.92	0.88	0.73 (rad/ps)	0.94 (rad/ps)
max ω_{max}	0.88	0.87	3.79 (rad/ps)	4.63 (rad/ps)
C_v	0.91	0.83	0.0008 (meV/ K/atom)	0.0010 (meV/ K/atom)
F_{vib}	0.82	0.80	2.92 (meV/ atom)	3.78 (meV/ atom)
S_{vib}	0.80	0.79	0.009 (meV/ K/atom)	0.012 (meV/ K/atom)

Regression model:

- Random-forest regression
- Equivariant inputs (Hessians of scalar descriptors)

Test system: $KZnF_3$

- Cubic perovskite at $0\,K$
- 121 non-equivalent mechanically stable minima found with USPEX

More specialized than a force field, but much cheaper

Beyond the BTE

The Allen-Feldman model

The BTE framework is only valid for propagating plane-wave-like modes. On shaky ground when (Ioffe-Regel crossover):

- $\Lambda \sim \pi/|q|$
- $\tau \sim \pi/\omega$

P. B. Allen and J. L. Feldman,
Phys. Rev. B 48 (1993) 12581:

- Vibrational modes (vibrons):

    Propagons: phonon-like
    Diffusons: delocalized, non-propagating
    Locons: localized, non-propagating

- Phonons and diffusons contribute to thermal transport
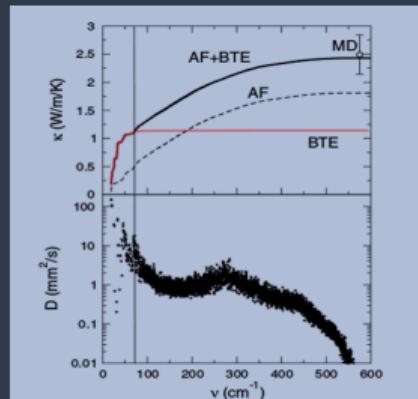
FIG. 4 (color online). Diffusivity of the vibrational modes of a core-shell SiNW with 3 nm diameter and *a*-Si thickness of 1 nm.

Source: D. Donadio, G. Galli,
Phys. Rev. Lett. 102 (2009) 195901

New contributions to the thermal conductivity

Unified theory of thermal transport in crystals and glasses

Michele Simoncelli, Nicola Marzari and Francesco Mauri
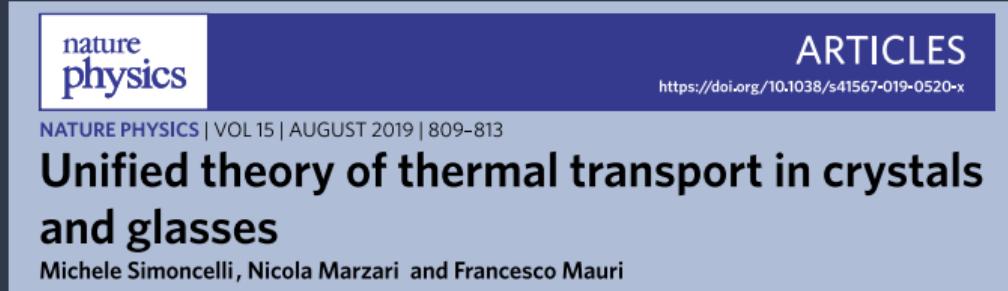
Additional non-diagonal term in the thermal conductivity:

$$\kappa^{\alpha\beta} = \kappa_{\mathrm{P}}^{\alpha\beta} + \frac{\hbar^2}{k_{\mathrm{B}}T^2}\frac{1}{\mathcal{V}N_{\mathrm{c}}}\sum_{\mathbf{q}}\sum_{s\neq s'}\frac{\omega(\mathbf{q})_s + \omega(\mathbf{q})_{s'}}{2}V^\alpha(\mathbf{q})_{s,s'}V^\beta(\mathbf{q})_{s',s}\times\frac{\omega(\mathbf{q})_s\overline{N}(\mathbf{q})_s(\overline{N}(\mathbf{q})_s+1)+\omega(\mathbf{q})_{s'}\overline{N}(\mathbf{q})_{s'}(\overline{N}(\mathbf{q})_{s'}+1)}{4(\omega(\mathbf{q})_s-\omega(\mathbf{q})_{s'})^2+(\Gamma(\mathbf{q})_s+\Gamma(\mathbf{q})_{s'})^2}\times(\Gamma(\mathbf{q})_s+\Gamma(\mathbf{q})_{s'})$$

Non-diagonal terms of the group velocity:

$$V_{\lambda,\lambda'}^{(\alpha)} = \underbrace{\boldsymbol{w}_{\lambda'}^* \cdot \frac{\partial\sqrt{D(q)}}{\partial q^{(\alpha)}}\boldsymbol{w}_\lambda}_{\text{automatic differentiation again!}}$$

Important when:

- Phonon frequencies are close (reference: linewidths)
- Non-diagonal elements significant

$$\kappa^{(\alpha\beta)} \propto \int\limits_0^\infty \left\langle J^{(\alpha)}(0) J^{(\beta)}(t) \right\rangle \mathrm{d}t, \text{ with } J = \frac{1}{V} \int x\dot{e}(x)\mathrm{d}^3x$$

Pros:

- Compact and elegant formalism
- Anharmonicity and net ionic displacements included (diffusion, liquids...)

Four kinds of problems, important for ab-initio for NN-based MD:

1. Arbitrary assignment of contributions to the energy to individual atoms
2. Expression of J compatible with periodic boundary conditions
3. Conceptually clear separation of diffusion from conduction in multicomponent systems
4. Poor convergence and noisy character of direct estimates of the average autocorrelation

Solutions by Baroni and coworkers

1. Gauge invariance vs. choice of atomic contributions to the energy (P. Pegolo, Master Thesis, Università degli Studi di Trieste)

2. Expression of J based on $\boldsymbol{R}_n - \boldsymbol{R}_m$ and $\frac{\partial \epsilon_n}{\partial \boldsymbol{R}_m}$ for an arbitrary potential

3. Spectra of energy and matter fluxes treated together [R. Bertossa *et al.*, Phys. Rev. Lett 122 (2019) 255901]

4. Cepstral analysis of $J^{(\alpha)}(t)$ to extract low-frequency behavior

Comparison of methods:
P. Pegolo, S. Baroni & F. Grasselli, npj Comput. Mater. 8 (2022) 24
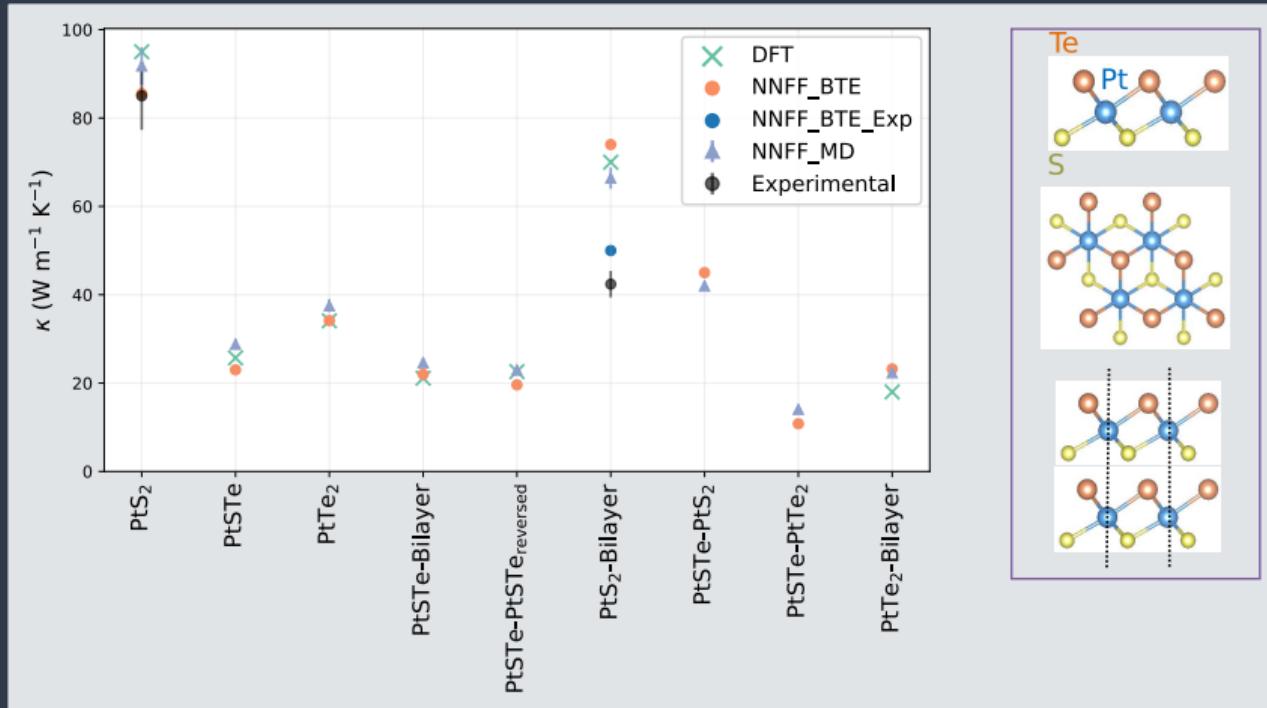
[LiJun Pan et al., unpublished]

Thermal Transport Calculations for Crystals and nanostructures based on the Boltzmann Transport Equation

Jesús Carrete Montaña <jesus.carrete.montana@tuwien.ac.at>

2023-06-14

TECHNISCHE UNIVERSITÄT WIEN