Hands-On Tutorial Workshop, July 29th 2014

Phonons & Thermal Transport

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CRYSTALLINE SOLIDS

Idealized Crystal Structure

Infinite grid of immobile atoms with perfect periodicity

cf. Christian Ratsch, Tuesday July 22

Real Materials

Everything moves!

cf. M. Rossi & L. Ghiringhelli, Friday July 25

Perfect periodicity disturbed!
FAILURES OF THE STATIC LATTICE MODEL


• **Inaccuracies** in the **equilibrium** properties at **0K**: 
  *Lattice Constants, Cohesive Energies, Elastic Constants,*...

• **Failure** to describe **thermodynamic equilibrium properties**: 
  *Specific Heat, Thermal Lattice Expansion, Phase Transformations,* ...

• **Failure** to describe **thermodynamic non-equilibrium properties**: 
  ✦ **Charge Transport**: 
    *Electrical AC/DC Conductivity, Superconductivity,*...
  ✦ **Heat Transport**: 
    *Thermal Conductivity, Transmission of Sound,*...
  ✦ **Coupling of Charge & Heat Transport**: 
    *Seebeck and Peltier Effect,*...
  ✦ **Interaction with Radiation**: 
    *X-Ray, Infrared, Neutron,* ...
I. THE HARMONIC CRYSTAL
The total energy $E$ is a $3N$-dimensional surface:

$$E = V(R_1, R_2, \cdots, R_N)$$

Approximate by Taylor Expansion around the Static Equilibrium $R_i^0$

$$E(R_0 + \Delta R) \approx E(R_0) + \cdots$$

Static Equilibrium Energy
The total energy $E$ is a 3N-dimensional surface:

$$E = V \left( \mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N \right)$$

Approximate by Taylor Expansion around the Static Equilibrium $\mathbf{R}_i^0$

$$E \left( \{ \mathbf{R}_0 + \Delta \mathbf{R} \} \right) \approx E \left( \{ \mathbf{R}_0 \} \right) + \sum_i \left. \frac{\partial E}{\partial \mathbf{R}_i} \right|_{\mathbf{R}_0} \Delta \mathbf{R}_i + \cdots$$

Forces vanish at $\mathbf{R}_0$
The total energy $E$ is a $3N$-dimensional surface:

$$E = V \left( R_1, R_2, \cdots, R_N \right)$$

Approximate by Taylor Expansion around the Static Equilibrium $R_i^0$.

$$E \left( \{ R_0 + \Delta R \} \right) \approx E \left( \{ R_0 \} \right) + \sum_i \left. \frac{\partial E}{\partial R_i} \right|_{R_0} \Delta R_i + \frac{1}{2} \sum_{i,j} \left. \frac{\partial^2 E}{\partial R_i \partial R_j} \right|_{R_0} \Delta R_i \Delta R_j$$

Harmonic Potential

Total Energy $E$
The total energy $E$ is a $3N$-dimensional surface:

$$E = V (R_1, R_2, \ldots, R_N)$$

**Warning:**
Harmonic Approximation is only valid for small displacements from $R^0$!
THE HARMONIC APPROXIMATION

\[ E(\{R_0 + \Delta R\}) \approx E(\{R_0\}) + \sum_i \left. \frac{\partial E}{\partial R_i}\right|_{R_0} \Delta R_i + \frac{1}{2} \sum_{i,j} \left. \frac{\partial^2 E}{\partial R_i \partial R_j}\right|_{R_0} \Delta R_i \Delta R_j \]

Static Equilibrium Energy from DFT

Determine **Hessian** aka the **Harmonic Force Constants** \( \Phi_{ij} \):

- **from Density-Functional Perturbation Theory**

- **from Finite Differences**

⇒ cf. *Christian Carbogno & Manuel Schöttler, Tutorial 6, Tuesday July 29*
THE HARMONIC APPROXIMATION

...in Molecules:

\[ N \quad \text{Number of atoms} \]

\[ \downarrow \]

Degrees of Freedom: \( 3N \)

Dimension of Hessian: \( 9N^2 \)

...in Crystalline Solids:

\[ N \quad \text{Number of atoms} \]

\[ \downarrow \]

Degrees of Freedom: \( 3N \)

Dimension of Hessian: \( 9N^2 \)

\[ \text{BUT:} \]

\[ N \rightarrow \infty \]
PERIODIC BOUNDARY CONDITIONS


Unit Cell with \( N_p \) atoms

Lattice vector: \( \mathbf{E}_0 \)

Fourier Transform

\[
D_{ij'}(\mathbf{q}) = \sum_j \frac{e^{i(\mathbf{q} \cdot (\mathbf{R}_j^0 - \mathbf{R}_{j'}^0))}}{\sqrt{M_{i'} M_{j'}}} \Phi_{i'j}
\]

Real Space:
Hessian \( \Phi_{ij} \) with \( i,j \to \infty \)

Reciprocal Space:
Dynamical Matrix \( D_{ij'}(\mathbf{q}) \) with \( i',j' \leq N_p \)

VIBRATIONS IN A CRYSTAL 101


**Real Space:**
Hessian $\Phi_{ij}$ with $i,j \to \infty$

**Fourier Transform**

$$D_{i'j'}(q) = \sum_j \frac{e^{i(q \cdot (R_j^0 - R_{j'}^0))}}{\sqrt{M_{i'}M_{j'}}} \Phi_{i'j}$$

**Reciprocal Space:**
Dynamical Matrix $D_{i'j'}(q)$ with $i',j' \leq N_p$

**Fourier Transform** can be truncated since
$\Phi_{ij} = 0$ for large $|R_j^0 - R_{j'}^0|$

Hessian $\Phi_{ij}$ with **finite** number of non-zero entries

Dynamical Matrix $D_{i'j'}(q)$ known for the **whole** reciprocal space
VIBRATIONS IN A CRYSTAL 101

e.g. N.W Ashcroft and N. D. Mermin, “Solid State Physics” (1976)
also see Björn Lange, Nuts and Bolts of DFT II, Tuesday July 22

Dynamical matrix:

\[ D_{i', j'}(q) = \sum_j \frac{e^{i(q \cdot (R_j^0 - R_{j'}^0))}}{\sqrt{M_{i'} M_{j'}}} \Phi_{i', j} \]

Equation of Motion becomes an Eigenvalue Problem:

\[ D(q) [\nu(q)] = \omega^2(q) [\nu(q)] \]

Analytical Solution in Real Space:

Superposition of Harmonic Oscillations

\[ R_j(t) = R_j^0 + \text{Re} \left( \sum_s \frac{A_s}{\sqrt{M_i}} e^{i(q \cdot (R_j^0 - R_{j'}^0) - \omega_s(q)t)} \cdot [\nu_s(q)]_{j'} \right) \]
For \( N_p \) atoms in the unit cell there are:

3 Acoustic modes:
- Atoms in unit cell in-phase
- Acoustic modes vanish at \( \Gamma \)
- Strong (typically linear) dispersion close to \( \Gamma \)

(3\( N_p \) - 3) Optical modes:
- Atoms in unit cell out-of-phase
- \( \omega > 0 \) at \( \Gamma \) (and everywhere else)
- Weak dispersion
\[ g(\omega) = \sum_s \int \frac{d\mathbf{q}}{(2\pi)^3} \delta(\omega - \omega(\mathbf{q})) = \sum_s \int \frac{dS}{(2\pi)^3} \frac{1}{|\nabla \omega(\mathbf{q})|} \]
The Harmonic Free Energy

\[ F^{ha}(T) = \sum_{0}^{\infty} z_{d} \left( \begin{array}{c} \sigma \left( \frac{1}{k_{B}T} \right) \\ \sigma \left( \frac{1}{k_{B}T} \right) \\ \vdots \end{array} \right) + z_{d} \left( \begin{array}{c} \sigma \left( \frac{1}{k_{B}T} \right) \\ \sigma \left( \frac{1}{k_{B}T} \right) \\ \vdots \end{array} \right) \]

The specific heat \( C_{V} \) is given by:

\[ C_{V} = T \left( \frac{\partial S}{\partial T} \right)_{V} = -T \left( \frac{\partial^{2} F(T)}{\partial T^{2}} \right)_{V} \]
THE HARMONIC FREE ENERGY

Quasi-harmonic approximation:

\[ F^{ha}(T) = \left( \frac{\partial}{\partial a} \right)_V a(T) + Z^d \eta(T) \]

\[ \alpha(T) = \frac{1}{a} \frac{da}{dT} \]

Compute \( F(T, V) \) by varying the lattice constants \( a \).
Electronic Structure Theory predicts the two polymorphs to be energetically degenerate.

**BUT:** Form I much more abundant!
THE ASPIRIN “HEADACHE”

Form I

Form II

ΔE (meV)

30
20
10
0
PBE+MBD
...+F_{ha}(0K)
...+F_{ha}(298K)

Form I more stable
THE ASPIRIN “HEADACHE”

Understanding polymorphism in organic crystals requires...

... accurate electronic structure theory
... correct description of many-body dispersion
... to account for nuclear motion
II. LIMITS OF THE HARMONIC APPROXIMATION
At elevated temperatures the harmonic approximation becomes increasingly inaccurate – and often terribly misleading!
Zirconia-based coatings play a crucial role in thermal barrier coatings.

THERMAL BARRIER COATINGS
PHASE DIAGRAM OF ZrO$_2$

- Monoclinic
- Tetragonal
- Cubic

Temperature range:
- $T < 1200^\circ$C

Structures:
- „Monoclinic“ Baddeleyite Structure
PHASE DIAGRAM OF ZrO$_2$

1200°C < $T$ < 2400°C

„Tetragonal“

P4$_2$/nnmc Structure
PHASE DIAGRAM OF ZrO$_2$

- Monoclinic
- Tetragonal
- Cubic

T > 2400°C

„Cubic“
Fluorite Structure
Cubic Zirconia exhibits a **soft mode (imaginary mode)**:

\[ \mathbf{D}(\mathbf{X}) \left[ \nu(\mathbf{X}) \right] = \omega^2(\mathbf{X}) \left[ \nu(\mathbf{X}) \right] \Rightarrow \omega_1^2(\mathbf{X}) < 0 \]
The Tetragonal-Cubic Phase Transition

Distance from cubic geometry \( dr = \sqrt{dx^2 + dy^2 + dz^2} \) always conserved!

Ferroelastic switches are an intrinsic feature of the dynamics in ZrO\(_2\).
ZrO\(_2\) exhibits **not one**, but **six degenerate** equilibrium configurations. 

Ferroelastic Switches between these configurations occur quite **frequently**. 

Severe violation of the harmonic approximation.
SUMMARY

We have introduced the harmonic approximation under periodic boundary conditions.

The harmonic approximation can be very useful to approximatively assess dynamic and thermodynamic effects at low temperatures.

The harmonic approximation becomes increasingly inaccurate at elevated temperatures and must be handled with care under such thermodynamic conditions.
III. HEAT TRANSPORT
HEAT TRANSPORT

Macroscopic Effect:

Fourier's Law:

\[ J = -\kappa \nabla T = -\alpha \rho c_V \nabla T \]

\[ \kappa = \kappa_{\text{photon}} + \kappa_{\text{elec.}} + \kappa_{\text{nucl.}} \]

Microscopic Mechanisms
**BASICS OF MACROSCOPIC TRANSPORT**

The Continuity Equation:  
(valid for any conserved quantity)  
\[
\frac{\partial T}{\partial t} + \nabla \cdot \mathbf{j} = 0
\]

Proportionality of flux and gradient:  
\[
\mathbf{j} = -\kappa \nabla T
\]

The Diffusion Equation:  
(also applies to mass & charge transport)  
\[
\frac{\partial T(r, t)}{\partial t} = \kappa \nabla^2 T(r, t)
\]

Analytic Solution:  
\[
T(r, t) = \frac{1}{(4\pi \kappa t)^{3/2}} \exp \left( -\frac{r^2}{4\kappa t} \right)
\]
**HARMONIC APPROXIMATION**

\[
R_j(t) = R_j^0 + \Re \left( \sum_s \frac{A_s}{\sqrt{M_i}} e^{i(q \cdot (R_j^0 - R_{j'}^0) - \omega_s(q)t)} \cdot [\nu_s(q)]_{j'} \right)
\]

\[
E = \frac{1}{2} \sum_s E_s = \frac{1}{2} \sum_s \sum_q |A_s|^2 \omega_s^2(q)
\]

\[
J = \frac{1}{2} \sum_s \sum_q |A_s|^2 \omega_s^2(q) \cdot \frac{\partial \omega_s(q)}{\partial q} \cdot \nabla T
\]

Thermal Conductivity diverges: \( \kappa \to \infty \)
The phonon-phonon interaction limits the vibrational thermal conductivity.

Deviations from the harmonic approximation limit the vibrational thermal conductivity.
Heat Transport Mechanisms

**Semi-empirical potentials:**
- + vast experience
- + established methodologies
- – accuracy is a question

**First-principles approaches:**
- + more accurate interactions
- – limited time and length scales
Boltzmann-Peierls-Transport-Equation describes the evolution of the phonon phase space distribution $f(\omega,q,t)$. 

Boltzmann-Peierls-Transport-Equation describes the evolution of the phonon phase space distribution $f(\omega, q, t)$.

\[ \kappa \sim \sum_s v_s^2 \omega_s^2 n_s (n_s + 1) \tau_s \]

- **Group velocity**
- **Frequency**
- **Equilibrium population**
- **Phonon lifetime**

Harmonic phonon theory

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(A) BOLTZMANN TRANSPORT EQUATION

Phonon Lifetimes from First Principles

• from Density Functional Perturbation Theory

• from fitting the forces in ab initio MD

• from fitting the phonon line width determined via ab initio MD

All these approaches give very accurate results for good thermal conductors at low temperatures.

Results are questionable at high levels of anharmonicity!
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Boltzmann-Transport-Eq. gives very accurate results for perfect crystals at low temperatures.
Thermal conductivity can be calculated by applying Fourier’s Law.

\[ \mathbf{J} = -\kappa \nabla T \]
FINITE SIZE EFFECTS

Finite Size Corrections

\[
\frac{1}{\kappa} \sim \left( \frac{1}{l_\infty} + \frac{4}{L_z} \right)
\]

mean free path

supercell length

Non-equilibrium MD exhibits strong finite-size artifacts in supercells typically accessible within DFT/AIMD.

FINITE SIZE EFFECTS


Non-equilibrium MD can suffer from non-linear artifacts in supercells typically accessible within DFT/AIMD.
### First-Principles Approaches

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Non-Equilibrium MD approaches are in principle exact, in DFT however prohibitively costly to converge accurately.
Heat

\[ T = T_{\text{hot}} \]  \hspace{1cm}  \[ T = T_{\text{cold}} \]

"LASER FLASH" MEASUREMENTS

Heat Diffusion Equation:

\[ \frac{\partial T(x,t)}{\partial t} + \alpha \frac{\partial^2 T(x,t)}{\partial x^2} = 0 \]

Extract the **heat diffusivity** \( \alpha \) by fitting \( T(x,t) \)

**LASER FLASH** MEASUREMENTS

Mimic the "Laser-Flash Measurements" in _ab initio_ MD simulations:

(A) Prepare two supercells: a **small hot** one and a **large cold** one.
In the **harmonic approximation**, the **positions** \( r_i \) and the **velocities** \( v_i \) are related to the **vibrational eigenfrequencies** \( \omega_s \) and -vectors \( e_s \).

\[
\begin{align*}
r_{0i} + \Delta r_i &= + \sum_s A_s(T) \cos (\Phi_s + \omega_s t) \quad \sqrt{M_i} \\
v_i &= - \sum_s A_s(T) \sin (\Phi_s + \omega_s t) \quad \sqrt{M_i} \cdot \omega_s \cdot e_s
\end{align*}
\]

**Maxwell-Boltzmann** distributed amplitudes

**random phase**

**harmonic approximation**

Setup of the Cell in Non-Equilibrium
Mimic the "Laser-Flash Measurements" in \textit{ab initio} MD simulations:

(A) Prepare two supercells: a \textbf{small hot} one and a \textbf{large cold} one.

(B) Let the \textbf{heat diffuse} via \textit{ab initio} MD and \textbf{monitor} the \textbf{temperature profile} $T(x,t)$. 
Monitor temperature of the central cell

The finite number of atoms leads to large temperature fluctuations.

„LASER FLASH“ SIMULATIONS
Fit to

\[ T(x, t) = T_{\text{cold}} + (T_{\text{final}} - T_{\text{cold}}) \sum_n (-1)^n \exp\left(-n^2\pi^2\alpha t\right) \]
How do the properties of the impurities affect the thermal conductivity of the system?
Vacancies

Thermal conductivity can be controlled via the impurities' mass!

APPLICATION TO IMPURITIES IN SI

APPLICATION TO IMPURITIES IN SI


Not all impurities are created equal!
FINITE SIZE EFFECTS

Finite Size Corrections

\[ \frac{1}{\kappa} \sim \left( \frac{1}{l_\infty} + \frac{4}{L_z} \right) \]

mean free path

supercell length

SiGe, Stillinger-Weber Potential,
Courtesy of Philip Howell, Siemens AG
Laser-flash approach exhibits strong finite-size artifacts in supercells typically accessible within DFT/AIMD.
Preparation of the supercell in non-equilibrium via the harmonic approximation allows to use rather small thermal gradients.
**First-Principles Approaches**

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**Laser-flash MD** yields accurate qualitative results at low temperatures within moderate computational costs. Quantitative predictions require finite size corrections, though.
The fluctuations of the forces in thermodynamic equilibrium is related to the generalized resistance in non-equilibrium for linear dissipative systems.


Brownian Motion:

The erratic motion of the particles is closely related to frictional force under perturbation.

Random walk in 2D

The fluctuations of the forces in thermodynamic equilibrium is related to the generalized resistance in non-equilibrium for linear dissipative systems.

The thermal conductivity is related to the autocorrelation function of the heat flux.

\[ \kappa \sim \int_{0}^{\infty} d\tau \left\langle J(0) \, J(\tau) \right\rangle_{eq} \]

Simulations of the thermodynamic equilibrium \quad Information about non-equilibrium processes
Heat Flux Autocorr. $\langle J(t) J(t+\tau) \rangle$ (a.u.)

Heat Flux (eVÅ/ps)

Temperature (K)
THE ATOMICISTIC HEAT FLUX


\[ J(t) = \frac{d}{dt} \left( \sum_i r_i(t) \varepsilon_i(t) \right) \]

\( r_i \cdots \) Position of atom \( i \)

\( \varepsilon_i \cdots \) Energy of atom \( i \)

Energy contribution \( \varepsilon_i \) of the individual atoms required!

⇒ Green-Kubo Method hitherto only used with classical potentials!
THE AB INITIO HEAT FLUX

\[
J(t) = \frac{d}{dt} \int \mathbf{r} \cdot \varepsilon(\mathbf{r}, t) \, d\mathbf{r}
\]

\[\varepsilon(\mathbf{r}, t) \quad \cdots \quad \text{Energy density}\]

**Energy Density** in Density Functional Theory:

\[
\int \varepsilon(\mathbf{r}, \{\mathbf{R}\}) \, d\mathbf{r} \quad \Leftrightarrow \quad \text{Harris-Foulkes Total Energy Functional}
\]

\[
\varepsilon(\mathbf{r}, \{\mathbf{R}\}) = \sum_i T_i + \sum_l \varepsilon_l f_{l}^{occ} |\Psi_l(\mathbf{r})|^2 - n(\mathbf{r}) v_{xc} [n(\mathbf{r})]
\]

\[
+ E_{xc} [n(\mathbf{r})] - \frac{1}{2} n(\mathbf{r}) v_{es}(\mathbf{r}) + \frac{1}{2} \sum_{ij} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} \delta (\mathbf{r} - \mathbf{R}_i)
\]
ASSESSING THE THERMAL CONDUCTIVITY

\[ \kappa = \frac{V}{3k_B T^2} \int_0^\infty d\tau \langle J(0) J(\tau) \rangle_{eq} \]

Fourier Trans.

\[ \kappa = \frac{V}{3k_B T^2} \lim_{\omega \to 0} |J(\omega)|^2 \]

Finite Size Artifacts artificially reduce the thermal conductivity at low frequencies!

PERIODIC BOUNDARY CONDITIONS
Small heat flux through boundaries leads to **huge change in energy barycenter**.
ELIMINATING THE FINITE SIZE ARTIFACTS


Helfands’ Heat Flux

\[
J(t) = \frac{d}{dt} \int \mathbf{r} \cdot \varepsilon(\mathbf{r}, t) \, d\mathbf{r} = \int \mathbf{r} \cdot \varepsilon(\mathbf{r}, t) \, d\mathbf{r} + \int \mathbf{r} \cdot \frac{d\varepsilon(\mathbf{r}, t)}{dt} \, d\mathbf{r}
\]

Convective Heat Flux

Hardys’ Heat Flux

\[
J_v = \int \mathbf{r} \cdot \frac{d\varepsilon(\mathbf{r}, t)}{dt} \, d\mathbf{r} = \int \mathbf{v} \cdot \sigma(\mathbf{r}) \, d\mathbf{r}
\]

Virial Heat Flux

\[\sigma(\mathbf{r}) \ldots \text{Stress density}\]
Formulas for analytical stress

F. Knuth, FHI

\[
\sigma_{ij} = \sigma_{ij}^{HF} + \sigma_{ij}^{MP} + \sigma_{ij}^{Pulay} + \sigma_{ij}^{kin} + \sigma_{ij}^{Jac}.
\]

\[
\sigma_{ij}^{HF} = \frac{1}{2V} \sum_{\alpha,\beta \neq \alpha} \left[ \frac{\partial \nu_{\beta}^{es,tot}(|R_{\alpha} - R_{\beta}|)}{\partial R_{i}^{\alpha}} \right] (R_{\alpha} - R_{\beta})_{j}
\]

\[
\sigma_{ij}^{MP} = \frac{1}{V} \sum_{\alpha} \int_{UC} dr \left[ n(r) - \frac{1}{2} n_{MP}(r) \right] \frac{\partial \nu_{\alpha}^{es,tot}(|r - R_{\alpha}|)}{\partial r_{i}} (r - R_{\alpha})_{j}
\]

\[
- \frac{1}{2V} \sum_{\alpha} \int_{UC} dr \frac{\partial n_{MP}(r - R_{\alpha})}{\partial r_{i}} (r - R_{\alpha})_{j} \nu_{es,tot}(r)
\]

\[
\sigma_{ij}^{Pulay} = \frac{2}{V} \sum_{k} \sum_{\alpha,l(\alpha)} \sum_{\beta,m(\beta)} f_{k} c_{kl} c_{km} \int_{UC} dr \frac{\partial \varphi_{l}(r - R_{\alpha})}{\partial r_{i}} (r - R_{\alpha})_{j} \left[ \hat{h}_{KS} - \epsilon_{k} \right] \varphi_{m}(r - R_{\beta})
\]

\[
\sigma_{ij}^{kin} = \frac{1}{V} \sum_{k} \sum_{\alpha,l(\alpha)} \sum_{\beta,m(\beta)} f_{k} c_{kl} c_{km} \int_{UC} dr \varphi_{l}(r - R_{\alpha})(r - R_{\alpha})_{j} \left[ \frac{\partial}{\partial r_{i}} \frac{\partial}{\partial r_{j}} \varphi_{m}(r - R_{\beta}) \right]
\]

\[
\sigma_{ij}^{Jac} = \frac{1}{V} \delta_{ij} \left[ E_{xc}[n] - \int dr n(r) \nu_{xc}(r) - \frac{1}{2} \int dr n_{MP}(r) \nu_{es,tot}(r) \right]
\]

ELIMINATING THE FINITE SIZE ARTIFACTS


FINITE SIZE ARTIFACTS ELIMINATED!

2x2x2 ZrO$_2$ - $T=1800K$

Hardys’ Heat Flux

Helfands’ Heat Flux
APPLICATION TO ZIRCONIA

Experiment:  

Classical MD:  
Heat Transport Mechanisms

First-principles approaches:
+ more accurate interactions
– limited time and length scales

Zirconia ZrO$_2$: Thermal Insulator
Heat Transport Mechanisms

First-principles approaches:
+ more accurate interactions
– limited time and length scales

pristine Silicon: good conductor
### First-Principles Approaches

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</tbody>
</table>

*Ab initio* Green-Kubo approach allows the **accurate** and **predictive** computation of lattice thermal conductivities \( \kappa \) at **arbitrarily high temperatures**!