A Survey of Theoretical Methods for Predicting the Thermal Properties of Materials

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The Concept of Thermal Conductivity

Fourier made fundamental contributions to the measurement of thermal conductivity. Fourier introduced the definition of thermal conductivity as

$$\kappa = \frac{Q\,L}{A\Delta T},$$

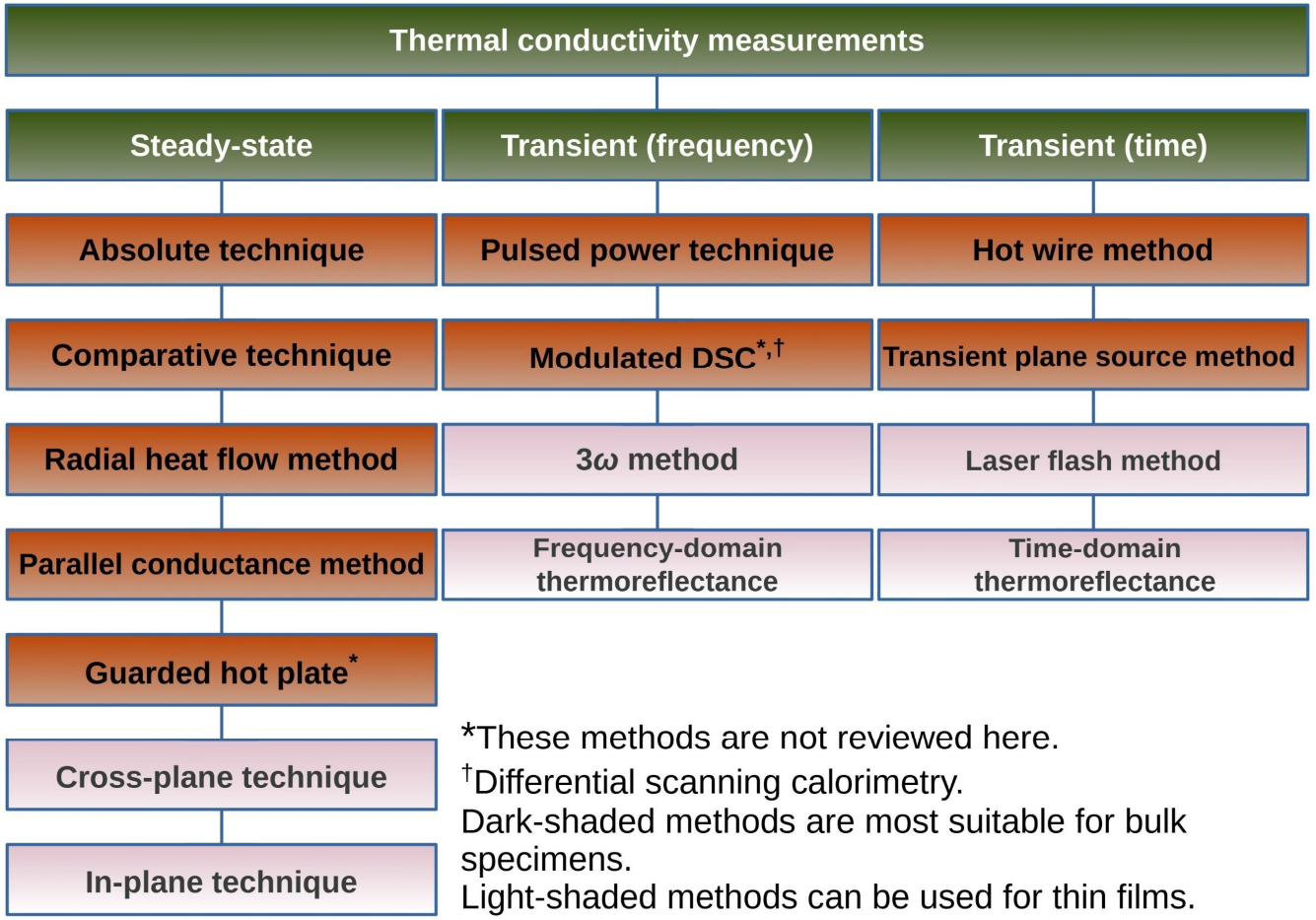
where Q is the transmitted heat rate (heat passed per time) through a distance L and perpendicular to a cross-section A, under a temperature difference ΔT.

In the years followed, Fourier introduced his general theory of heat flux in terms of temperature gradient:

$$\boldsymbol{Q} = -\kappa \boldsymbol{\nabla} T$$

where $\boldsymbol{Q}$ is the flowing heat per unit of area and during a unit of time or *heat flux*, κ is the thermal conductivity, and ∇T is the gradient of temperature.

Most Common Experimental Techniques



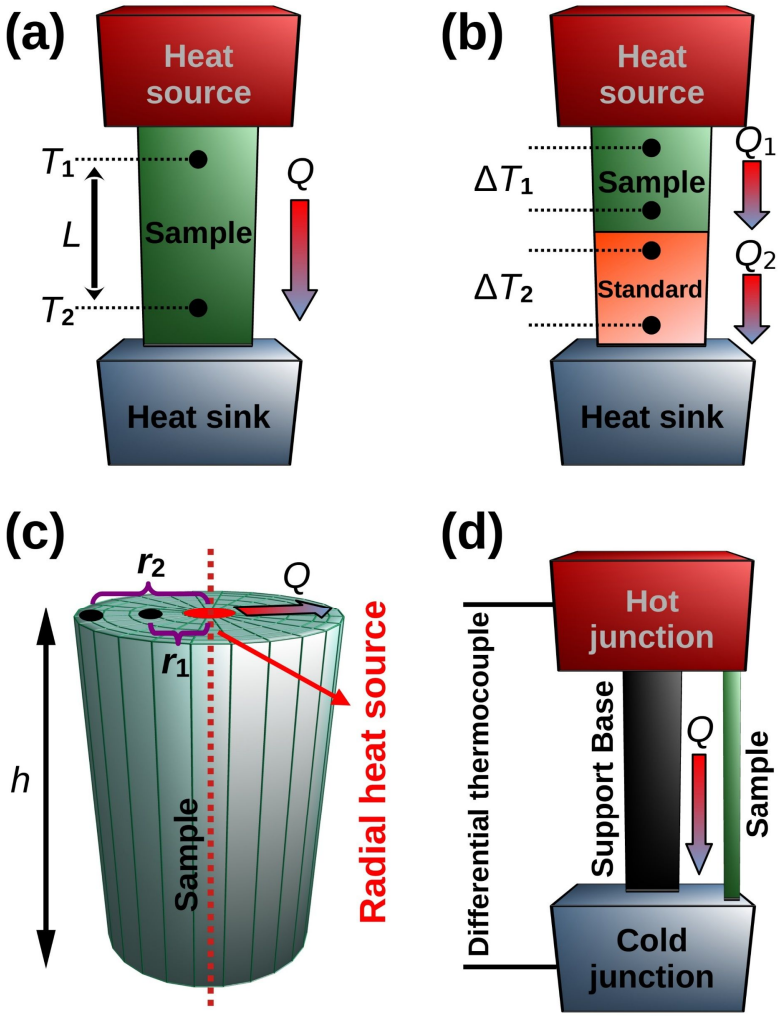
*These methods are not reviewed here.

†Differential scanning calorimetry.

Dark-shaded methods are most suitable for bulk specimens.

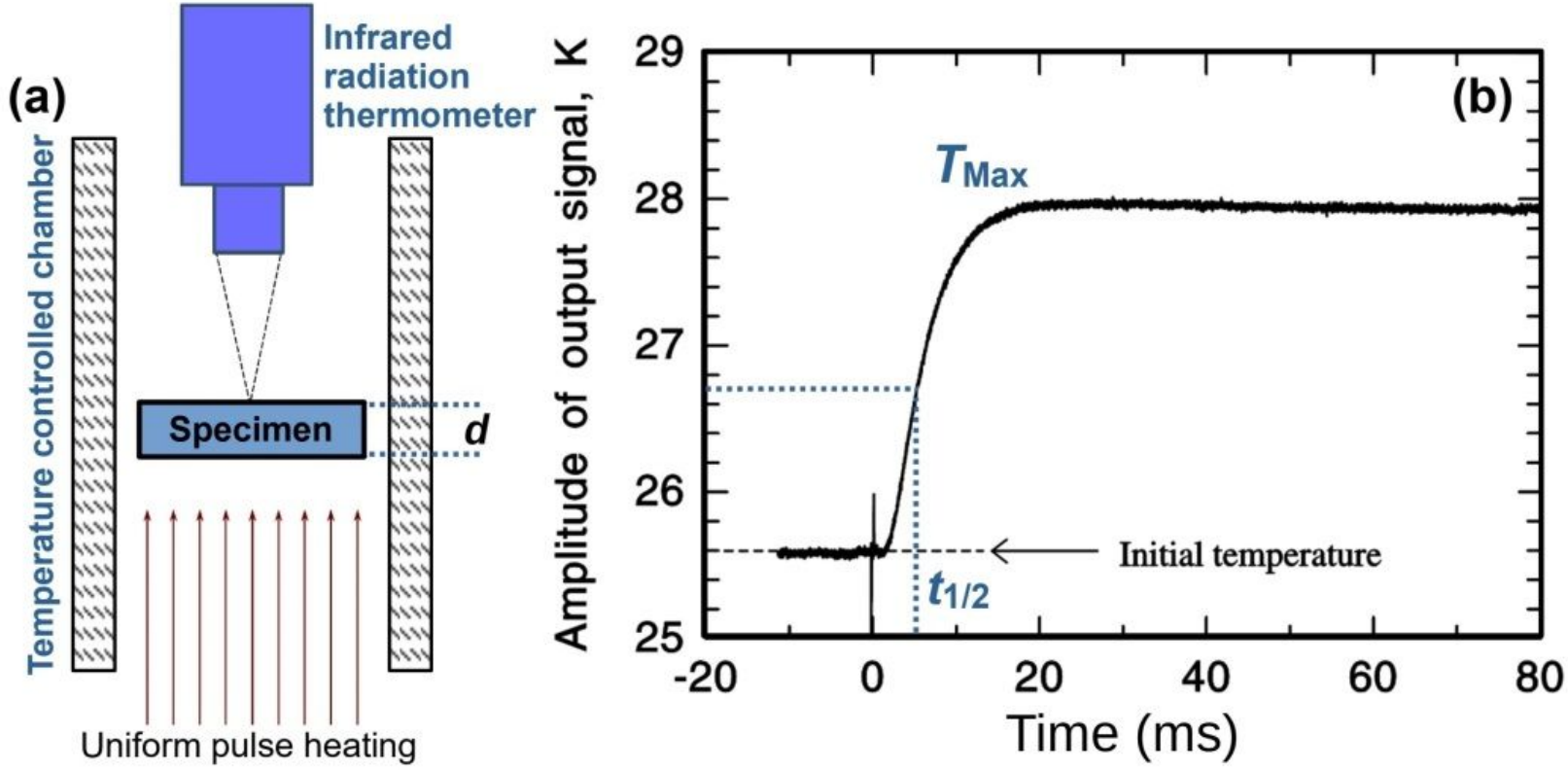
Light-shaded methods can be used for thin films.

Steady-State Methods



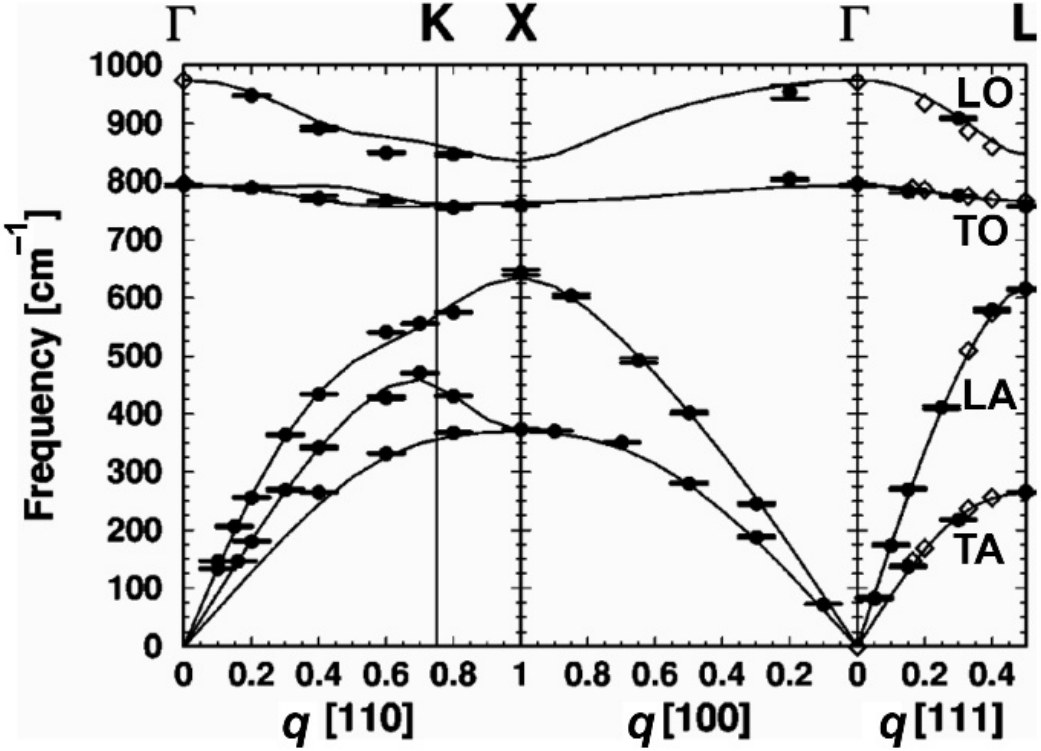
Schematic representation of four steady-state techniques for measuring the thermal conductivity in bulk materials: (a) Absolute method; (b) Comparative method; (c) Radial heat flow method; (d) Parallel thermal conductance method. Temperature sensors are marked with black circles.

Transient-State Methods



(a) Schematic representation of the laser flash apparatus and (b) typical $T(t)$ curve. Copyrights 2001 The Institute of Physics and 2005 Springer.

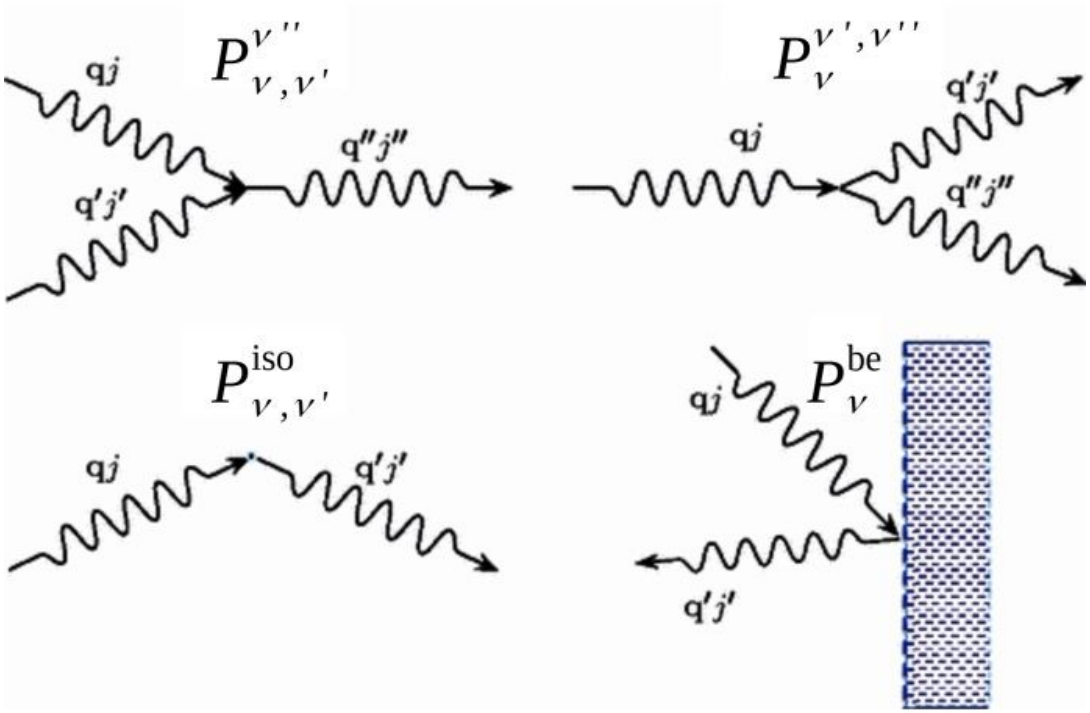
The Concept of Phonons



Phonon dispersion relations in SiC. Copyright 2002 American Institute of Physics.

- The concept of *phonons*, first proposed by Tamm in 1932
- Representing the quanta of the collective vibrational energy of oscillating atoms within a lattice
- Like a bouncing spring, phonon energy depends on the mass of the oscillating atoms the amplitude of the oscillation, and the interatomic force constant (IFC),
- IFC is a concept similar to the spring constant
- The behaviour of phonons in solids is best described by the phonon dispersion relations, which shows what phonon energies (or frequencies as $E = hv$, with h being the Plank's constant) are permissible for any given crystal momentum ($\boldsymbol{q}$)

Phonon Dynamics and Lattice Thermal Conductivity



Phonon-phonon, isotope, and boundary scattering of phonon of mode *v* with vector ***q*** and branch index *j*.
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BTE lattice dynamics method

In the linear regime, the microscopic expression for the heat flux ($\boldsymbol{Q}$), carried by phonons in the direction of the temperature gradient, is expressed as:

$$\boldsymbol{Q} = \frac{1}{N_0 \Omega} \sum_{\nu} \hbar \omega_{\nu} \boldsymbol{c}_{\nu} n_{\nu}.$$

here ħ is the reduced Plank's constant and ω_v is the angular frequency of a phonon of mode *v,* meaning that $\hbar\omega_v$ is the energy of phonon of mode *v* with vector $\boldsymbol{q}$ and branch index *j*. N_0 is the number of wave vectors in the Brillouin zone, and Ω is the unit cell volume. $\boldsymbol{c}_{\nu}$, defined as $\nabla_{\boldsymbol{q}} \omega_v$, is the group velocity of phonons of mode *v*, and n_v is the out-of-equilibrium phonon distribution function. n_v follows the Bose-Einstein distribution as phonons are bosons:

$$n_{\nu} = \frac{1}{e^{\frac{\hbar \omega_{\nu}}{k_B T}} - 1}.$$

Computational Implementation of BTE

To calculate thermal conductivity based on an anharmonic lattice dynamic by solving BTE, one must first obtain the harmonic and anharmonic IFCs. The former needs the second-order derivatives of the total potential energy with respect to the atomic displacements, and the latter requires the third-order derivatives. Anharmonic lattice dynamic calculations have been developed in open-source packages such as:

ShengBTE: https://www.shengbte.org

AlmaBTE: https://almabte.bitbucket.io

Phono3py: https://atztogo.github.io

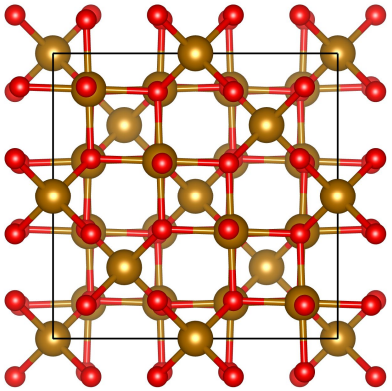
AFLOW-AAPL: https://doi.org/10.1038/s41524-017-0046-7

AlaMode: https://alamode.readthedocs.io/en/latest/intro.html

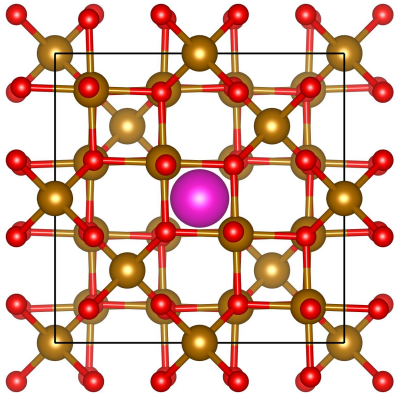
Compressive sensing lattice dynamics: https://doi.org/10.1103/PhysRevB.100.184308

Reflections on the BTE-IFC Method

- It is only applicable to crystalline solids
- The calculation of IFC based on density functional method can be hefty, especially given the high convergence thresholds (for forces and sampling points over the Brillouin zone (*k*-points)
- In complex structures (including dopants, defects, and dislocations) the number of required configurations calculated with density functional theory rises rapidly



Pristine Fe_3O_4:
54 Configurations



Eu doped Fe_3O_4:
240 Configurations

- In some lucky cases where good forcefield libraries are available, one can substitute the density functional calculations with classical lattice dynamics calculations, resulting in huge computational savings

Molecular Dynamics based Methods
Equilibrium: Green-Kubo

A system under an equilibrium molecular dynamics simulation has a constant average temperature and a zero average heat flux. Nevertheless, because of the instantaneous fluctuations in temperature, there is a finite heat flux at each instant of time. In the Green-Kubo method, the lattice thermal conductivity of the system is related to the time required for such fluctuations to dissipate according to:

$$\kappa_{\alpha\beta} = \frac{1}{k_B T^2 \Omega} \int_0^\infty \langle Q_\alpha(0) Q_\beta(t) \rangle dt,$$

where k_B is Boltzmann's constant, T the temperature of the system, Ω is the system volume, and $Q_\alpha(0)$ and $Q_\beta(t)$ are the instantaneous heat current in the α and β directions at the beginning and time t, respectively. The angular brackets denote the ensemble's average.

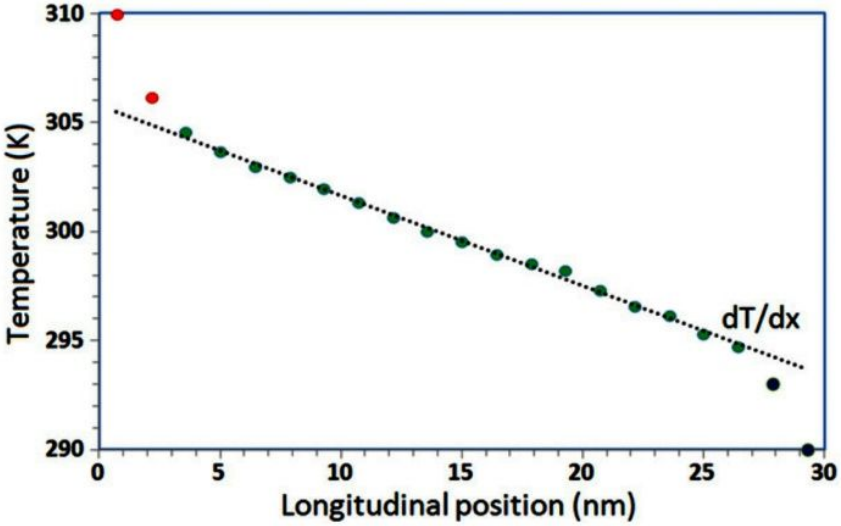
The main challenges in the Green-Kubo thermal conductivity calculation are the difficulties associated with carrying out the time integral up to infinity (a very long time in reality) and ensuring its convergence.

Molecular Dynamics Based Methods
Non-Equilibrium: Green-Kubo

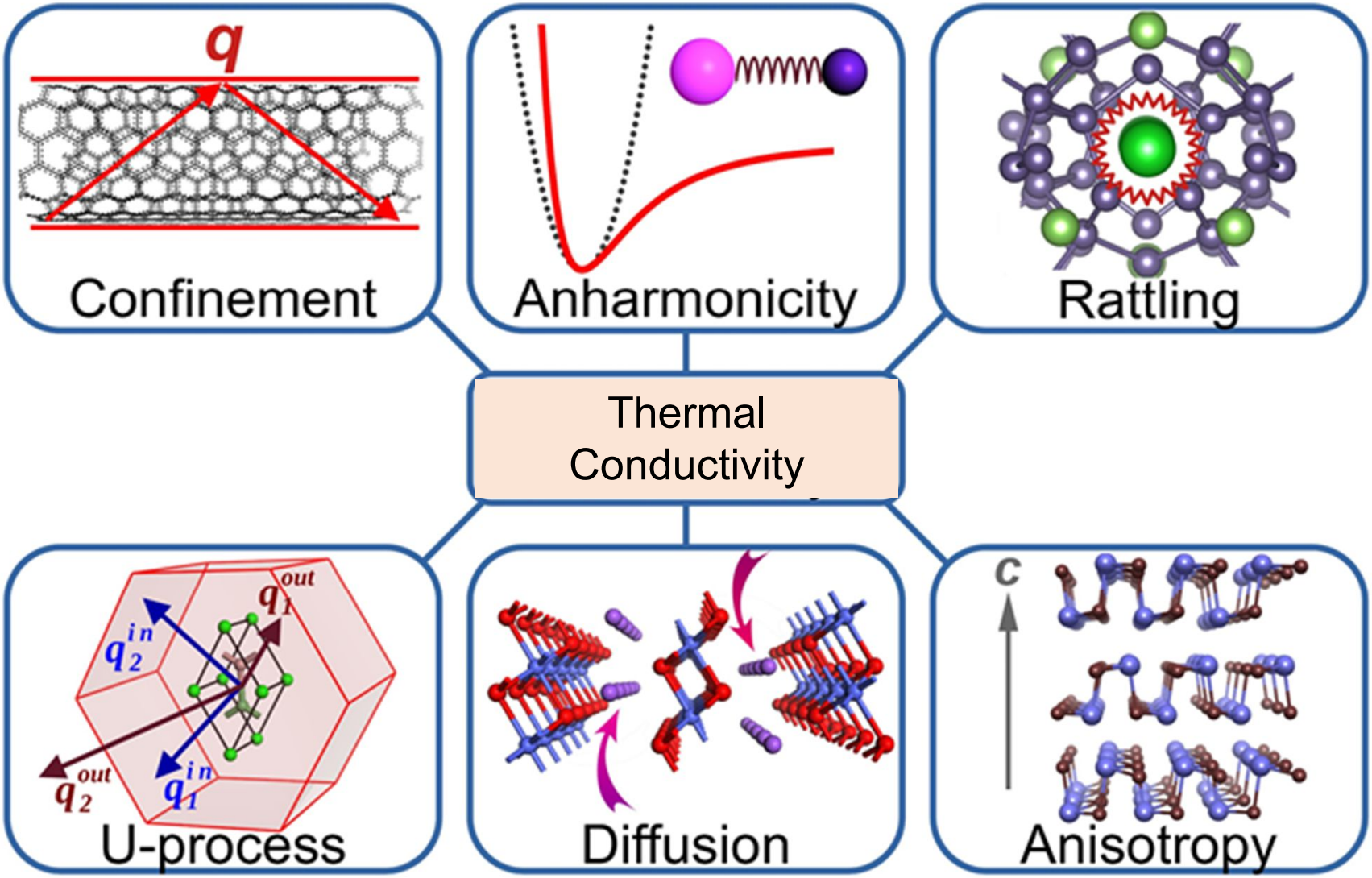
In nonequilibrium molecular dynamics, the thermal conductivity is calculated from the heat flux ratio to temperature gradient, similar to experiments based on Fourier's law. The usual approach for running such simulation is to impose a known heat flux and calculate the resulting temperature gradient.

Heat Exchange is done by interchanging the velocities of the mentioned atoms by introducing an elastic collision between them. The velocities arising from such a collision are then assigned to the atoms before continuing the simulation. Such a collision conserves the total kinetic energy, potential energy, and linear momentum of the system during heat exchange between the sections. The average heat flux in this scheme is calculated according to:

$$Q_i = \frac{1}{2ANt_0} \sum_{n=1}^{N/\nu_t} \frac{1}{2} m_h \left(\boldsymbol{v}_h'^2(n\nu_t) - \boldsymbol{v}_h^2(n\nu_t) \right)$$



Typical temperature gradient obtained from NEMD simulation. Copyright 2012 Elsevier.


q
Confinement
Anharmonicity
Rattling
Thermal
Conductivity
q_2^{in}
q_1^{out}
q_2^{out}
q_1^{in}
U-process
Diffusion
c
Anisotropy

Conclusions and Further Readings

- We reviewed the experimental and theoretical concepts in thermal conductivity
- thermal conductivity can be attributed to two sources of conductions in solids; electrons, and phonons; The latter being more important for fusion applications
- Thermal conductivity can be generally measured either by a steady-state method or by a transient method,
- Phonon analysis provides deep and accurate insight into materials' thermal behaviour.
- Luckily, the phonon dispersion relations for any given materials can be calculated using *ab initio* methods, providing a powerful predictive tool for guiding and optimizing the experimental efforts
- However, as material complexity grows, the computational costs becomes untrackable quickly
- Alternatively, thermal conductivity can be calculated using molecular dynamics where, for instance, the inverse of the experimental is simulated by establishing a known temperature gradient across a large supercell and calculating heat flow to obtain thermal conductivity
- In any case, developing new and accurate forcefield libraries for molecular dynamics seems to be the best strategy forward

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Low thermal conductivity: fundamentals and theoretical aspects in thermoelectric applications

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ABSTRACT

The thermoelectric effect allows direct and reversible conversion of thermal energy into electricity. As a result, thermoelectric generators and coolers can be an essential part of the solution to today's energy challenges by reducing adverse effects on the environment. Nonetheless, further progress in thermoelectric research critically depends on designing novel thermoelectric materials that substantially exceed the current efficiency limits. As the thermoelectric performance is inversely proportional to the material's thermal conductivity, the design and discovery of materials with low thermal conductivity and robust electronic properties are of paramount importance. However, this quest for materials with low thermal conductivity is arguably the most challenging aspect of optimizing the thermoelectric modules. In this review, we first introduce the historical, experimental, and computational aspects of the concept of thermal conductivity. We then explore in detail the theoretical foundations of intrinsically low thermal conductivity in bulk and low-dimensional materials. We specifically examine how density functional and molecular dynamics calculations help identify low thermal conductivity characteristics such as bond anharmonicity, weak bonding of a rattling atom, cation disorder, and diffusion. Furthermore, we present high throughput computational screening strategies for discovering new materials with low thermal conductivity by discussing the recent advances in the relevant computational tools.

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A review of recent progress in thermoelectric materials through computational methods

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Abstract

Reducing our overwhelming dependence on fossil fuels requires groundbreaking innovations in increasing our efficiency in energy consumption for current technologies and moving towards renewable energy sources. Thermoelectric materials can help in achieving both goals. Moreover, because of recent advances in high-performance computing, researchers more increasingly rely on computational methods in discovering new thermoelectric materials with economically feasible performance. In this article, significant thermoelectric materials discovered through these computational methods are systematically reviewed. Furthermore, the primary computational tools that aid the design of the next-generation thermoelectric materials are introduced and discussed. These techniques include various levels of density functional theory, electronic transport simulations, and phonon calculations.