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Modeling thermoelectric materials and devices

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Recent advances in modeling and simulation suggest thermoelectric devices can be competitive with existing refrigeration and power generation technologies.

The thermoelectric effect, a conversion between thermal and electrical energy, was discovered in the early part of the 19th century. It is the basis for how a thermocouple measures temperature and has been used in niche applications for refrigeration and power generation since the 1950s.

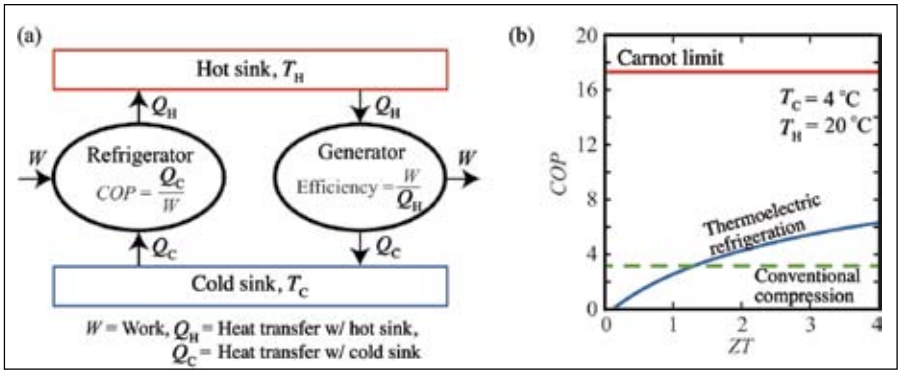
Thermoelectric devices have the advantage of containing no moving parts, making them quiet, durable and reliable. It is only recently that advances in materials development, theory and computational tools have suggested that thermoelectric devices can compete with traditional refrigeration and power generation technologies.[1–5]

Modeling and simulation have an important role in the development of materials and devices for thermoelectric energy conversion applications. Atomistic modeling tools (e.g., density functional theory calculations and molecular dynamics simulations) provide strategies for the design of nanostructured materials and help to elucidate the underlying physical phenomena. Continuum modeling at the device-scale, using thermodynamic cycles, heat transfer analysis and finite-element method calculations, is critical for optimizing the integration of thermoelectric materials with devices and for predicting how these devices will interact with their environment.

Thermodynamic cycle and device-level energy balance

A thermoelectric device can be used for refrigeration or for power generation. The schematic diagram in Figure 1(a) shows that, in refrigeration, electrical power is supplied and thermal energy is moved from a cold sink to a hot sink. The device performance is quantified by the coefficient of performance, defined as the thermal load taken from the cold sink divided by the work input. Figure 1(a) shows that, for power generation, heat transfer from a hot sink to a cold sink produces electrical power. The device performance is quantified by its efficiency, defined as the generated power divided by the thermal load from the hot sink. The maximum COP (coefficient of performance) or efficiency is set by the Carnot limit, $T_C/(T_H-T_C)$. It is a function of the temperatures of the hot and cold sinks, as shown in Figure 1(b).

The remainder of this article discusses thermoelectric refrigeration.



(Credit: TMcGaughey.)

Figure 1. (a) Thermodynamic cycles for refrigeration and power generation. In a thermoelectric refrigerator, work input as electrical power allows for heat removal from a cold sink. In a thermoelectric generator, heat transfer from a hot sink produces an electrical potential. (b) Coefficient of performance for a refrigerator operating at room temperature.

The modeling tools and techniques discussed, however, are equally applicable to power generation.

A specific definition of a thermoelectric refrigerator starts by considering the single thermoelectric module shown in Figure 2. The module consists of two legs, made from different thermoelectric materials, one *n*-type and one *p*-type. The legs are connected in series electrically through metal contacts but are in a parallel arrangement from the standpoint of heat transfer between the hot and cold sinks. In a real device, hundreds of thermoelectric modules are electrically connected in series.

An expression for the maximum COP based on the electrical and thermal properties of the legs can be obtained by performing an energy balance on the module.[6] In the thermoelectric refrigerator, a voltage is applied across the module, leading to the flow of electrical current. Two separate energy conversion mechanisms develop. First, there is Peltier cooling at the cold junction (leading to the absorption of energy from the cold sink) and Peltier heating at the hot junction (leading to the release of energy to the hot sink). The magnitudes of the heating and cooling are given by $(S_p - S_n)IT = SIT$, where S_p and S_n are the Seebeck coefficients of the *p*- and *n*-type materials, respectively, I the current and T the junction temperature. The Seebeck coefficient is a temperature-dependent material property that describes the voltage induced in a material in the presence of a temperature gradient. It is positive for a *p*-type material and negative for an *n*-type material.

The current flow leads to Joule heating as well as the desired Peltier heating and cooling in the legs. Joule heating is undesirable, because it adds to the heat load at the cold junction, which the Peltier cooling must remove. The strength of the Joule heating is related to the current flow and to the electrical conductivities (σ) of the thermoelectric materials, which will be taken to be same for the *n*- and *p*-type materials in this analysis.

The temperature difference between the hot and cold sinks leads to parasitic heat conduction through the legs and an additional, undesirable, heat load at the cold junction. The magnitude of the heat conduction is related to the thermal conductivity (k) of the legs, which will be taken to be the same for the *n*- and *p*-type materials in this analysis.

An expression is obtained for the COP in terms of the materials properties, leg geometries, temperatures of the hot and cold sinks and the electrical current by performing an energy balance at the hot and cold junctions, including the thermal loads, Peltier heating and cooling, Joule heating and thermal conduction. Increased current leads to increased Peltier heating and cooling (desirable) but also to increased Joule heating (undesirable). There is an optimal current flow that leads to a maximum COP, given by

$$\mathrm{COP} = [T_C/(T_H - T_C)]\,\{[(1 + ZT)^{1/2} - (T_H/T_C)]/[(1 + ZT)^{1/2} + 1]\} \quad (1)$$

This expression for the maximum COP contains the dimensionless parameter ZT, defined by

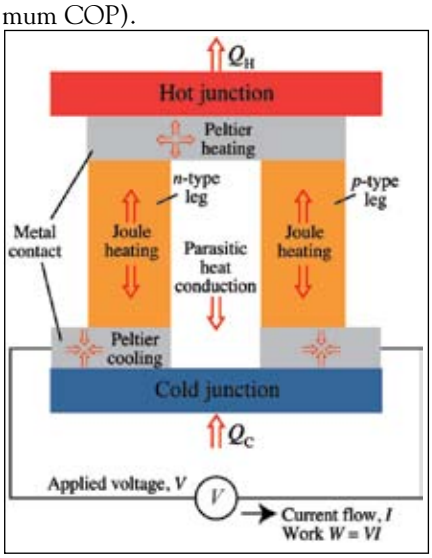
$$ZT = (S^2\sigma/k)[(T_H + T_C)/2] \quad (2)$$

which is the thermoelectric figure of merit. The product $S^2\sigma$ in the numerator is called the power factor. Although there is no theoretical limit to ZT, the COP approaches the Carnot limit, $T_C/(T_H - T_C)$, as ZT approaches infinity, as shown in Figure 1(b).

The minds of thousands of scientists and engineers during the past 60 years have been occupied devising schemes for maximizing ZT by manipulating the Seebeck coefficient, electrical conductivity and thermal conductivity. However, device-level modeling needs to be addressed before discussing how ZT can be predicted from theory and of the strategies that have emerged for increasing ZT.

The model described by equations (1) and (2) is a simplification of a real device. Issues which need to be considered that make the maximum COP impossible for real devices to achieve.

- First, it is difficult to find *n*- and *p*-type materials with the same electrical and thermal conductivities (an assumption in the expression for maximum COP).



(Credit: TMcGaughey.)

Figure 2. Schematic diagram of a single thermoelectric refrigerator module. The hot and cold junctions are electrically insulating. This module comprises the detail that is the oval marked "Refrigerator" in Figure 1(a).

• Second, the electrical contact resistances at material interfaces (e.g., between the thermoelectric legs and the metal contacts, and between the hot and cold sinks and the thermoelectric device) lead to a smaller current flow for a given applied voltage. At the same time, thermal contact resistances at these interfaces benefit the system by decreasing the parasitic heat conduction losses. Interfacial effects become more important as thermoelectric devices are decreased to millimeter scales and below.

• Third, heat transfer to the device—which typically will be operated at temperatures below ambient conditions—by radiation and convection from the surroundings, increases the thermal load at the cold junction and negatively affects performance.

• Fourth, in the presence of a potentially large temperature difference, all material properties become temperature (and, thus, location) dependent.

These factors affect the device performance by changing the optimal current at which the device should be operated and decreasing the COP that can be realized.

These effects cannot be included accurately in a simple analytical model, and require more detailed modeling using numerical techniques, such as finite-element analysis. Although significantly more costly than analytical models from a computational perspective, finite-element studies provide an important link between modeling and performance of real devices.

Predicting TE properties

The following section explains how researchers are using modeling to predict the three relevant materials properties–electric conductivity, Seebeck coefficient and thermal conductivity–and how modeling facilities strategies for maximizing *ZT*.

Electrical conductivity describes how easy it is for electrons to move through a material. Qualitatively, the electrical conductivity is related to the material's Fermi level, which indicates the energy of the highest occupied electron state. In metals, where the Fermi level lies in the conduction band, there are free electrons, and the electrical conductivity is high (approximately 10^7 siemens per meter). In an *undoped* semiconductor, where the Fermi level lies between the valence band and the conduction band, the electrons are tightly bound to the atomic nuclei, and the electrical conductivity is very low (much less than 1 siemen per meter). In *doped* semiconductors—the materials typically used in thermoelectric energy conversion applications—the electrical conductivity can be made close to that of metals.

The **Seebeck coefficient** describes the relationship between an applied voltage and the induced temperature difference (or vice-versa). The Seebeck coefficient also is related to the material's Fermi level. The magnitude of the Seebeck coefficient is approximately 10 microvolts per kelvin for metals and approximately 100–500 microvolts per kelvin for doped semiconductors (positive for *p*-type and negative for *n*-type). Recall from the device-level discussion that the difference between the Seebeck coefficients of the *p*- and *n*-type materials to calculate the thermoelectric figure of merit *ZT*.

Thermal conductivity describes how easy it is for thermal energy to transfer through a material by conduction. For solids at room temperature, thermal conductivity varies from about 0.01 watts per meter kelvin for aerogels to a few thousand watts per meter kelvin for carbon nanotubes and graphene. Glass has a room-temperature thermal conductivity of 1.4 watts per meter kelvin and silicon, 140 watts per meter kelvin. Thermal conduction in a solid results from the transport of electrons ($k_{electron}$), which dominate in metals, and phonons (k_{phonon}), which dominate in semiconductors and dielectrics. A phonon is a quasi particle (it has no mass) that carries energy waves generated by the vibrations of the atoms. Like a water wave, which carries energy while imparting no net displacement to the individual molecules, a phonon carries energy through a solid with no net mass transfer. Because it is a wave, a phonon has a frequency, wavelength and velocity.

To predict electrical conductivity, the Seebeck coefficient and the electronic contribution to the thermal conductivity requires knowledge of a material's electronic band structure (i.e., the energy levels of all the electrons in the system) and the mobility of the electrons. The mobility often is expressed using a relaxation time, which gives the average time between the collisions of an electron with other electrons, defects, system boundaries and phonons. Alternatively, the mean free path (the distance an electron travels between collisions) is used. Because electrons are quantum mechanical entities, their behavior is governed by the Schrödinger equation, and quantum-based calculations are required. Various techniques are available, but increases in accuracy come at very large increases in computational power, requiring microprocessor clusters or supercomputers.

Density functional theory is the most commonly used quantum-based approach. Traditional density functional theory underestimates the electronic band gap; recently it has been modified to address this issue, typically by making the calculations more complex. It is more challenging to predict the electron relaxation times than the band structure, and simplifying assumptions typically are made (e.g., that all electrons have the same relaxation time). Once researchers determine the electronic band structure and relaxation times, they then can calculate the electrical conductivity, Seebeck coefficient and electronic contribution to the thermal conductivity using solutions of the Boltzmann transport equation and definitions of the electrical and thermal fluxes.

Calculating the phonon contribution to the thermal conductivity is analogous to that of electrons: It requires the phonon band structure (i.e., how the phonon frequencies are related to their wavelengths) and relaxation times. These quantities can be predicted using molecular dynamics simulations and/or lattice dynamics calculations. In a molecular dynamics simulation, the

positions and velocities of a collection of atoms are predicted using Newton's second law. Because this approach uses the classical framework of Newton's laws of motion, it is suitable only at high temperatures (typically above the Debye temperature, the temperature above which all thermal vibrations are fully activated), where quantum effects on the phonon mode populations are small. In a lattice dynamics calculation, the atoms are treated as a mass–spring system, leading to a multiple degree-of-freedom vibration problem. Linear (harmonic) analysis allows for the calculation of the frequencies, whereas the relaxation times are obtained by perturbing the harmonic solution with higher-order terms. Lattice dynamics calculations are performed in a quantum framework, allowing for the consideration of lower temperatures than what can be modeled in a molecular dynamics simulation.

The required inputs to a molecular dynamics simulation or a lattice dynamics calculation are the forces that the atoms in the thermoelectric material exert on each other. These forces can come from two sources. The first source uses quantum-mechanics-based density functional theory calculations. Although highly accurate and allowing for all the thermoelectric properties to be predicted using the same framework, this type of phonon calculation is computationally demanding, and the theoretical techniques are still being developed. Only in the past five years have the first fully quantum predictions of the phonon contribution to thermal conductivity been made on simple materials (e.g., silicon), but the good agreement found with experiment is encouraging. This quantum-based approach is only feasible as a means to provide the input to lattice dynamics calculations. The computational time required to use quantum calculations to predict the forces between atoms makes it prohibitive to use quantum-based molecular dynamics simulations to predict phonon properties.

Empirical interatomic potentials are the second source for predicting the forces between atoms. A potential is typically an algebraic expression that provides the energy and forces between pairs or triplets of atoms based on their relative positions. The forms of these potentials are selected to capture the nature of the bonding in a specific material (e.g., electrostatic, covalent and van der Waals), and free parameters are chosen so as to reproduce experimental data or predictions from quantum calculations, such as the lattice constant, bulk modulus or defect energies. Because of their simple algebraic form, potentials are used to calculate the forces between atoms many orders of magnitude faster than quantum calculations, allowing for very fast lattice dynamics calculations and molecular dynamics simulations of sufficient length to predict phonon properties.

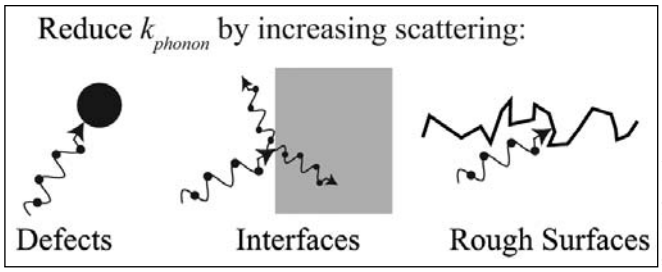


Figure 3. The phonon contribution to thermal conductivity can be reduced by adding defects, interfaces and free surfaces that can scatter phonons. Limits to thermal conductivity are now being reached, but there is still potential to increase the Seebeck coefficient by manipulating the electronic band structure.

The disadvantage of this approach is that most of the potentials are fit to structural and mechanical properties and do a poor job of predicting thermal properties (e.g., phonon frequencies and thermal conductivity).

Although using potentials to drive lattice dynamics calculations or molecular dynamics simulations can capture the qualitative trends found by experiment (e.g., how thermal conductivity varies with temperature), they typically do not have good quantitative predictive power. In recent years, however, more effort has been put into developing potentials using phonon properties as input, suggesting that this approach, which is orders of magnitude faster than quantum-based methods, may yet prove to be suitable for accurately predicting the thermal performance of thermoelectric materials.

This discussion on how to predict the electrical conductivity, Seebeck coefficient and thermal conductivity is valid for bulk materials, which was the major focus of thermoelectric research up to the 1990s. Since then, nanostructured materials have emerged as exciting candidates for increasing ZT. Such materials may contain free surfaces, as in a nanowire, or interfaces spaced as closely as a few nanometers, as in a superlattice, which creates additional scattering sites for electrons and phonons. Predictions of how electrons and phonons interact with interfaces can also be made using density functional theory calculations, molecular dynamics simulations and lattice dynamics calculations.

Although modeling of a bulk material can be performed at the unit-cell level, modeling a free surface or interface requires much larger computational domains and resources. Furthermore, much of the theoretical methodology for modeling free surfaces and interfaces is still under development.

Maximizing the figure of merit

The above explanation of thermoelectronic properties and modeling provides a backdrop for looking at the development of thermoelectronic materials during the past half-century.

The emphasis for thermoelectric refrigeration has been on finding materials that maximize ZT to realize a COP as close to the Carnot limit as possible. To compete with traditional technologies, ZT greater than 3 is required.

Although high values of ZT also are desired in power generation, recent emphasis on waste heat recovery (e.g., from the tailpipe of a car) points to a need for thermoelectric materials that are inexpensive, safe and easily pro-

cessed with less emphasis on high *ZT* values.

The definition of *ZT* in Equation (2) shows that it is desirable to maximize the Seebeck coefficient (to maximize the Peltier heating and cooling), maximize the electrical conductivity (to minimize Joule heating) and minimize thermal conductivity (to minimize the parasitic heat flow from the hot junction to the cold junction). The ideal thermoelectric material is a so-called phonon-glass, electron-crystal and has the low thermal conductivity of a glass (where the atoms are disordered) but the high electrical conductivity of a crystal (where the atoms are ordered). In bulk materials, these three properties are not independent and their relationship hinders *ZT*. Metals, for example, have a high electrical conductivity but high thermal conductivity and low Seebeck coefficient, making them not useful for thermoelectric energy conversion.

In the initial development of thermoelectric materials in the 1950s and 1960s, doped semiconductors attracted attention because of the ability to control their electronic band structure and achieve *ZT* values slightly lower than 1. Bismuth and it compounds were the best materials, but issues regarding abundance and toxicity were barriers to large-scale commercialization. Also, the available *ZT* was simply not high enough to make thermoelectric refrigerators and generators compete with existing technologies. (The exception was niche applications, such as power generation in deep-space probes, where the excellent durability and reliability of thermoelectric devices offset low efficiencies.) More abundant materials, such as silicon, suffered from high bulk thermal conductivities, leading to *ZT* values on the order of 0.01 and were of essentially no interest.

A major breakthrough came in the late 1990s, when it was realized that restricting semiconductors to small dimensions (e.g., thin films, nanowires and superlattices) could dramatically decrease their thermal conductivity while maintaining good electrical properties. This thermal conductivity decrease occurs because the phonon mean free path is typically longer than the electron mean free path. Appropriately spaced boundaries in a material (either interfaces or free surfaces) can significantly increase phonon scattering, as shown in Figure 3, but not affect electron scattering.

Thus, much of the effort in thermoelectric materials design during the past 15 years has focused on decreasing the phonon contribution to the thermal conductivity.[3–5] Initial efforts have probed ordered nanostructures, such as superlattices (periodic one-dimensional arrangement of nanometer-sized layers) or bulk materials with regularly spaced quantum dots. *ZT* values of about 2 have been reported, but these materials, (e.g., Bi_2Te_3/Sb_2Te_3 superlattices,) suffer from slow and costly production.

Noting that the success of superlattices comes from the high density of internal interfaces and not the periodicity, researchers have moved toward making bulk-like materials with nanometer-sized grains, with encouraging results.

Nanostructures with free surfaces also show promise for thermoelectric energy conversion, and experimental measurements of roughened silicon nanowires show dramatic decreases in thermal conductivity, pushing *ZT* toward unity. Atomic-level modeling is important in understanding these measurements so that the underlying physical mechanisms can be identified and exploited in the design of new materials.

In recent years, researchers have also explored bulk materials, with a particular interest in those with large unit-cells,[2] such as skutterudites, which contain angstrom-sized internal pores. Phonon transport in these materials can be hindered by the presence of "rattler" atoms inside these pores or through the small-scale disorder present at the unit cell level.

Outlook for modeling and thermoelectric materials

Current research trends suggest that a lower bound to the phonon contribution to thermal conductivity (approximately 1 watt per meter·kelvin) has been reached. Additional gains will be marginal and will not allow for the still-needed increases in *ZT*. Effort is shifting toward the electron transport properties, with a focus on increasing the Seebeck coefficient through quantum confinement and adding resonant impurity states to distort the electronic band structure.

Because of advances in theoretical tools and computational power, modeling of thermoelectric materials and devices has emerged as an important component in the progress of pushing *ZT* higher and identifying new materials. Although modeling alone cannot be used to design new materials, it is important in screening materials more efficiently than can be done through experimental fabrication and characterization. Modeling also allows for identification of the basic physical phenomena that govern the transport of charge and heat, allowing for new insights into how materials can be tailored to optimize their thermoelectric properties.

About the author

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References

[1]A. Majumdar, "Thermoelectricity in Semiconductor Nanostructures," *Science*, **303**, 777–78 (2004).

[2]G.J. Snyder and E.S. Toberer, "Complex Thermoelectric Materials," *Nat. Mater.*, **7**, 105–14 (2008).

[3]A.J. Minnich, M.S. Dresselhaus, Z.F. Ren and G. Chen, "Bulk Nanostructured Thermoelectric Materials: Current Research and Future Prospects," *Energy Environ. Sci.*, **2**, 466–79 (2009).

[4]D.L. Medlin and G.J. Snyder, "Interfaces in Bulk Thermoelectric Materials," *Curr. Opin. Colloid Interface Sci.*, **14**, 226–35 (2009).

[5]M. Zeberjadi, K. Esfarjani, M.S. Dresselhaus, Z.F. Ren and G. Chen, "Prespectives on Thermoelectrics: From Fundamentals to Device Applications," *Energy Environ. Sci.*, **5**, 5147–62 (2012).

[6]M. Kaviany, *Principles of Heat Transfer*. Wiley, New York, 2002. ■