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Diffusive and ballistic thermo-electric transport

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Abstract. The efficiency of existing thermoelectric power generators is much lower than mechanical engines. We discuss the similarities and differences between solid-state thermoelectric devices and other thermal engines. In nanostructured materials, non-equilibrium energy and current transport could be important. We describe the transition between ballistic and diffusive regimes and how this can alter the thermoelectric effects and improve the energy conversion efficiency.

As the world strives to meet the huge demand for electricity, sustainable energy technologies are attracting significant attention. Currently, however, renewable energy sources such as solar and wind, supply only a small fraction of the electricity consumed due, primarily, to their relatively high cost. An untapped source of low-cost sustainable energy is heat. Energy from fossil fuels, in fact, is first converted to heat before generating electricity or mechanical motion. The progress in improving the efficiency of power plants and internal combustion engines has been slow. State-of-the-art thermal engines operate close to the Curzon-Ahlborn limit of efficiency at maximum output power\(^1,2\) (30-40\%, see Fig. 1) but, the majority of the energy produced is wasted in the form of low quality heat. Solid-state thermoelectric devices allow direct conversion of heat to electricity. However, due to their moderate energy conversion efficiency and relatively high cost, their use has been mainly limited to radioisotope thermal generators (RTG) for deep space satellites and remote power generation.

Efficiency of thermoelectric devices is determined by their material’s figure-of-merit, \(Z\), which is the ratio of the Seebeck coefficient squared times the electrical conductivity divided by thermal conductivity. \(ZT\) values (where \(T\) is the absolute temperature) remained close to 1 from 1950’s to 2000. As a result, the energy conversion efficiency of commercial TE generators is lower than the thermal

Fig. 1. Energy conversion efficiency versus ratio of ambient to heat source temperatures\(^1,2\). \(ZT\) curves correspond to the maximum output power case\(^1\). The dots represent the observed efficiencies of the existing thermal power plants\(^2\).
engines by a factor of 4 to 6. During the last ten years there has been extensive work where nanostructured materials\cite{3,4} are used to engineer, for example, the thermal conductivity of the material with very little impact on electrical transport. $ZT \sim 1.5$ to 1.8 has been demonstrated by several groups\cite{4}. Even though there seems to be a long way to go before thermoelectric power generators approach the efficiency of mechanical engines, thermoelectrics can still have a big impact in solving our energy challenge. This is because solid-state thermoelectric power generators are scalable; they can work with heat sources of various dimensions with a wide range of hot and cold temperatures. A cheap, low efficiency thermoelectric system can have a huge impact on waste heat recovery applications and in topping cycle power generation.

In this talk we review the fundamental differences between mechanical engines and solid-state thermoelectrics. Conversion of heat into electricity requires taking energy from random degrees of freedom and converting it into directed current. The process is inherently limited by the 2\textsuperscript{nd} law of thermodynamics. However we are far from this limit. One of the key differences between thermoelectric devices and conventional thermal engines is the cyclic nature of the latter where the working gas is brought in contact with a hot reservoir and then a cold reservoir whereas thermoelectric devices are in contact with both reservoirs at the same time\cite{5}. Another key difference is the phase transition\cite{6} in the working gas which allows storing a lot of energy in internal degrees of freedom (latent heat) and limiting the amount of heat leakage\cite{7}. The efficiency at maximum output power of thermoelectric devices is compared with other thermal engines and quantum dot devices and the relation with the Curzon-Ahlborn limit will be described\cite{1}.

In nanostructured materials, it is possible to change the effective “bulk” properties of the material and engineer the electrical and thermal transport properties. This is well described with standard Boltzmann transport. Tradeoffs in “artificially” engineered nanomaterials are similar to existing bulk semiconductors. On the other hand, in heterogeneous meta-materials, when the size of the constituent materials is smaller than the electron or phonon mean-free-paths, it is possible to create a non-equilibrium population of carriers. Two examples, thermionic refrigerators\cite{8,9} and non-linear Peltier coolers\cite{10} will be briefly described.

Finally, we emphasize that thermoelectric figure-of-merit is also important from a “microscopic” point of view. Shastry\cite{11} has recently shown that $ZT$ (or more correctly the ratio $Z^*T/(1+Z^*T)$) is the fundamental coupling parameter between electrical charge transport and thermal energy transport by electrons in a material. Here $Z^*$ is the high frequency figure-of-merit. $Z^*T/(1+Z^*T)$ plays the same role as $C_p/C_v - 1$ which is the coupling constant between sound and energy modes in anharmonic lattices or in superfluid systems. $C_p$ and $C_v$ are the constant pressure and the constant volume heat capacities. Materials with high thermoelectric figure-of-merit can be useful since charge and energy transport
can be strongly coupled at a microscale level\textsuperscript{7,12} thus leading to the design of new information processing and energy conversion devices.

References