Do Thermoelectric Materials in Nanojunctions Display Material Property or Junction Property?

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The miniaturization of thermoelectric nanojunctions raises a fundamental question: do the thermoelectric properties of the bridging materials in nanojunctions remain to display material properties or show junction properties? In order to answer this question, we investigate the Seebeck coefficient $S$ and the thermoelectric figure of merit $ZT$ especially in relation to the length characteristics of the junctions from the first-principles approaches. For $S$, the metallic atomic chains reveal strong length characteristics related to strong hybridization in the electronic structures between the atoms and electrodes, while the insulating molecular wires display strong material properties due to the cancelation of exponential scalings in the DOSs. For $ZT$, the atomic wires remain to show strong junction properties. However, the length characteristics of the insulation molecular wires depend on a characteristic temperature $T_0 = \sqrt{\beta/\gamma}$ around 10 K. When $T \ll T_0$, where the electron transport dominates the thermal current, the molecular junctions remain to show material properties. When $T \gg T_0$, where the phonon transport dominates the thermal current, the molecular junctions display junction properties.

Nanoscale thermoelectric devices can be considered as the new types of devices which can be embedded into integrated chip sets to assist the stability of devices by converting the accumulated waste heat into useful electric energy. There has been an ever increasing interest in the thermoelectric properties of nanojunctions, partially motivated by the recent experiments demonstrating the capability of measuring the Seebeck coefficients in the molecular junctions. As the Seebeck coefficients are relevant not only to the magnitude but also to the slope of density of states (DOSs), they can reveal more detailed information about the electronic structures of the materials sandwiched in the nanojunctions beyond what the conductance measurements can provide. The Seebeck coefficients have been applied to explore the electronic structures of molecular junctions using functional substitutions for the bridging molecules. Theoreticians have proposed using gate fields and external biases as means to modulate the Seebeck coefficients in nanojunctions. Much research has been devoted to the study of Seebeck coefficients, but little is known about the fundamental thermoelectric properties in nanojunctions.

Indeed, the miniaturization of thermoelectric nanojunctions raises a fundamental question: do bridging thermoelectric material in nanojunctions show material properties or junction properties? Thermoelectric bulk crystals usually show material properties, where the thermoelectric physical quantities are irrelevant to the sizes and shapes of materials. In addition, recent experiments on Seebeck coefficients in molecular junctions also reveal strong signals of material properties. These experiments have observed that Seebeck coefficients are insensitive to the number of molecules in junctions and show rather weak dependence on the lengths of the bridging molecules, which is in sharp contrast to the conductance which shows strong exponential dependence on the lengths of molecules. However, the bridging materials in nanojunctions may have strong interactions with the contacts. From this point of view one can say thermoelectric quantities can display the junction characteristics. Considering the examples and the reason quoted above, it is therefore not obvious whether the thermoelectric quantities of the bridging materials in nanojunctions display junction properties or material properties.

In this letter, we will show that the thermoelectric quantities in nanojunctions unnecessarily display entire material properties or junction properties. To demonstrate this point, this study investigates two important thermoelectric quantities, the Seebeck coefficient ($S$) and the thermoelectric figure of merit ($ZT$), in (metallic) aluminum atomic junctions and (insulating) molecular junctions. It shows that metallic atomic chains reveal strong junction properties while the insulating molecular wires partially possess the material properties, where $S$ reveals the material property and $ZT$ displays the junction property at temperatures larger than the characteristic temperature $T_0$.

To answer the question, we have developed a theory with analytical expressions for $S$ and $ZT$ allied to a fully self-consistent first-principles calculation in the framework of the density functional theory (DFT). It allows us to numerically calculate $S$ and $ZT$ and subsequently investigate these quantities analytically. We focus on the subject on whether $S$ and $ZT$ depend on the characteristics of the junctions, especially on the dependence on length-characteristic of junctions. Before turning to the detailed discussion, let us begin with a brief introduction on how to calculate $S$ and $ZT$. First, we consider that the junction consists of source-drain electrodes, with distinct chemical potentials $\mu_{L(R)}$ and temperatures $T_{L(R)}$, as independent electron and phonon reservoirs. When an additional infinitesimal temperature $\Delta T$ is applied across the junction, an extra voltage $\Delta V$ is induced to compensate the electric current induced by the temperature gradient $\Delta T$ across the junction. We then derive the...
expressions for $S$ (defined as $S = \Delta V/\Delta T$) and the electron thermal conductance (defined as $\kappa_{el} = \Delta J_Q^e/\Delta T$), where $J_Q^e$ is the thermal current conveyed by the electrons which also carry the electric current).

$$S = -\frac{1}{e} \frac{K_L^e + K_R^e}{K_L^e + K_R^e}$$

$$\kappa_{el} = \frac{1}{h} \sum_{i=L,R} (K_i^e S + K_i^e T_i)$$

where $K_n^{L(R)} = -\int dE \left( E - \mu_{L(R)} \right) \frac{\partial f_k(E)}{\partial E} \tau(E)$, and the transmission function $\tau(E) = T^R(E) = T^L(E)$, which is a direct consequence of the time-reversal symmetry. It has been assumed that the left and right electrodes serve as independent electron and phonon reservoirs where the electron population is described by the Fermi-Dirac distribution function, $f_k(E) = \frac{1}{\exp ((E - \mu)/k_B T) + 1}$, and $k_B$ is the Boltzmann constant. The transmission functions are computed using the wave functions obtained self-consistently in the DFT framework [14, 15]. We should notice that the above equations are suitable for describing $S$ and $\kappa_{el}$ in nanojunctions operated under finite external biases, where two electrodes can have different temperatures.

In addition, the differential conductivity, typically insensitive to temperature in cases where direct tunneling is the major transport mechanism, can be expressed as

$$\sigma = \frac{e}{2} \int dE \sum_{i=L,R} f_k(E) (1 - f_k(E)) \tau(E) / k_B T_i.$$  

So far, the physical quantities ($S$, $\sigma$, and $\kappa_{el}$) which have been discussed are related to the electron transport. It must be noted that the heat current is conveyed by the electrons and phonons simultaneously. The phonon thermal conductance ($\kappa_{ph}$) usually dominates the combined thermal conductance $\kappa = \kappa_{el} + \kappa_{ph}$ at high temperatures. The complete discussion on $ZT$ shall include the essential ingredient $\kappa_{ph}$; thus $ZT$ can be expressed as follows:

$$ZT = \frac{S^2 \sigma}{\kappa_{el} + \kappa_{ph}},$$

where $T = (T_L + T_R)/2$ is the average temperature of the source-drain electrodes. We estimate the phonon thermal conductance following the approaches of Patthon and Geller [16]. It is assumed that the nanojunction is a weak elastic link, with a given stiffness which can be evaluated from the total energy calculations, attached to the electrodes modeled as phonon reservoirs. The phonon thermal conductance (defined by $\kappa_{ph} = \Delta J_Q^ph/\Delta T$) is given by:

$$\kappa_{ph} = \frac{\pi K^2}{h k_B} \int dE E^2 N_L(E) N_R(E) \sum_{i=L,R} \frac{n_i(E)(1 + n_i(E))}{T_i}.$$  

where $n_i(E) = 1/[\exp(E/k_B T_i) - 1]$ and $N_{L(R)}(E) \approx C \cdot E$ is the Bose-Einstein distribution function and the spectral density of phonon states in the left (right) electrode, respectively. The stiffness of the bridging nanostructure is $K = Y A/l$, where $Y$ is the Young’s modulus and $A$ ($l$) is its cross-section (length).

We have numerically computed $S$ and $ZT$ using Eqs. [10] to [13] along with the transmission functions obtained self-consistently in the DFT framework, as shown in Figs. [1] and [2]. To elaborate the properties of the Seebeck coefficient and the thermonic figure of merit, we will limit our discussion to the linear response regime (i.e., $\mu_L \approx \mu_R = \mu$) and $T_L = T_R = T$. After expanding $S$, $\kappa_{el}$, and $\kappa_{ph}$ in terms of the temperature $T$, we obtain the analytical expressions for the $S$ and $ZT$.

$$S \approx \alpha T,$$

where $\alpha = -\pi^2 k_B^2 \frac{\partial \mu}{\partial E} / (3e \tau(\mu))$. We have noted that the Seebeck coefficient depends on the magnitude and the slope of the transmission function, and is linearly proportional to $T$ at low temperatures.

$$ZT \approx \frac{\alpha^2 \sigma T^3}{\beta T + \gamma(l) T^3},$$

where we have expanded $\kappa_{el}$ and $\kappa_{ph}$ up to the lowest order in $T$, i.e., $\kappa_{el} \approx \beta T$, and $\kappa_{ph} \approx \gamma(l) T^3$. The prefactor $\beta$ is the thermonic figure of merit, $\alpha = \beta \gamma(l) / (3\hbar)$ and $\gamma(l) = 8\pi^2 k_B^2 C A^2 Y^2 / (15h^2)$, respectively. One may notice that there is a characteristic temperature $T_0 = \sqrt{\beta / \gamma(l)}$, which is around $10 \text{K}$ for the alkane thiols molecular junctions and is negligibly small for aluminum atomic junctions. When $T \ll T_0$, the electron thermal conductance dominates and $ZT \approx \alpha S^2 T / \kappa_{el} \approx [\alpha^2 \sigma / \beta]^2$, which is irrelevant to the length-characteristic of the junction and is proportional to $T^2$ as temperatures increase. When $T \gg T_0$, the phonon thermal conductance dominates and $ZT$ tends to have a saturation value of $ZT \approx \sigma S^2 T / \kappa_{ph} \approx \sigma^2 \sigma / \gamma(l)$, which is related to the length of the junction. The above analytic expressions provide a convenient means for analyzing the length characteristic of $S$ and $ZT$ in nanojunctions.

Before turning to the detailed discussion on the thermonic properties in nanojunctions, we must draw attention to the reason why nanojunctions display material properties for $S$ and $ZT$. The Seebeck coefficients are directly related to the transmission functions, which are determined by the electronic structures of the crystal materials irrelevant to the size and shape of the material, leading to the material properties for $S$. Furthermore, the conductance $\sigma$ and the combined thermal conductance $\kappa = \kappa_{el} + \kappa_{ph}$ are proportional to the contact surface and inversely proportional to the length scale in the bulk crystal materials, which leads to the material properties for $ZT$ due to the cancelation of the geometric factors in the conductance $\kappa$ and the combined thermal conductance $\kappa$. However, whether the thermonic materials in nanojunctions remain to display material properties or show junction properties have not yet been fully realized.
the thermal conductance \( \kappa \) of 3-Al atomic chain and its energy diagram (inset) where the Seebeck coefficient \( S \) now, let us look closely into the properties of the thermal current, and thus \( ZT \), the (insulating) alkanethiol junctions and the (metallic) aluminum atomic junctions. Alkanethiols \((CH_2)_n-SH\), denoted as \( C_n \), are a good example of reproducible junctions which can be fabricated \([18, 19]\). Alkanethiols with \( n = 1 \) (alkanethiol) and \( n = 2 \) (alkanediol) are conveyed by electron transport. When \( T \ll T_0 \), the phonon transport dominates the thermal current and thus \( ZT \approx \sigma S^2 T/\kappa_{el} \). As shown in the inset of Fig. 1(d), \( ZT \) is independent of the lengths of the \( C_n \) molecules and displays material properties. This result can be explained quite naturally by the cancelation of the exponential scaling in \( \sigma \) and \( \kappa_{el} \) because both the electric current (with conductance \( \sigma \)) and the electron thermal current (with thermal conductance \( \kappa_{el} \)) are conveyed by electron transport. When \( T \gg T_0 \), the phonon transport dominates the thermal current and thus \( ZT \approx \sigma S^2 T/\kappa_{ph} \). As shown in the main body of Fig. 1(d), \( ZT \propto l^3 \exp (-\xi l) \) because of \( \sigma \propto \exp (-\xi l) \) [see the inset of Fig. 1(b)], and \( \kappa_{ph} \propto l^{-2} \) [see Fig. 1(c)]. In this case, \( ZT \) displays junction properties.

Finally, we will examine the dependence of \( S \) and \( ZT \) on the lengths of the metallic aluminum (Al) atomic junctions \([17]\). An Al atomic chain is an ideal testbed for studying the charge transport at the atom-scale level [see the inset of Fig. 2(a) for a schematic of the aluminum atomic junction \([23, 24, 25, 26]\)]. This study has observed that \( S \) and \( ZT \) depend on the geometric characteristic of the junctions and show the junction properties in any case, which is in sharp contrast to the \( C_n \) junctions. At a fixed temperature, it has been observed that \( ZT \) and the magnitude of \( S \) increase as the number of Al atoms increases, as shown in Figs. 2(a) and (d). The increase of the Seebeck coefficients is due to the increase of the slopes in the transmission functions at the Fermi levels. The reason for this may be due to the strong hybridization between the electronic structures of atoms and the electrodes. The negative sign of the Seebeck coefficients indicates that the metallic Al atomic junctions are n-
type [the Fermi energy is closer to the lowest unoccupied molecular orbital (LUMO)].

In conclusion, this study has raised and answered an important fundamental question in thermoelectric nanojunctions: do the thermoelectric materials in nanojunctions remain to display material properties or show junction properties? To answer this question, we have developed a theory with analytical expressions for $S$ and $ZT$ allied to a fully self-consistent first-principles calculation in the DFT framework. Using the insulating alkane-thiol molecular junctions and metallic aluminum junction as examples, this study concludes that the thermoelectric quantities in nanojunctions do not necessarily display material properties or junction properties. The metallic atomic chains reveal strong length characteristics related to the strong hybridization in the electronic structures between the atoms and electrodes, while the insulating molecular wires display strong material properties due to the cancelation of exponential scalings in the DOSs. For $S$, the metallic atomic chains reveal strong length characteristics related to the strong interactions between the electronic structure of atoms and the electrodes, while the insulating molecular wires show independence from the lengths of molecules, thus displaying strong material properties due to the cancelation of exponential scalings in the density of states. It may be worth pointing out the cancelation may not be complete in real experiments due to other effects; the important point is, the strong exponential scaling behavior with the lengths of the junctions should be canceled. For $ZT$, the atomic wires remain to show strong junction properties. However, the length characteristics of the insulation molecular wires depends on a characteristic temperature $T_0 = \sqrt{\beta/\gamma(l)}$ around 10 K. When $T \ll T_0$, where the electron transport dominates the thermal current, the molecular junctions remain to show material properties. When $T \gg T_0$, where the phonon transport dominates the thermal current, the molecular junctions display junction properties. The length characteristic of the $C_n$ molecules is according to $ZT \propto l^2 \exp(-\xi l)$. The different length-scaling behaviors between the thermal current conveyed by the electrons and the thermal current conveyed by the phonons offer the key to the understanding of characteristic temperature and the behavior of $ZT$. We believe that this study is a substantial step towards the understanding of the thermoelectric properties in nanojunctions, and we hope that this study will generate more experimental and theoretical explorations in the properties of thermoelectric nanojunctions.

We are grateful to Prof. N. J. Tao for helpful discussions. The authors thank MOE ATU, NCTS and NCHC for support under Grants NSC 97-2112-M-009-011-MY3, 097-2816-M-009-004 and 97-2120-M-009-005.

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