Efficiency of Energy Conversion in Thermoelectric Nanojunctions

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Using first-principles approaches, this study investigated the efficiency of energy conversion in nanojunctions, described by the thermoelectric figure of merit ZT. We obtained the qualitative and quantitative descriptions for the dependence of ZT on temperatures and lengths. A characteristic temperature: $T_0 = \sqrt{\beta/\gamma(l)}$ was observed. When $T \ll T_0$, $ZT \propto T^2$. When $T \gg T_0$, ZT tends to a saturation value. The dependence of ZT on the wire length for the metallic atomic chains is opposite to that for the insulating molecules: for aluminum atomic (conducting) wires, the saturation value of ZT increases as the length increases; while for alkanethiol (insulating) chains, the saturation value of ZT decreases as the length increases. ZT can also be enhanced by choosing low-elasticity bridging materials or creating poor thermal contacts in nanojunctions.

There has been renewed interest in the study of thermoelectricity motivated by its possible application in energy-conversion devices at the nanoscale level [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. Recent experiments on the Seebeck coefficient, which is insensitive to the number of molecules in the junction, shed light on the possibility of the implementation of thermoelectric devices at the atomic level [4]. Nanoscale energy-conversion devices can convert waste heat energy into useful electric power and stabilize miniature electronic devices by reducing the temperature. The Seebeck coefficient, which is related not only to the magnitude but also to the slope of density of states, can provide more information than current-voltage characteristics [1, 2, 3, 4]. Measurement of the Seebeck coefficient has been applied to explore the effect of chemical structure on the electronic structure of molecular junctions [5]. The gate field has been theoretically proposed as a means of modulating the conduction mechanism between p-type [the Fermi energy is closer to the highest occupied molecular orbital (HOMO)] and ntype [the Fermi energy is closer to the lowest unoccupied molecular orbital (LUMO)] via the sign of the Seebeck coefficient [3, 11]. Although much research has been devoted to the study of Seebeck coefficient, little is known about the efficiency of energy conversion in nanojunctions [8]. The objective of this research was to provide greater insight into this subject.

Molecular tunneling junctions consist of source-drain electrodes as independent electron and heat reservoirs with distinct temperatures $[T_{L(R)}]$ and chemical potentials $[\mu_{L(R)}]$. The efficiency of energy conversion depends on several factors: the electrical conductance (σ) , the Seebeck coefficient (S), the electron thermal conductance (κ_{el}) and the phonon thermal conductance (κ_{ph}) . The efficiency can be described by the dimensionless thermoelectric figure of merit [9]:

$$ZT = \frac{S^2 \sigma}{\kappa_{el} + \kappa_{ph}} T,$$
(1)

where $T = (T_L + T_R)/2$ is the average temperature in the source-drain electrodes. The ideal thermoelectric molecular junction would have a large S, a large σ and a small combined thermal conductance $(\kappa_{el} + \kappa_{ph})$. Thermoelectric materials with a large σ are usually accompanied by a large κ_{el} , which makes the enhancement of the thermoelectric figure of merit a challenging task.

In this Letter, we reported first-principles calculations of the thermoelectric figure of merit in nanojunctions. It aimed to obtain a qualitative and quantitative descriptions of ZT for temperatures and lengths of the nanojunctions. The self-consistent density functional theory (DFT) was performed together with the derivation of an analytical expression for ZT to investigate its dependence on the temperatures and lengths of nanojunctions. As an example, this study investigated ZT for the aluminum atomic (conducting) wires and the alkanethiol (insulating) molecules in a nanojunction in the linear response regime. It was found $ZT \propto T^2$ at low temperatures, while ZT tended to a saturation value at high temperatures. The dependence of ZT on the wire lengths for the metallic atomic chains was opposite to that for the insulating molecules: longer conducting wires and shorter insulating molecules had better efficiency of energy conversion. The results of this study may be of interest to experimentalists attempting to develop thermoelectric nanoscale devices.

First, we started by a brief introduction of the DFT calculations for a molecule sandwiched between two bulk electrodes with external source-drain bias. The effective single-particle wave functions of the whole system were calculated in scattering approach by solving the Lippmann-Schwinger equation with exchange and correlation energy included within the local density approximation iteratively until the self-consistency was obtained. The effective single-particle wave function $\Psi_E^{L(R)}(\mathbf{r}, \mathbf{K}_{||})$ represents the electron incidents from the left (right) electrode with the energy E and component of the momentum $\mathbf{K}_{||}$ parallel to the electrode surface [12, 13, 14]. These left- and right-moving wave functions, weighting with the Fermi-Dirac distribution function according to their energies, were applied to calculate the electric current I and the thermal current conveyed by the transport electrons J_Q^{el} , via the following expressions: $I = \frac{2e}{\hbar} \int dE \left[f_E^R(\mu_R, T_R) \tau^R(E) - f_E^L(\mu_L, T_L) \tau^L(E) \right] \text{ and }$

$$\begin{split} J_Q^{el} &= \frac{2}{\hbar} \int dE \left[(E - \mu_R) f_E^R \tau^R(E) - (E - \mu_L) f_E^L \tau^L(E) \right], \\ \text{where } \tau^{L(R)}(E) \text{ is the transmission function of } \\ \text{the electron with energy } E \text{ incident from the left} \\ (\text{right) electrode.} \quad \text{The transmission function can } \\ \text{be computed using the wave functions obtained } \\ \text{self-consistently in DFT calculations according to} \\ \tau^{L(R)}(E) &= \frac{\pi \hbar^2}{mi} \int d\mathbf{R} \int d\mathbf{K}_{||} I_{EE}^{LL(RR)}(\mathbf{r},\mathbf{K}_{||}), \text{ where } \\ I_{EE'}^{LL(RR)} &= \left[\Psi_E^{L(R)} \right]^* \nabla \Psi_{E'}^{L(R)} - \nabla \left[\Psi_E^{L(R)} \right]^* \Psi_{E'}^{L(R)} \text{ and } d\mathbf{R} \\ \\ \text{represents an element of the electrode surface. It is assumed that the left and right electrodes served as independent electron and phonon reservoirs with the electron population described by the Fermi-Dirac distribution \\ \end{split}$$

function, $f_E^{L(R)} = 1/(\exp((E - \mu_{L(R)})/k_B T_{L(R)}) + 1)$, where k_B is the Boltzmann constant, and $\mu_{L(R)}$ and $T_{L(R)}$ are the chemical potential and the temperature in the left (right) electrode, respectively. The external source-drain bias is defined by: $V_B = (\mu_R - \mu_L)/e$.

Then, we briefly described the method used to calculate the electrical conductance, the Seebeck coefficient and the thermal conductance conveyed by electron transport. We considered the extra electric and thermal current induced by an additional infinitesimal temperature (ΔT) and voltage (ΔV) symmetrically distributed across the junction:

$$\Delta I = I(\mu_L, T_L + \frac{\Delta T}{2}; \mu_R, T_R - \frac{\Delta T}{2}) + I(\mu_L + \frac{e\Delta V}{2}, T_L; \mu_R - \frac{e\Delta V}{2}, T_R) - 2I(\mu_L, T_L; \mu_R, T_R),$$
(2)

and

$$\Delta J_Q^{el} = J_Q^{el}(\mu_L, T_L + \frac{\Delta T}{2}; \mu_R, T_R - \frac{\Delta T}{2}) + J_Q^{el}(\mu_L + \frac{e\Delta V}{2}, T_L; \mu_R - \frac{e\Delta V}{2}, T_R) - 2J_Q^{el}(\mu_L, T_L; \mu_R, T_R), \quad (3)$$

respectively. After expanding the Fermi-Dirac distribution function to the first order in ΔT and ΔV , we obtained the Seebeck coefficient (defined by $S = \Delta V/\Delta T$) by letting $\Delta I = 0$ and the electron thermal conductance (defined by $k_{el} = \Delta J_{O}^{el}/\Delta T$):

$$S = -\frac{1}{e} \frac{\frac{K_1^L}{T_L} + \frac{K_1^R}{T_R}}{K_0^L + K_0^R},$$
(4)

$$\kappa_{el} = \frac{1}{h} \sum_{i=L,R} [K_1^i eS + \frac{K_2^i}{T_i}],\tag{5}$$

where $K_n^{L(R)} = -\int dE \left(E - \mu_{L(R)}\right)^n \frac{\partial f_E^{L(R)}}{\partial E} \tau(E)$, and $\tau(E) = \tau^R(E) = \tau^L(E)$, a direct consequence of the time-reversal symmetry. In addition, the differential conductance, typically insensitive to temperature in cases where direct tunneling is the major transport mechanism, may be expressed as:

$$\sigma = \frac{e}{2} \int \sum_{i=L,R} \frac{f_E^i(1-f_E^i)}{k_B T_i} \tau(E) dE.$$
(6)

So far, the physical quantities that have been discussed have been related to the propagation of electrons. However, in most cases, the thermal current is dominated by the contribution from phonon transport. In the absence of the phonon thermal conductance, the research on ZT is incomplete. To consider the phonon contribution to ZT, it is assumed that the nanojunction is a weak elastic link, with a given stiffness that may be evaluated from total energy calculations, attached to the electrodes modeled as phonon reservoirs. We estimate the contribution of the thermal current from phonon scattering (J_Q^{ph}) , following the approach of Patthon and Geller [15]. After expanding the Bose-Einstein distribution function to the first order of ΔT in the expression of phonon thermal current, the phonon thermal conductance(defined by $k_{ph} = \Delta J_Q^{ph} / \Delta T$) is obtained:

$$\kappa_{ph} = \frac{\pi K^2}{\hbar k_B} \int dE E^2 N_L(E) N_R(E) \sum_{i=L,R} \frac{n_i(E)(1+n_i(E))}{T_i^2}$$
(7)

where $n_{L(R)} \equiv 1/(e^{E/K_B T_{L(R)}} - 1)$ and $N_{L(R)}(E) \simeq CE$ is the Bose-Einstein distribution function and the spectral density of phonon states in the left (right) electrode, respectively. The stiffness of the bridging nano-structure is: K = YA/l, where Y is the Young's modulus and A (l) is its cross-section (length).

Finally, ZT could be calculated by applying Eqs. (4) to (7). The Seebeck coefficient and the electron (phonon) thermal conductance can be characterized by the power law expansions: $S \approx \alpha T$, $\kappa_{el} \simeq \beta \left[T + \eta T^3\right] \approx \beta T$ and $\kappa_{ph} = \gamma(l)T^3$ in the common range of temperatures $(T_L \approx T_R = T)$ and in the linear response regime $(\mu_L \approx \mu_R = \mu)$, where $\alpha = -\pi^2 k_B^2 \frac{\partial \tau(\mu)}{\partial E} / (3e\tau(\mu));$ $\beta = 2\pi^2 k_B^2 \tau(\mu) / (3h); \ \eta = (\pi k_B \partial \tau(\mu) / \partial E)^2 / (3\tau(\mu)^2)$ and $\gamma(l) = 8\pi^5 k_B^4 C^2 A^2 Y^2 / (15\hbar l^2)$. Consequently, the thermoelectric figure of merit in the nanojunctions has a simple form,

$$ZT \approx \frac{\alpha^2 \sigma T^3}{\beta T + \gamma(l)T^3},$$
 (8)





FIG. 1: Aluminum atomic junctions at $V_B = 0.01$ V: (a) Schematic of 3-Al atomic chain and its Energy diagram. The Al-Al bond distance was about 6.3 a.u.; (b) Electrical conductances σ vs T; (c) Electron thermal conductances κ_{el} vs T; (d) Seebeck coefficients S vs T; (e) Phonon thermal conductances κ_{ph} vs T ($Y = 1.2 \times 10^{13}$ dyne/cm²); (f) Phonon thermal conductances κ_{ph} vs T ($Y = 5.0 \times 10^9$ dyne/cm²); (g) Log(ZT) vs T (for $Y = 1.2 \times 10^{13}$ dyne/cm²); (h) ZT and Log(ZT) (Inset) vs T (for $Y = 5.0 \times 10^9$ dyne/cm²).

which is valid in small bias and low temperature regimes.

The properties of the thermoelectric figure of merit now can be discussed using Eq. (8). There was a characteristic temperature, $T_0 \equiv \sqrt{\beta/\gamma(l)}$, for ZT in the nanojunctions. When $T \ll T_0$, the thermal current was dominated by the contribution from the electron transport $(k_{ph} \ll k_{el})$, which led to ZT increasing as the temperature increased: $ZT \approx \sigma S^2 T/k_{el} \approx \left[\alpha^2 \sigma/\beta\right] T^2$. Similarly, when $T \gg T_0$, the thermal current was dominated by the contribution from the phonon transport $(k_{ph} \gg k_{el})$, which led to a saturation of ZT at a constant value related to the length of the junction: $ZT \approx \sigma S^2 T/k_p \approx \alpha^2 \sigma/\gamma(l)$. To increase ZT it was first necessary to reduce k_{ph} by choosing low-elasticity bridging wires or creating poor thermal contacts in the nanojunctions, such that $ZT \approx \sigma S^2 T/k_{el}$. It is worth noting that σ and k_{el} roughly canceled each other out in the contribution of ZT because both were proportional to $\tau(\mu)$. It then followed that $ZT \propto S^2T$ and, thus, that the material with a large Seebeck coefficient was of key importance to increasing ZT. The characteristic mark of such a material in the nanojunctions is a sharp peak around the Fermi levels in the DOS [11], and the Seebeck coefficient may be optimized by applying the gate field [3, 11]. In addition, it was noted that α and σ depend on the length of the junction in a way related to the mate-

FIG. 2: Alkanethiol junctions at $V_B = 0.01$ V: (a) Electric conductance σ vs T; (b) Electron thermal conductances κ_{el} vs T; (c) Seebeck coefficients S vs T; (d) Phonon thermal conductance κ_{ph} vs T ($Y \simeq 2.3 \times 10^{12}$ dyne/cm²); (e) ZT vs T ($Y \simeq 2.3 \times 10^{12}$ dyne/cm²); (f) ZT vs T (for Y =0 dyne/cm²).

rial properties of bridging wires, which is reflected in the distinguished features of ZT on the length dependence. This point was explained using two catalogs of nanojunctions: the aluminum atomic (conducting) wires and the alkanethiol (insulating) chains, as discussed below.

Aluminum atomic wire is ideal for studying charge transport at the atom-scale [see Fig. 1(a) for a schematic of the aluminum junction] [16, 17, 18, 19]. As shown in Fig. 1(b), the conductance was relatively insensitive to the chain length (typically around 1 $G_0 = 2e^2/h \approx$ 77 μS) apart from the possible 4-atom periodicity due to a filling factor of 1/4 in the π orbitals [20]. As shown in Fig. 1(c), the magnitude of electron thermal conductance was linear in temperatures, $\kappa_{el} \approx \beta T$. At a fixed temperature, the dependence of the magnitude of κ_{el} on the number of Al atoms was the same as that of σ , owing to the fact that both σ and κ_{el} were proportional to $\tau(\mu)$. As shown in Fig. 1(d), the magnitude of the Seebeck coefficient was linear in temperature, $S \approx \alpha T$, with the negative sign showing that the carrier was ntype. At a fixed temperature, it was observed that the magnitude of the Seebeck coefficient increased considerably as the number of Al atoms increased. The increase of the Seebeck coefficient was due to the increase of the slope in the DOS at the Fermi level. These features may be related to the fact that the Fermi level was close to the LUMO in the Al wires. Fig. 1(e) shows the phonon thermal conductance: $\kappa_{ph} = \gamma(l)T^3$, for the Young modulus using $Y = 1.2 \times 10^{13}$ dyne/cm² from

the total energy calculations [21]. As seen, $\kappa_{ph} \gg \kappa_{el}$ was due to the large Young modulus. Fig. 1(g) shows the thermoelectric figure of merit with κ_{ph} calculated using $Y = 1.2 \times 10^{13} \text{ dyne/cm}^2$ from the total energy calculations. The increase in the number of Al atoms sharply increased the saturation value of ZT because of the sharp increase in the Seebeck coefficient by the number of Al atoms according to $ZT \propto S^2$. The thermoelectric figure of merit reached the saturation value, $ZT \rightarrow \alpha^2 \sigma / \gamma(l)$ when $T \gg T_0$. Since the mechanical elasticity of the Al wires could be delicate to the detailed geometry in the contact region which was unknown in the real experiment, as Fig. 1(f) shows the phonon thermal conductance κ_{ph} for another possible value, $Y = 5.0 \times 10^9 \text{ dyne/cm}^2$ from controlled tensile experiments on nanoscale Al films [22]. As shown in Fig. 1(h), it is worth noting that ZTcould be strongly enhanced by a smaller κ_{ph} . In such cases, the thermal current conveyed by electron transport dominated so that $ZT \approx (\alpha^2 \sigma/\beta) T^2$ and ZT was strongly enhanced.

Alkanethiols $[CH_3(CH_2)_{n-1}SH$, denoted as $C_n]$ are a good example of reproducible junctions that can be fabricated [23, 24]. In contrast to the conductor behavior of aluminum wires, alkanethiol chains are insulators. It has been established that non-resonant tunneling is the main conduction mechanism in alkanethiol junctions. Consequently, the conductance is small and decreases exponentially with the length of wire, as $\sigma = \sigma_0 \exp(-\xi l)$ where l is the length of alkanethiol chain and $\xi \approx 0.78$ $Å^{-1}$ [25, 26, 27, 28, 29], as shown in Fig. 2(a). By exploiting the periodicity in the $(CH_2)_2$ group of the alkanethiol chains, the wave functions of the C_n junctions were calculated by a simple scaling argument, which led to exponential scaling in the transmission function $\tau(E)$. As shown in Fig. 2(b), the magnitude of electron thermal conductance was linear in temperatures, $\kappa_{el} \approx \beta T$. At a fixed temperature, the magnitude of κ_{el} decreased exponentially with n, the number of carbon atoms in Cn, owing to the scaling behavior of $\tau(E)$. As shown in Fig. 2(c), the magnitude of the Seebeck coefficient was linear in temperature as $S \approx -\pi^2 k_B^2 \frac{\partial \tau(\mu)}{\partial E} / (3e\tau(\mu)) T$, and its dependence on the number of carbon atoms was canceled due to the same scaling factor $\exp(-\xi l)$ for both $\tau(\mu)$ and $\frac{\partial \tau(\mu)}{\partial E}$. As shown in Fig. 2(c), thermal conductance increased as the temperature increased as $\kappa_{ph} = \gamma(l)T^3$ for the Young modulus calculated with total energy calculations [21]. At a fixed temperature, κ_{ph} decreased as n^{-2} due to $\gamma(l) \propto l^{-2}$ (see Fig. 2(d)). Due to the small transmission probability for the insulating alkanethiol chains, the electron thermal conductance (note: $k_{el} \propto \sigma$) was much suppressed so that $\kappa_{el} \ll k_{ph}$, as shown in Fig. 2(b) and (d). Consequently, the characteristic temperature T_0 was low in the alkanethiol chains, and the T^2 regime for ZT was significantly suppressed. As shown in Fig. 2(e). ZT decreased as the number of carbon atoms increased for $T \gg T_0$, due to the saturation value of $ZT \approx \alpha^2 \sigma / \gamma(l) \propto l^2 \exp{(-\xi l)}$. Neverthe less, there was enough experimental evidence to show that the junctions had poor thermal contacts for certain samples [30]. These samples quickly frustrated at much smaller biases. The frustration of these samples could have been due to poor heat dissipation by the thermal current via phonon transport when the local heating was triggered by an external bias larger than the threshold value [18, 31]. In such cases, the bridging nano-structure effectively has a very small Young modulus. In the limit of extremely poor thermal contacts (effectively, $k_{ph} = 0$, σ and k_{el} canceled the length dependence), which led to $ZT \propto \alpha^2 \sigma_0 T^2 / \beta$ and implied that ZT was independent of the wire length as shown in Fig. 2(g).

In conclusion, self-consistent DFT calculations were performed to study the efficiency of energy conversion in nanojunctions. There was a characteristic temperature of T_0 for ZT: when $T \ll T_0$, $ZT \to (\alpha^2 \sigma/\beta) T^2$; when $T \gg T_0$, $ZT \to \alpha^2 \sigma / \gamma(l)$. Of key importance to increasing the efficiency of energy conversion was using materials with a large Seebeck coefficient. Such materials were usually characterized by a sharp peak around the Fermi levels in the DOS. Efficiency could be further optimized by applying the gate field, choosing low-elasticity bridging materials or creating poor thermal contacts in nanojunctions. The relation between ZT and the wire lengths depended on the material properties: for aluminum atomic (conducting) wires, the saturation value of ZT increased as the length increased; while for the alkanethiol (insulating) chains, the saturation value of ZT decreased as the length increased. The conclusions of this study may be beneficial to research attempting to increase the efficiency of energy conversion in nano thermoelectric devices.

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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- ²¹ The aluminum (alkanethiol) junction consisted of an Al atomic chain (a C₄ molecule) sandwich between two Al (Au) electrodes that were modeled as electron jellium with $r_s \approx 2$ ($r_s \approx 3$). The following parameters were used for the junctions: the effective cross-section chosen was A = 23.1 a.u.² (21.4 a.u.²) for the aluminum (alkanetiol)

junction. The spectral densities of electrodes were evaluated using the longitudinal and transverse sound velocities for Al (Au), $v_l = 6.35 (3.2) \times 10^5$ cm/s and $v_t = 3.1 (1.2) \times 10^5$ cm/s, respectively. The Young's modulus of aluminim (alkanethiol) wire, $Y \simeq 1.2 \times 10^{13}$ dyne/cm² ($Y \simeq 2.3 \times 10^{12}$ dyne/cm²), was calculated with total energy calculations and was found to be almost independent of the length of the wires.

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