Supplementary material for: Significantly Enhanced thermoelectric performance by twist angle dependent phonon interference effect

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Here, we illustrated the theoretical details about the thermoelectric transport properties of molecular junctions. This additional file includes:

- Supporting information about the details of theoretical method, skipping the difficult theoretical derivation, will be easily used for numerical calculations..
- Aligned band structure of graphene leads (armchair edge) and the molecular energy level of central molecules.

1. Conventional nonequilibrium Green's function (NEGF) method

In the framework of NEGF method, the calculation of electron and phonon transport properties are unified.¹ The first step is the calculation of phonon and electron Hamiltonian, which can be obtained by using many commercial or open-source software package, such as VASP, Atomistic tooltix (ATK), Quantum-Espresso (QE/PWscf), SIESTA, LAMMPS (for phonon only) and so on. After that, the Hamiltonian of phonon and electron can be written as the matrix form and partitioning by left (*L*), center (*C*), right (*R*):

For convenience, we express the phonon and electron in an unified form by carriers energy E ($E = \omega$ with the n = 2 for phonon, E = E with the n = 1 for electron). And the retarded (r) and advanced (a) Green's function read as:

$$G_{C}^{r}(E) = G_{C}^{a}(E)^{\dagger} = \left[(E + i\eta)^{n} - H_{C} - \Sigma_{L} - \Sigma_{R} \right]^{-1}$$
(2)

where $\eta > 0$ is an infinitesimal parameter (10⁻⁵ in this work), and the retarded self-energy:

$$\Sigma_{L(R)} = H_{CL(CR)} g_{L(R)}^r H_{LC(RC)}$$
(3)

The surface Green's functions $g_{L(R)}^r$ are given by:

$$g_{L(R)}^{r}(E) = \left[(E + i\eta)^{n} S_{L(R)} - H_{L(R)}^{00} - \Sigma_{L(R)}^{00} \right]^{-1}$$
(4)

where $S_{L(R)}$ is identity matrix for phonon or overlap matrix for electron, and $\Sigma_{L(R)}^{00} = H_{L(R)}^{10(01)} g_{L(R)}^r H_{L(R)}^{01(10)}$. Clearly, this surface self-energy and surface Green's function can be solved recursively.² It generally obtained by decimation techniques. And then, the total transmission function with coupling matrices $\Gamma_{L(R)} = i[\Sigma_{L(R)} - \Sigma_{L(R)}^{\dagger}]$ can then be computed from the Caroli formula:

$$T(E) = \operatorname{Tr}\left[\Gamma_{R}G_{C}^{r}\Gamma_{L}G_{C}^{a}\right]$$
(5)

2. Thermoelectric parameters calculation

Once the transmission function is obtained, the Seebeck coefficient (S), conductance (σ) and electrical thermal conductance (κ_e) can be obtained by:³

$$S(\mu,T) = -\frac{1}{eT} \left(\frac{L_1}{L_0} \right)$$
(6)

$$\sigma(\mu,T) = -\frac{2e^2}{h}L_0\tag{7}$$

$$k_{e}(\mu,T) = -\frac{2}{hT} \left(L_{2} - \frac{L_{1}^{2}}{L_{0}} \right)$$
(8)

where *h* is Plank constant, *T* is temperature, *e* is elementary charge, and L_n is Lorentz function, which expressed as:

$$L_n(\mu,T) = \int_{-\infty}^{\infty} T(E)(E-\mu)^n \frac{\partial f_E}{\partial E} dE$$
(9)

where f_E is Fermi-Dirac distribution function. Since the phonon thermal conductance is uncorrelated to chemical potential μ , it is a constant value at a specific temperature. Finally, the *ZT* value is determined by the well-known relations:

$$ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_p} T \tag{10}$$

3. Individual phonon mode transmission probability

The transmission probability of individual phonon modes that originated from graphene leads are given by the transmission matrix:^{4, 5}

$$t_{mn} = \frac{2i\omega}{a_L a_R} \sqrt{V_R} \left[U_R^r \right]^{-1} \mathbf{i} \left[U_R^{a\dagger} \right]^{-1} \sqrt{V_L}$$
(11)

where $\mathbf{i} = d_R^{00} K_{RC} D_C^r K_{CL} d_L^{00}$, and the $a_{L(R)}$ is the lattice constant of left (right) leads along the transport direction, *m* and *n* is the vibration degree of freedom of the left and right leads respectively. The eigenvector matrices $U_{L(R)}^{a(r)}$ are obtained from diagonalizing the Bloch matrices:

$$F_{L(R)}^{a(r)}U_{L(R)}^{a(r)} = \Lambda_{L(R)}^{a(r)}U_{L(R)}^{a(r)}$$
(12)

where

$$F_L^a = \left[\left(H_L^{10} g_L^r \right)^{-1} \right]^{\dagger}$$
⁽¹³⁾

$$F_{R}^{r} = g_{R}^{r} H_{R}^{10}$$
(14)

and the velocities matrices are given by:

$$V_{L(R)} = \frac{a_{L(R)}}{2\omega} U_{L(R)}^{a(r)} \Gamma_{L(R)}^{00} U_{L(R)}^{a(r)}$$
(15)

where $\Gamma_{L(R)}^{00} = i \left[\Pi_{L(R)}^{00} - \left(\Pi_{L(R)}^{00} \right)^{\dagger} \right]$. In addition, this method can also apply to calculate electronic transport. The transmission probability that contribute from different phonon mode of left or leads is read as:

$$T_L^m(\omega) = \sum_n |t_{mn}|^2$$
$$T_R^n(\omega) = \sum_n |t_{mn}|^2$$

Equivalent to Caroli's formula, the total phonon transmission of left and right leads is given by:

$$T_L(\omega) = T_R(\omega) = Tr(tt^{\dagger}) = Tr(t^{\dagger}t)$$

4. Phonon transmission eigenchannel decomposition

To better understand the phonon interference effect, it is necessary to clarify the phase change of propagating lattice wave. For this purpose, we adopt the phonon transmission eigenchannel decomposition method as described in manuscript.⁶ For simplicity, we skip the theoretical derivation and go straight to the key steps of numerical calculation. It starts with the spectral function A_C , which is given by terms of the Green's functions as follows:

$$A_{C} = A_{C}^{B} + \sum_{Z=L,R} A_{C}^{Z} = i \Big[D_{C}^{r} - D_{C}^{r\dagger} \Big]$$

$$= \sum_{L,R} D_{C}^{r} \Gamma_{L(R)} D_{C}^{r\dagger} + 4i\eta \omega D_{C}^{r} D_{C}^{r\dagger}$$
(16)

Where A_C^Z is contributed from left/right leads, and A_C^B is contributed from the bound state of central molecular. Then, the spectral function of specific leads (*L* or *R*) can be decomposed for:

$$\begin{aligned} \mathcal{A}_{C}^{L(R)}(\omega) &= \sum_{m} \mathscr{H}_{m}^{\bullet}(\omega) \mathcal{A}_{m}(\omega) \mathscr{H}_{m}^{\bullet}(\omega)^{\dagger} \\ &= \frac{\pi}{\omega} \sum_{m} \mathscr{L}_{m}^{\bullet}(\omega) \mathscr{L}_{m}^{\bullet}(\omega)^{\dagger} \end{aligned}$$
(17)

Diagonalizing the spectral function matrix we can obtain the eigenvalues λ_m and the scattering state $\mathcal{G}_m^{(\omega)}(\omega)$. Then the transmission probability matrix is given by:

$$\tau_{mn} = \frac{\pi}{\omega} \mathcal{G}_{m}^{\prime}(\omega)^{\dagger} \Gamma_{R} \mathcal{G}_{n}^{\prime}(\omega) = \frac{\pi}{\omega} [\mathcal{O}(\omega)^{\dagger} \Gamma_{R} \mathcal{O}(\omega)]_{mn}$$
(18)

where $U(\omega) = [\xi_1, \xi_2, ..., \xi_m]$. Diagonalizing this transmission probability matrix, we will obtain the transmission eigenvector $c_{m\mu}$ and transmission eigenvalue τ_{μ} . In this way, the total phonon transmission spectra are decomposed into the contribution of different phonon transmission eigenchannels in the central region of device. And the eigenchannel Ψ_{μ} in central region is given by:

$$\Psi_{\mu}(\omega) = \sum_{m} c_{m\mu}(\omega) \xi_{m}^{0}(\omega)$$
⁽¹⁹⁾

Finally, the complex displacements of eigenchannels are given by:

$$Q_{\mu}(\omega) = \sum_{i \in C, \alpha} \frac{s(\omega)}{\sqrt{m_i}} |\Psi_{\mu}(\omega)| e^{i\theta_{i\alpha,\mu}(E)}$$
(20)

where $s(\omega)$ is a frequency dependent scaling factor of complex displacement vector, m_i is mass of *i*-th

atom. Here, the $\theta_{i\alpha,\mu}(E)$ is the phase angle of transmission eigenchannel. This information is included in

the imaginary part of the complex displacement of eigenchannels Ψ_{μ} .

5. Band structure and molecular energy spectrum

To illustrate the electronic properties are less affect by the twist angle, we calculated the band structure of graphene leads and molecular energy spectrum of central molecules, as shown in left panel of Figure. S1. The band structure of graphene leads clearly show semiconducting property (with around 0.2 eV band gap). The central molecular energy spectrum as a function of twist angles are calculated, as shown in the right panel of Figure. S1. For convenience, we aligned the molecular energy levels and band structure of graphene (Fermi level as the reference). One can see that molecular energy levels near Fermi level are located within the band gap of graphene. This illustrated the zero electronic transmission of the intermediate coupling molecular junction near the Fermi level. In addition, the isolated discrete energy level leads to localization of electronic state and thus results in the slope of transmission function changes in every discrete energy levels. Therefore, the Seebeck coefficient will undergo the unsystematic changes on the upper and lower sides of every discrete energy levels. In addition, one can see that the molecular energy spectrum is almost unaffected by twist angle.



Figure. S1 (a) Band structure of graphene leads. (b) Molecular energy spectrum of central molecules.

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