Equilibrium and nonequilibrium thermoelectric efficiency of monolayer molybdenum diselenide/gold junctions

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Transition metal dichalcogenide devices are composed of a two-dimensional (2D) sheet connected to metallic electrodes. The interface between the 2D material and metallic junction significantly affects the performance of the device. Herein, we investigate the equilibrium and nonequilibrium thermoelectric performance of a device composed of MoSe₂ as the central region and Au(111) as the electrode by combining density functional theory and Green's function formalism. In the linear response regime, the maximum of the thermopower is directly related to the length of the MoSe₂, and the figure of merit increases linearly with temperature so it is more than one at 600 K. In the nonequilibrium regime, the differential thermopower is strongly dependent on the external potential difference. In addition, thermoelectric efficiency approaches one when the electrochemical potential of the colder electrode is higher than that of the hotter one and the temperature difference is tuned. Findings unveil that the thermopower of the TMD-based junctions can be significantly tuned under nonequilibrium conditions, demonstrating their potential for thermoelectric applications.

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I. INTRODUCTION

Transition metal dichalcogenide (TMD) monolayers are among the most important two-dimensional (2D) materials. Structural diversity, having a tunable direct band gap [1–4], having spin and valley degrees of freedom [5–9], the emergence of high-temperature magnetization [10–13], strongly bound excitons [14–16], and observing superconductivity [17–20] are among the outstanding electronic properties of such materials, which make them distinguished in the world of 2D materials. Monolayer MoSe₂ has attracted a lot of attention in recent years due to the fact that it can be easily synthesized by micromechanical exfoliation method. Various applications for this single layer have been investigated, including field effect transistors [21], optoelectronic components [4,22], catalytic applications [23], spintronics, and valleytronics [24].

High-quality TMD monolayers with large sizes are usually grown by epitaxy and chemical vapor deposition methods on different substrates [25,26]. Devices designed based on TMD monolayers have metal electrodes. The interaction of the TMD monolayer with a metal substrate or electrode can significantly affect its electronic properties. In addition, these interactions can lead to the emergence of unique characteristics. The involvement of out-of-plane *d* orbitals, specifically in the TMD valence band, leads to the band renormalization of the monolayer due to the interaction with the substrate [27,28]. The TMD-metal junction can lead to a local Schottky barrier and modulate the work function of the TMD monolayer [29]. Increasing the annealing temperature can greatly increase the hybrid between the TMD and the substrate, so both the structural phase transition and the electronic phase transition from semiconductor to metal are observed [30]. An increase in van der Waals interaction between the TMD and the metal substrate can lead to the transition of *n*-type TMD-Au Schottky contact to a *p*-type one with reduced energy barrier height [31]. Recently, we have shown that the twist engineering between the TMD and the metal substrate is an efficient way for tuning the electronic band gap of the TMD [32].

A lot of energy is wasted in electronic devices as heat. Thermoelectric materials have a high potential to solve the energy problem because they can convert wasted heat into electricity. To have high thermoelectric efficiency, a material should have good thermopower and electrical conductivity, and, on the other hand, it should have a low thermal conductivity. Dimension reduction can improve materials' thermoelectric efficiency because of the phonon thermal conductivity reduction due to phonon boundary scattering. TMDs are suitable candidates for thermoelectric applications due to the inherent gap and favorable phonon and electron transport properties. Valley degeneracy, confinement of the carriers in 2D, and high effective mass make TMD monolayers important competitors for existing bulk thermoelectric materials with high figure of merit (ZT) such as Bi₂Te₃, SnTe, and PbTe. Unlike these bulk thermoelectric materials that have limited applications due to toxicity and poor chemical stability, TMDs are chemically stable and nontoxic. Recently, much theoretical research has been done on the thermoelectric properties of 2D materials [33-44]. In this research, people have investigated the thermoelectric properties of a sheet or a ribbon without considering the role of electrodes. Real devices have metal electrodes that can affect the thermoelectric efficiency of the device. Also, the majority of research has focused on the equilibrium regime (linear response regime) in which a very small temperature

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difference is applied at the two ends of the material. In the devices, the potential difference between the two electrodes can cause the appearance of a temperature gradient and, as a result, the system is out of equilibrium.

In this paper, we simulate a device consisting of a single layer of MoSe₂ and two Au(111) electrodes. Part of the $MoSe_2$ sheet with a length of L is suspended and the other part is placed on the Au substrate. Recently, Thomas et al. designed a similar geometry with quasiepitaxial $WS_2/Au(111)$ interfaces and with a suspended WS₂ region using oriented porous metallic network technique [45]. We have investigated the equilibrium and nonequilibrium thermoelectric properties of the MoSe₂/Au(111) junction using a combination of density functional theory (DFT) and Green's function formalism. In the equilibrium condition, a small temperature difference is applied between electrodes, while in the nonequilibrium case there are both a large temperature gradient and a voltage difference between the two electrodes. We find that not only the length of the suspended part but also the profile of the temperature gradient and voltage difference are important parameters to tune the thermoelectric efficiency of the junction.

II. COMPUTATIONAL DETAILS

Electronic properties of a MoSe₂/Au(111) junction are calculated using DFT and projected augmented wave formalism [46]. A generalized gradient approximation in the form of Perdew-Burke-Ernzerhof was adopted for the exchangecorrelation functional [47]. To take into account the van der Waals interactions, the dispersion correction by using Grimme's DFT-D3 scheme was considered [48]. The energy convergence value between two consecutive steps was chosen as 10^{-6} eV and a maximum force of 0.001 eV/Å was allowed on each atom. To simulate the Au slab, five-layer Au(111) was simulated, where two bottom layers were fixed during the optimization. The surface of the Au slab was allowed to be reconstructed, consistent with experimental findings. A 20 Å vacuum slab was considered to avoid the interaction between the supercell with its image. The Brillouin zone of the MoSe₂/Au(111) junction was sampled by a $15 \times 15 \times 1$ K-point mesh according to Monkhorst-Pack method [49].

To study the transport properties of the $MoSe_2/Au(111)$ junction-based device, SIESTA package was used [50]. In this package, the electrodes are considered to be semi-infinite and the transport occurs along the z direction. Each electrode has 1 nm length and is composed of 58 atoms. The K-point along the transport direction was 100 and it sets to be 15 along the transverse direction. The norm-conserving Troullier-Martins pseudopotential [51] was used to describe the core electrons and the Perdew-Burke-Ernzerhof generalized gradient approximation was employed as the exchange-correlation functional. The cutoff energy was 100 Ha and a double-zeta single-polarized basis set was used to describe the valance electrons.

III. RESULTS AND DISCUSSION

A. MoSe₂/Au junction

The optimized MoSe₂ monolayer has a space group symmetry of p-6m2 and a point group of D_{3h} and a lattice constant



FIG. 1. (a) Top and side view of optimized single-layer MoSe₂ on Au(111) surface. The unit cell is shown by black lines. (b) MoSe₂projected band structure and DOS of the structure. The Fermi level is set as the energy reference.

of 3.32 Å, which is in good agreement with previous experimental and theoretical results [52-54]. The band structure of the MoSe₂ monolayer is plotted in Fig. S1 (see Supplemental Material [55]). The monolayer is a semiconductor with a direct band gap at the K point. The size of the band gap is equal to 1.46 eV, which is in agreement with previous reports [56,57]. The optimized structure of Au(111) has a lattice constant of 2.88 Å, hence, a $\sqrt{3} \times \sqrt{3}$ superlattice of MoSe₂ monolayer is matched with a 2×2 lattice of Au(111) with a strain less than 0.5%. Figure 1(a) shows the structure of $MoS_2/Au(111)$. The vertical distance between the lowest layer of Se atoms and the highest layer of gold atoms is equal to 2.73 Å, indicating the weak van der Waals interaction between the layers and is consistent with the value of 2.3 Å reported in experimental papers [58]. The gold surface is slightly disturbed due to the presence of the MoSe₂ layer, however, the displacement of the gold atoms relative to its equilibrium state is in the order of picometers. These disturbances are observed only in the topmost layer of the gold slab, confirming the weak interaction of the substrate with the monolayer.

Figure 1(b) shows the band structure projected on MoSe₂ orbitals and the density of states. Due to the weak interlayer interaction, no noticeable change in the band gap size of the MoSe₂ monolayer is observed. The change in the location of the edges of the valence and conduction bands is due to band folding (see Fig. S1 of the Supplemental Material [55]). As is clear, the edge of the conduction band is closer to the



FIG. 2. Schematic of the considered devices that include two electrodes and an active area. In the active region, some part of MoSe₂ with length *L* is freestanding. The left electrode has a temperature of *T* and a chemical potential of μ , while the temperature of the right electrode is $T+\Delta T$ and its chemical potential is $\mu+qV$.

Fermi level, which is attributed to the *n*-type doping of the monolayer due to the gold substrate. Experimental reports also confirmed a small injection of electrons from the gold substrate to MoSe₂ by the core-level x-ray photoelectron spectroscopy spectrum [58]. The conduction band edge is visible at an energy of about 0.55 eV, which is consistent with the value of 0.61 eV observed in the scanning tunneling spectroscopy (STS) spectrum [58,59]. The band gap reported in experimental works for monolayer MoSe₂ on Au(111) is in the range of 1.4-1.9 eV [58-60], which is in good agreement with our results. Examining the partial density of states (PDOS) spectrum reveals that the MoSe₂ monolayer is still a semiconductor on the gold substrate. Analyzing the PDOS of Mo and Se atoms depicted in Fig. S2 (see Supplemental Material [55]) reveals that the *d* orbitals of Mo atoms form valence and conduction bands. Due to being placed on the substrate, the symmetries of MoSe₂ are slightly broken so d_{xz} and d_{yz} orbitals are not degenerate. This is due to interlayer interaction perpendicular to the MoSe₂ plane. As is clear from Fig. S2 (see Supplemental Material [55]), the conduction band edge belongs to the d_{7^2} orbitals, while the d_{xy} and $d_{x^2-y^2}$ in-plane orbitals also participate in the valence band.

Figure 2 schematically shows the devices considered in this paper. The device consists of two electrodes and an active area. In the central region, a part of the MoSe₂ monolayer with length L is suspended. Therefore, the flow of charge and energy must pass through this channel. Recently, Thomas et al. designed a similar geometry with quasiepitaxial $WS_2/Au(111)$ interfaces and with a suspended WS_2 region using oriented porous metallic network technique [45]. The temperature, T, and chemical potential, μ , of the left electrode are constant during the simulation, as long as a temperature, ΔT , and voltage gradient, qV, is applied to the right electrode in nonequilibrium conditions. Carriers are transferred from the hotter region (right electrode) to the colder region (left electrode), which induce a potential difference, ΔV , at the left electrode. Considering the ballistic transport, the flow of charge and energy through the device can be described by the following relations:

$$I_e(V, \Delta T) = \frac{2e}{h} \int dE T_e(E) (f_L(E, \mu, T) - f_R(E, \mu + qV, T + \Delta T)), \qquad (1)$$

$$I_q^{\alpha}(V, \Delta T) = \frac{2}{h} \int dE T_e(E) (f_L(E, \mu, T) - f_R(E, \mu + qV, T + \Delta T)) (E - \mu_{\alpha}), \quad (2)$$

where $T_e(E) = \Gamma_L G^r(E) \Gamma_R G^a(E)$ is the transmission coefficient, where Γ_{α} is the broadening function of the electrode α , dependent on the quality of the coupling between the electrode and the central region. $G^{r(a)}$ denotes the retarded (advanced) Green's function. $f_{\alpha}(E, \mu_{\alpha}, T_{\alpha})$ is the Fermi-Dirac distribution function in which $\mu_{\alpha}(T_{\alpha})$ stands for the chemical potential (temperature) of the electrode α .

Figure 3(a) shows the transmission of the device with L = 2.25 nm. Inset shows the transmission coefficient for different lengths in the logarithmic scale. Due to the presence of the suspended part of MoSe2, the active area of the device is a semiconductor, which can be distinguished from the gap of the transmission coefficient. To highlight the role of the substrate, we also computed the transmission coefficient of a freestanding MoSe₂ device without gold electrodes for comparison. Although the size of the band gap is the same in the two cases, significant differences are observed in the transmission spectrum. The substrate not only approaches the conduction band edge to the Fermi level indicating *n*-type doping but also increases the slope of the transmission coefficient near the band edges, which is important for thermopower. The doping of the channel by substrate results in the asymmetry of the transport properties of the device. The calculated transmission spectrum is similar to the STS results presented in the experimental reports [27,58]. Decreasing the L does not have a significant effect on the amount of the gap and, on the contrary, it has a significant effect on the behavior of the transmission coefficient far from the gap. The transmission coefficient for other lengths is plotted in Fig. S3 (see Supplemental Material [55]).

The density of states of the device is shown in Fig. 3(b). The density of states of the whole device shows metallic behavior, which is due to the presence of the gold substrate. The density of states of the freestanding part has good agreement with the transmission coefficient of the system. Although the whole DOS shows metallic behavior, the transmission coefficient demonstrates that the device is a semiconductor. The underlying physics for such a contrast is attributed to the suspended part of the monolayer. Indeed, two sides of the suspended part are conductive but the semiconducting nature of the central region suppresses the electron transmission in the real space and around the Fermi level in the energy space. As is clear in Fig. 1, d orbitals of Mo atoms have the most contribution around the valence and conduction bands. The partial density of states also confirms that in the energy range of -2 to 2 eV, the *d* orbitals of Mo atoms have the most important contribution in the transport inside the device. In Figs. 3(c) and 3(d), we have plotted the eigenstates of the transmission coefficient matrix for the two peaks A and B, shown in Fig. 3(a). It is clear from Figs. 3(c) and 3(d) that d_{72} orbitals of Mo atoms are responsible for the transport around peak A in the conduction band. Cut-plane view also confirms this finding. On the other hand, the hybridization of d_{xy} and $d_{x^2+y^2}$ orbitals are responsible for the transport in the B region. These results are consistent with the contribution of different



FIG. 3. (a) Transmission coefficient of the device with L = 2.25 nm. Transmission coefficient of freestanding MoSe₂ is also depicted for comparison. (b) Total density of states and partial density of states projected on the freestanding and supported part of MoSe₂. Also, partial density of states of the freestanding part of the channel is also drawn. (c), (d) Isosurface and cut plane of the transmission eigenstates of peaks A and B in (a), respectively.

d orbitals in the valence and conduction bands, discussed in Fig. 1.

In the following, we simulate three devices with lengths of L = 3.25, 2.25, and 1.25 nm and study their thermoelectric properties in equilibrium (linear response regime) and nonequilibrium regimes in detail.

B. Equilibrium thermoelectric properties

In the equilibrium state (linear response regime), the temperature gradient and the potential difference applied to the right electrode are very small, so we can expand the Fermi-Dirac distribution function of the right electrode to the first order in terms of V and ΔT . In this way, the electron conductance and thermopower of the device are equal to

$$G = e^2 L_0, \tag{3}$$

$$S = -\frac{L_1}{eTL_0},\tag{4}$$

where L_n are the Onsager integrals as

$$L_n = \frac{2}{h} \int dE (E - \mu)^n T_e(E) \left(-\frac{\partial f}{\partial E} \right).$$
 (5)

The dependence of the thermopower on the length of the suspended region, *L*, is illustrated in Fig. 4. The *n*-type nature of $MoSe_2/Au(111)$ junction is also confirmed by analyzing the thermopower. Indeed, the peak of the *n*-type carrier (positive energy) is closer to the Fermi level. In L = 3.25 nm,

the maximum thermopower is observed for both *n*- and *p*-type carriers at a temperature of 500 K. The variation in the maximum thermopower for the carriers versus the electrode temperature also confirms this result as depicted in Fig. 4. Up to a temperature of about 450 K, there is a noticeable gap between the *n*- and *p*-type peaks, vanishing with a further increase in temperature. This behavior can be clearly seen in Fig. S4 (see Supplemental Material [55]). In all devices, the *p*-type thermopower is more than the *n*-type one. However, the electron-hole asymmetry strongly depends on the size of *L*. By reducing the length of *L*, first, the gap between the *n*- and *p*-type peaks increases significantly at low temperatures. Second, much higher temperatures are needed to reach the maximum thermopower.

In the device with L = 2.25 nm, the maximum thermopower is observed at a temperature of 650 K, while the thermopower does not reach the maximum for the device with L = 1.25 nm even up to T = 700 K. By decreasing L, the probability of electron tunneling from one lead to the other through the channel increases, leading to the reduction of the thermopower. In addition, the electron-hole asymmetry in thermopower for two types of carriers increases significantly with decreasing length. The maximum thermopower of the device increases significantly with the increase of L, so when L becomes 2.6 times (3.25 nm versus 1.25 nm), the maximum ratio of *p*-type carriers in two devices becomes 3.6. The inset of Fig. 3 shows the increase of the transmission in the channel by reducing L. It is well-known that the electrical conductance decreases with the increase of the channel length supported



FIG. 4. Variation of thermopower as a function of temperature and chemical potential for (a) L = 3.25 nm, (b) L = 2.25 nm, and (c) L = 1.25 nm. Maximum of thermopower of *n*- and *p*-type carriers as a function of temperature for corresponding *L* is depicted in (d)–(f).

with the results depicted in the inset. The thermopower has a reverse relation with the conductance, so the increase in the length results in the increase of the thermopower. To consider the effect of the substrate on the thermoelectric properties of the devices, we increased (decreased) the vertical distance between the MoSe₂ and Au monolayer by 10% compared to the optimized state. In this way, the interaction between the two materials was weakened (strengthened). Figure 5 shows the thermopower for the device with L=3.25 nm in three different interlayer distances. By reducing the vertical distance, the *p*-type peak moves toward the Fermi level, while the *n*-type peak moves to the higher energies. It is consistent with the transition of the *n*-type TMD-Au Schottky barrier to the *p*-type one with increase of the vdW interaction [31]. By increasing the vertical distance, we see a slight increase in the magnitude of the thermopower. On the other hand, at all considered heights, the maximum thermopower of *p*-type carriers is higher than that of *n*-type carriers. In Fig. 5(b), we investigate the amount of electron-hole asymmetry of thermopower at three assumed heights as a function of temperature. We defined electron-hole asymmetry as $\zeta = \frac{\max(S^p)}{\max(S^n)}$, where S^{β} represents the thermopower of the β -type carrier. It is clear that at low temperatures, the electron-hole asymmetry is greater in the conditions where the interaction of the substance with the substrate is stronger so $\zeta = 1.3$, and increasing the temperature leads to the decrease of the electron-hole asymmetry. For the case of h = 2.8 Å, a strange increase in the electron-hole asymmetry of thermopower is observed around room temperature. At temperatures above 500 K, the electron-hole asymmetry is independent of the strength of the interaction of the monolayer with the substrate and reaches a saturation level close to $\zeta \approx 1.06$.

As it is clear from Figs. 4 and 5, the thermopower of the designed device is in the range of $1000 \,\mu\text{V/K}$ at room temperature. The magnitude and behavior of thermopower are in good agreement with a recent paper about the thermopower

of a few-layer $MoSe_2$ calculated with a similar approach [61]. It is higher than the value of $127 \,\mu V/K$, recently reported for a device composed of the graphene nanoribbon [62], and about 80 $\mu V/K$ reported for the graphene sheet obtained due to strong inelastic scattering [63] and magnetic field [64]. The advantage of proposed devices over graphene is due to a



FIG. 5. (a) Thermopower of a device with L = 3.25 nm as a function of the chemical potential at room temperature for three different vertical distances between MoSe₂ and Au (111) substrate. (b) electron-hole asymmetry of Thermopower as a function of the temperature.

larger band gap of MoSe₂. Hippalgaonkar *et al.* [65] reported a thermopower of 600 μ V/K for monolayer MoS₂ at room temperature close to values obtained in this research. Zhao *et al.* [66] reported a thermopower of 150 μ V/K for holedoped tin SnSe₂ crystal that is lower than the value obtained in this paper. The thermopower of a bilayer PtSe₂ is as high as of 1000 μ V/K, comparable with our results [67]. The high thermopower of bilayer PtSe₂ is because of the semimetalsemiconductor transition and doping. Yoshida *et al.* reported a thermopower of 300 μ V/K for ultrathin WSe₂ by controlling the gate voltage and doping [68].

Thermoelectric efficiency of each device in the linear response regime is determined by a dimensionless quantity as figure of merit defined as $ZT = \frac{S^2 GT}{\kappa}$. κ is the thermal conductance of the device composed of the lattice part, $\kappa_{\rm ph}$, and the electronic part, κ_e . The electronic part of the thermal conductance is described using Onsager integrals as

$$\kappa_e = \frac{1}{T} \left(L_2 - \frac{L_1^2}{L_0} \right).$$
(6)

The phonon thermal conductance of the device in the linear response regime is given by

$$\kappa_{\rm ph} = \int \omega \frac{(\hbar\omega)^2}{2\pi k_B T^2} T_{\rm ph}(\omega) \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2},\tag{7}$$

where $T_{\rm ph}$ denotes the phonon transmission coefficient.

To estimate the thermoelectric efficiency of the device, we considered the phonon thermal conductance of the suspended MoSe₂ monolayer because the direct calculation of the phonon thermal conductance of the device is a big computational challenge due to a large number of atoms. The phonon thermal conductance of the considered devices is definitely smaller than the thermal conductivity of the pure MoSe₂ single layer due to the interaction of the single layer with the substrate; therefore, the reported ZT is the minimum thermoelectric efficiency of the device. The phonon band structure was calculated using PHONOPY package [69] to obtain the phonon transmission spectra of the monolayer MoSe₂. For this purpose, we first converted the hexagonal primitive cell into a $\sqrt{3} \times 1 \times 1$ rectangular cell and then repeated it into a $3 \times 5 \times 1$ supercell containing 90 atoms. To calculate the phonon transmission of the MoSe₂ monolayer in the ballistic regime, we counted the number of phonon bands crossing a specific energy. To make the calculations accurate, we considered a dense mesh of $300 \times 300 q$ points. Figures S5 and S6 (see Supplemental Material [55]) show the phonon dispersion and phonon thermal conductance of the MoSe₂ monolayer. The phonon dispersion and thermal conductance of MoSe₂ are in good agreement with previous results [70].

Figure 6(a) shows the figure of merit of the device with L = 3.25 nm. Two prominent peaks are observed on both sides of the Fermi level, caused by the two main peaks of thermopower. The results show that increasing the electrode temperature can significantly increase the figure of merit so $ZT \approx 1$ at temperatures above 550 K. ZT peak in *p*-type doping is larger than n-type due to the electron-hole asymmetry of the thermopower. The ZT obtained for free-standing monolayer MoSe₂ is in good agreement with results presented



FIG. 6. (a) Figure of merit as a function of chemical potential and temperature. (b) Figure of merit as a function of temperature for different channel lengths and MoSe₂.

in Ref. [70] used the same methodology. The obtained ZT is higher than the one reported in Ref. [71] for monolayer $MoSe_2$ that is due to different approach used in the latter. Kumar and Schwingenschlogl used the Boltzmann transport theory for calculating the thermopower and power factor based on the constant relaxation time. In addition, they employed the self-consistent iterative approach to calculate the phonon thermal conductivity.

To have a better understanding of the effect of the substrate on the ZT, we have plotted the figure of merit of the freestanding MoSe₂ monolayer in Fig. S4 (see Supplemental Material [55]). As is clear, the location of ZT peaks is symmetrical with respect to the Fermi level and, on the other hand, the *n*-type peak is larger. This shows that the gold substrate leads to the asymmetry of the thermoelectric characteristic of the single layer and changes the participation of the carriers. To study the effect of channel length on the ZT, the maximum of ZT as a function of temperature for three lengths is plotted in Fig. 6(b). We have also plotted the dependence of the maximum of the ZT of the suspended monolayer MoSe₂ for comparison. By increasing the length of L from 1.25 nm to 2.25 nm, the maximum of ZT increases significantly and a further increase in the channel length has no effect on it. Therefore, lengthening the channel cannot lead to an increase in the efficiency of the device. Although the reported ZT for the devices is their minimum limit, it is interesting that up to 550 K the minimum ZT of the devices is higher than the maximum of the figure of merit of the suspended monolayer MoSe₂. This increase is due to the reduction of the electron thermal conductivity of the junction compared to the pure suspended sample.

The figure of merit of the proposed device is about 1 at T = 600 K, which is higher than experimental results for TMD-based devices. Kong *et al.* [72] reported a ZT of 0.14 at T = 720 K for highly oriented MoS₂ polycrystals with MoO₂ nanoinclusions. The value of ZT becomes 0.14 for highly oriented MoS₂ polycrystals when VMo₂S₄ is used as nanoinclusions [73]. SnSe₂ nanoflake exhibits a figure of merit of 0.15 at T = 610 K [74] that is significantly lower than our case. Guilmeau *et al.* reported a ZT of 0.45 at 800K for TiS₂ by intercalating Cu atoms [75].



FIG. 7. (a) The nonequilibrium thermopower and (b) differential thermopower calculated as a function of applied bias and temperature gradient with L = 3.25 nm. (c), (d) Variation of nonequilibrium thermopower and differential thermopower versus voltage for different *L*s at $\Delta T = 100$ K.

C. Nonequilibrium thermoelectric properties

In this section, we consider the nonequilibrium transport through the junction where a voltage difference, V, and a temperature gradient, ΔT is applied to the right electrode. The temperature gradient induces an extra current in the device, and the nonequilibrium thermopower can be defined as [76,77]

$$S(V, \Delta T) = -\left(\frac{\Delta V}{\Delta T}\right)_{I_{e}(V+\Delta V, \Delta T)=I_{e}(V,0)},$$
(8)

where ΔV is the voltage induced in the left electrode to cancel the current induced by the temperature gradient. In the nonequilibrium regime, we can also define the differential thermopower as [77]

$$S_d(V, \Delta T) = -\frac{\left(\frac{\partial I_e}{\partial \Delta T}\right)_V}{\left(\frac{\partial I}{\partial V}\right)_{\Delta T}},\tag{9}$$

where $(\frac{\partial x}{\partial y})_z$ denotes the partial derivative of x with respect to y when the z is fixed. Note that the denominator in the Eq. (9) is the electrical conductance.

Figures 7(a) and 7(b) show the nonequilibrium thermopower and differential thermopower as a function of the voltage applied to the right electrode and the temperature gradient, respectively. Due to the fact that the chemical potential of the left electrode is set equal to the Fermi level, the thermopower is negative in all applied voltage ranges, demonstrating the participation of electrons in the transport of charge and energy inside the device. As is clear from Fig. 7(a), by setting the chemical potential equal to the Fermi level, the range of changes in the nonequilibrium thermopower in low temperature gradients is very large, and the dependence of the thermopower on the voltage of the right electrode decreases significantly with the increase of the temperature gradient. With respect to the transmission spectrum, the transport occurs through the states above the Fermi level where the first state is visible in the energy of 0.5 eV. When the voltage bias is positive, the right electrode becomes the source and can inject the electron from that state to the left electrode. On the contrary, when the bias is negative the left electrode becomes the source. In addition to the voltage bias, the temperature gradient is the other electron injection source that always flows the electrons from the right lead toward the left. For the positive bias, the injection of the electrons from both the bias and the temperature gradient is in the same direction, from the right electrode to the left one, so the induced voltage in the left electrode is the maximum. As a consequence, the thermopower significantly enhances, as demonstrated in Figs. 7(a)and 7(c). When the bias is negative, the direction of electron flow induced by the temperature gradient is opposite to that induced by the voltage, so the thermopower is very small.

The interesting point is that, unlike the equilibrium state, the thermopower is strongly dependent on L. As is clear in Fig. 7(c), a sharp increase in the thermopower of the device with L = 3.25 nm is observed, while the range of thermopower changes in the device with L = 1.25 nm is very small. The highest nonequilibrium thermopower is recorded at L = 3.25 nm, and V = 0.2 V because the right electrode has a chemical potential greater than the left electrode and the temperature gradient is not very large, which is due to the nature of the *n*-type junction. In this situation, by maintaining the chemical potential of the right electrode and increasing the temperature difference, we see a decrease in thermopower. The further increase of the temperature gradient leads to the participation of holes in the transport through the states below the Fermi level and from the colder electrode (left) to the hotter one (right), thus reducing the share of electrons. Indeed, electrons below the chemical potential of the right electrode excite the above of chemical potential by an increase of the temperature. This scenario is reversed when the chemical potential of the right electrode is lower than that of the left. When $\mu_R - \mu_L = -0.2$ V, in low-temperature gradients, the thermopower is close to zero, which is due to the suppression of the current because the Fermi level of both electrodes is lower than the available electronic states in the device. An increase in the temperature gradient leads to an increase in the participation of electrons and, as a result, an increase in the magnitude of the thermopower with a negative sign. The dependence of nonequilibrium thermopower on V and ΔT for L = 1.25, 2.25 nm is drawn in Fig. S8 (see Supplemental Material [55]).

Differential thermopower shows a different behavior compared to thermopower. In each temperature gradient, we see an initial increase in S_d with increasing voltage and then decreasing its magnitude. The critical voltage at which the maximum S_d occurs depends on ΔT . In a very small temperature difference, $\Delta T \approx 50$ K, S_d starts to increase from zero, but as the temperature gradient increases, its value deviates from zero. The dependence of S_d on temperature gradient strongly depends on the sign of the applied voltage. As long as the chemical potential of the left electrode is higher and plays the role of the source, S_d experiences an increase and then a decrease until a critical temperature gradient. The story is reversed when the right electrode turns into a source so the magnitude of S_d decreases uniformly as the temperature gradient increases. This phenomenon is related to the asymmetry of the transmission coefficient of the junction. The $MoSe_2/Au(111)$ junction is an *n*-type junction, which makes the transmission coefficient asymmetric with respect to the Fermi level of the device. This asymmetry is the root of the difference observed in the behavior of the device under the application of temperature gradient or voltage difference. Figure 7(d) also confirms that, unlike the equilibrium thermoelectric characteristics, the thermoelectric characteristics of the device in the nonequilibrium regime are strongly dependent on L.

To investigate the effect of MoSe₂ interaction with the substrate on the nonequilibrium thermoelectric behavior of the device, we examine the thermopower and differential thermopower for stronger and weaker interactions between the monolayer and the substrate in Fig. S8 (see Supplemental Material [55]). In general, increasing the interaction between the layers leads to the improvement of the thermoelectric characteristics of the device. Of course, this improvement is strongly dependent on the voltage sign. Changes are very noticeable in negative voltages, while no significant difference is observed in positive voltages. Therefore, in this junction, as long as the source electrode and the hotter electrode are separated, the interaction effect between the monolayer and the substrate has a very important effect on the thermoelectric behavior.

In our device, considering that $T_R > T_L$, the electrons are transferred from the right electrode to the left one by temperature gradient, leading to the work $W(V, \Delta T)$. The power output of the device can be defined using the energy current relation, Eq. (2), as follows:

$$P(V, \Delta T) = I_a^R(V, \Delta T) - I_a^L(V, \Delta T).$$
(10)

Therefore, the nonequilibrium thermoelectric efficiency of the device can be defined as the ratio of power to heat removed from the right electrode as follows:

$$\eta = \frac{P(V, \Delta T)}{I_a^R(V, \Delta T)} = 1 - \frac{I_q^L(V, \Delta T)}{I_a^R(V, \Delta T)}.$$
(11)

Figure 8 shows the thermoelectric efficiency of the device with L = 3.25 nm. In Fig. 8(a), where the dependence of η on voltage and temperature gradient is plotted at room temperature and, with $\mu_L = E_f$, it is clear that the thermoelectric efficiency can approach one when the colder electrode plays the role of the source. The voltage required to reach the maximum efficiency directly relates to the temperature gradient. The larger the temperature gradient, the larger the negative voltage needed to achieve an efficiency close to one. On the other hand, as long as the hotter electrode is the source, the thermoelectric efficiency in the considered voltage range cannot be more than 40%. In this situation, increasing the temperature gradient leads to improving the efficiency of the device. On the other hand, in constant voltage, the changes of η depend on the sign of the voltage. In negative voltages and in the range -0.25 V < V < -0.07 V, increasing the temperature gradient leads to a decrease in efficiency.

The dependence of the efficiency on the temperature of the left electrode and the temperature gradient is described in Fig. 8(b). Here, we set V = -0.1 V, corresponding to high efficiency at room temperature according to Fig. 8(a). As the results show, the thermoelectric efficiency of the device strongly depends on the temperature difference and the temperature of the left electrode. When the temperature difference between the two electrodes is small, the temperature on the left side should be around 300 K to have high efficiency. By increasing the temperature gradient between two electrodes, high efficiency can be achieved at lower temperatures. Therefore, not only the temperature of the left electrode but also the temperature difference between the two electrodes is a very important parameter to adjust the thermoelectric efficiency of the device.

IV. CONCLUSION

In this paper, we designed a device composed of monolayer $MoSe_2$ coupled to Au(111) electrodes. We investigated the thermoelectric efficiency of the device by combining DFT and Green's function formalism. We considered different lengths of monolayers and analyzed equilibrium and nonequilibrium thermoelectric efficiencies of the device. The transmission coefficient of the device exhibits a gap of 1.5 eV and the $MoSe_2/Au(111)$ junction exhibits *n*-type characteristics. In the equilibrium condition in which the temperature gradient and voltage difference are small, the maximum thermopower and the gap between *n*- and *p*-type carriers are strongly



FIG. 8. Efficiency of device with L = 3.25 nm as a function of (a) voltage bias and temperature gradient, and (b) temperature and temperature gradient.

dependent on the length of the central region. In addition, the minimum figure of merit of the device is 1.1, indicating its potential for thermoelectric application. In the nonequilibrium condition, a large temperature and voltage difference is applied to one electrode while the temperature of the other electrode is fixed. Our results demonstrate that the magnitude of the thermopower and differential thermopower are strongly related to arrangement of the chemical potential of two electrodes. We found that when the hotter electrode has a chemical potential lower than the colder electrode and

[1] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. 105, 136805 (2010).

- [2] T. Eknapakul, P. King, M. Asakawa, P. Buaphet, R.-H. He, S.-K. Mo, H. Takagi, K. Shen, F. Baumberger, T. Sasagawa *et al.*, Nano Lett. **14**, 1312 (2014).
- [3] M. Drüppel, T. Deilmann, P. Krüger, and M. Rohlfing, Nat. Commun. 8, 2117 (2017).
- [4] Y.-H. Chang, W. Zhang, Y. Zhu, Y. Han, J. Pu, J.-K. Chang, W.-T. Hsu, J.-K. Huang, C.-L. Hsu, M.-H. Chiu *et al.*, ACS Nano 8, 8582 (2014).
- [5] C. Jin, J. Kim, M. I. B. Utama, E. C. Regan, H. Kleemann, H. Cai, Y. Shen, M. J. Shinner, A. Sengupta, K. Watanabe *et al.*, Science **360**, 893 (2018).
- [6] H. Yuan, X. Wang, B. Lian, H. Zhang, X. Fang, B. Shen, G. Xu, Y. Xu, S.-C. Zhang, H. Y. Hwang *et al.*, Nat. Nanotechnol. 9, 851 (2014).
- [7] F. Wu, T. Lovorn, E. Tutuc, I. Martin, and A. H. MacDonald, Phys. Rev. Lett. **122**, 086402 (2019).
- [8] C. Zhao, T. Norden, P. Zhang, P. Zhao, Y. Cheng, F. Sun, J. P. Parry, P. Taheri, J. Wang, Y. Yang *et al.*, Nat. Nanotechnol. 12, 757 (2017).
- [9] R. Suzuki, M. Sakano, Y. Zhang, R. Akashi, D. Morikawa, A. Harasawa, K. Yaji, K. Kuroda, K. Miyamoto, T. Okuda *et al.*, Nat. Nanotechnol. 9, 611 (2014).

the temperature difference between two electrodes is about 50 K, the thermoelectric efficiency of the device approaches one.

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- [10] M. Bonilla, S. Kolekar, Y. Ma, H. C. Diaz, V. Kalappattil, R. Das, T. Eggers, H. R. Gutierrez, M.-H. Phan, and M. Batzill, Nat. Nanotechnol. 13, 289 (2018).
- [11] W. Yu, J. Li, T. S. Herng, Z. Wang, X. Zhao, X. Chi, W. Fu, I. Abdelwahab, J. Zhou, J. Dan *et al.*, Adv. Mater. **31**, 1903779 (2019).
- [12] X. Zhang, Q. Lu, W. Liu, W. Niu, J. Sun, J. Cook, M. Vaninger, P. F. Miceli, D. J. Singh, S.-W. Lian *et al.*, Nat. Commun. **12**, 2492 (2021).
- [13] L. Meng, Z. Zhou, M. Xu, S. Yang, K. Si, L. Liu, X. Wang, H. Jiang, B. Li, P. Qin *et al.*, Nat. Commun. **12**, 809 (2021).
- [14] Z. Ye, T. Cao, K. O'brien, H. Zhu, X. Yin, Y. Wang, S. G. Louie, and X. Zhang, Nature (London) 513, 214 (2014).
- [15] J. Kunstmann, F. Mooshammer, P. Nagler, A. Chaves, F. Stein, N. Paradiso, G. Plechinger, C. Strunk, C. Schüller, G. Seifert *et al.*, Nat. Phys. **14**, 801 (2018).
- [16] E. C. Regan, D. Wang, E. Y. Paik, Y. Zeng, L. Zhang, J. Zhu, A. H. MacDonald, H. Deng, and F. Wang, Nat. Rev. Mater. 7, 778 (2022).
- [17] Y. Li, H. Zheng, Y. Fang, D. Zhang, Y. Chen, C. Chen, A. Liang, W. Shi, D. Pei, L. Xu *et al.*, Nat. Commun. **12**, 2874 (2021).
- [18] C. Rubio-Verdú, A. M. García-García, H. Ryu, D.-J. Choi, J. Zaldívar, S. Tang, B. Fan, Z.-X. Shen, S.-K. Mo, J. I. Pascual *et al.*, Nano Lett. **20**, 5111 (2020).

- [19] Y.-T. Hsu, A. Vaezi, M. H. Fischer, and E.-A. Kim, Nat. Commun. 8, 14985 (2017).
- [20] S. C. De la Barrera, M. R. Sinko, D. P. Gopalan, N. Sivadas, K. L. Seyler, K. Watanabe, T. Taniguchi, A. W. Tsen, X. Xu, D. Xiao *et al.*, Nat. Commun. 9, 1427 (2018).
- [21] B. Chamlagain, Q. Li, N. J. Ghimire, H.-J. Chuang, M. M. Perera, H. Tu, Y. Xu, M. Pan, D. Xaio, J. Yan *et al.*, ACS Nano 8, 5079 (2014).
- [22] N. R. Pradhan, Z. Lu, D. Rhodes, D. Smirnov, E. Manousakis, and L. Balicas, Adv. Electron. Mater. 1, 1500215 (2015).
- [23] H. Shu, D. Zhou, F. Li, D. Cao, and X. Chen, ACS Appl. Mater. Interfaces 9, 42688 (2017).
- [24] Y. Zhang, T.-R. Chang, B. Zhou, Y.-T. Cui, H. Yan, Z. Liu, F. Schmitt, J. Lee, R. Moore, Y. Chen *et al.*, Nat. Nanotechnol. 9, 111 (2014).
- [25] T. H. Choudhury, X. Zhang, Z. Y. Al Balushi, M. Chubarov, and J. M. Redwing, Annu. Rev. Mater. Res. 50, 155 (2020).
- [26] F. G. Aras, A. Yilmaz, H. G. Tasdelen, A. Ozden, F. Ay, N. K. Perkgoz, and A. Yeltik, Mater. Sci. Semicond. Process. 148, 106829 (2022).
- [27] A. Bruix, J. A. Miwa, N. Hauptmann, D. Wegner, S. Ulstrup, S. S. Grønborg, C. E. Sanders, M. Dendzik, A. Grubisic Čabo, M. Bianchi, J. V. Lauritsen, A. A. Khajetoorians, B. Hammer, and P. Hofmann, Phys. Rev. B 93, 165422 (2016).
- [28] J. A. Miwa, S. Ulstrup, S. G. Sørensen, M. Dendzik, A. G. Čabo, M. Bianchi, J. V. Lauritsen, and P. Hofmann, Phys. Rev. Lett. 114, 046802 (2015).
- [29] A. Boehm, J. J. Fonseca, K. Thürmer, J. D. Sugar, C. D. Spataru, J. T. Robinson, and T. Ohta, Nano Lett. 23, 2792 (2023).
- [30] B. T. Blue, G. G. Jernigan, D. Le, J. J. Fonseca, S. D. Lough, J. E. Thompson, D. D. Smalley, T. S. Rahman, J. T. Robinson, and M. Ishigami, 2D Mater. 7, 025021 (2020).
- [31] R. Luo, W. W. Xu, Y. Zhang, Z. Wang, X. Wang, Y. Gao, P. Liu, and M. Chen, Nat. Commun. 11, 1011 (2020).
- [32] Q. Wu, M. Bagheri Tagani, L. Zhang, J. Wang, Y. Xia, L. Zhang, S.-Y. Xie, Y. Tian, L.-J. Yin, W. Zhang *et al.*, ACS Nano 16, 6541 (2022).
- [33] M. Zare, B. Z. Rameshti, F. G. Ghamsari, and R. Asgari, Phys. Rev. B 95, 045422 (2017).
- [34] S. N. Sadeghi, M. Zebarjadi, and K. Esfarjani, J. Mater. Chem. C 7, 7308 (2019).
- [35] M. A. Mohebpour, S. I. Vishkayi, and M. B. Tagani, Phys. Chem. Chem. Phys. 22, 23246 (2020).
- [36] H. Karbaschi, N. Nouri, M. Rezaei, and G. Rashedi, Nanotechnology 31, 375403 (2020).
- [37] M. A. Mohebpour, B. Mortazavi, X. Zhuang, and M. B. Tagani, Phys. Rev. B 106, 125405 (2022).
- [38] M. Zare, Phys. Rev. B 99, 235413 (2019).
- [39] M. A. Mohebpour, B. Mortazavi, T. Rabczuk, X. Zhuang, A. V. Shapeev, and M. B. Tagani, Phys. Rev. B 105, 134108 (2022).
- [40] M. A. Mohebpour, S. M. Mozvashi, S. I. Vishkayi, and M. B. Tagani, Sci. Rep. 11, 23840 (2021).
- [41] S. B. Touski and N. Ghobadi, J. Phys. D 54, 485302 (2021).
- [42] A. Patel, D. Singh, Y. Sonvane, P. Thakor, and R. Ahuja, ACS Appl. Mater. Interfaces 12, 46212 (2020).
- [43] T. Nian, Z. Wang, and B. Dong, Appl. Phys. Lett. 118, 033103 (2021).
- [44] M. B. Tagani, Phys. Rev. B 107, 085114 (2023).

- [45] C. J. Thomas, J. J. Fonseca, C. D. Spataru, J. T. Robinson, and T. Ohta, ACS Nano 15, 18060 (2021).
- [46] G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996).
- [47] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- [48] S. Grimme, S. Ehrlich, and L. Goerigk, J. Comput. Chem. 32, 1456 (2011).
- [49] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
- [50] D. Sánchez-Portal, P. Ordejon, E. Artacho, and J. M. Soler, Int. J. Quantum Chem. 65, 453 (1997).
- [51] N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).
- [52] X. Li, M.-W. Lin, J. Lin, B. Huang, A. A. Puretzky, C. Ma, K. Wang, W. Zhou, S. T. Pantelides, M. Chi *et al.*, Sci. Adv. 2, e1501882 (2016).
- [53] V. Villafañe, M. Kremser, R. Hübner, M. M. Petrić, N. P. Wilson, A. V. Stier, K. Müller, M. Florian, A. Steinhoff, and J. J. Finley, Phys. Rev. Lett. 130, 026901 (2023).
- [54] Y. Xia, B. Wang, J. Zhang, Y. Feng, B. Li, X. Ren, H. Tian, J. Xu, W. Ho, H. Xu *et al.*, 2D Mater. 5, 041005 (2018).
- [55] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevB.108.075431 for the band structure of the free-standing monolayer, PDOS of the monolayer, transmission coefficient as a function of L, temperature-dependent thermopower, and additional information about non-linear thermopower.
- [56] X. Wang, Y. Gong, G. Shi, W. L. Chow, K. Keyshar, G. Ye, R. Vajtai, J. Lou, Z. Liu, E. Ringe *et al.*, ACS Nano 8, 5125 (2014).
- [57] Y.-H. Choi, D.-H. Lim, J.-H. Jeong, D. Park, K.-S. Jeong, M. Kim, A. Song, H.-S. Chung, K.-B. Chung, Y. Yi *et al.*, ACS Appl. Mater. Interfaces 9, 30786 (2017).
- [58] J. Lu, D.-L. Bao, K. Qian, S. Zhang, H. Chen, X. Lin, S.-X. Du, and H.-J. Gao, ACS Nano 11, 1689 (2017).
- [59] S. Yasuda, R. Takahashi, R. Osaka, R. Kumagai, Y. Miyata, S. Okada, Y. Hayamizu, and K. Murakoshi, Small 13, 1700748 (2017).
- [60] Q. Wu, X. Fu, K. Yang, H. Wu, L. Liu, L. Zhang, Y. Tian, L.-J. Yin, W.-Q. Huang, W. Zhang *et al.*, ACS Nano 15, 4481 (2021).
- [61] M. G. Rosul, X. Wang, K. Esfarjani, and M. Zebarjadi, Phys. Rev. B 105, 115412 (2022).
- [62] Q.-Y. Li, T. Feng, W. Okita, Y. Komori, H. Suzuki, T. Kato, T. Kaneko, T. Ikuta, X. Ruan, and K. Takahashi, ACS Nano 13, 9182 (2019).
- [63] J. G. Checkelsky and N. P. Ong, Phys. Rev. B 80, 081413(R) (2009).
- [64] F. Ghahari, H.-Y. Xie, T. Taniguchi, K. Watanabe, M. S. Foster, and P. Kim, Phys. Rev. Lett. **116**, 136802 (2016).
- [65] K. Hippalgaonkar, Y. Wang, Y. Ye, D. Y. Qiu, H. Zhu, Y. Wang, J. Moore, S. G. Louie, and X. Zhang, Phys. Rev. B 95, 115407 (2017).
- [66] L.-D. Zhao, G. Tan, S. Hao, J. He, Y. Pei, H. Chi, H. Wang, S. Gong, H. Xu, V. P. Dravid *et al.*, Science **351**, 141 (2016).
- [67] H. Moon, J. Bang, S. Hong, G. Kim, J. W. Roh, J. Kim, and W. Lee, ACS Nano 13, 13317 (2019).
- [68] M. Yoshida, T. Iizuka, Y. Saito, M. Onga, R. Suzuki, Y. Zhang, Y. Iwasa, and S. Shimizu, Nano Lett. 16, 2061 (2016).
- [69] A. Togo and I. Tanaka, Scr. Mater. 108, 1 (2015).

- [70] W. Huang, H. Da, and G. Liang, J. Appl. Phys. 113, 104304 (2013).
- [71] S. Kumar and U. Schwingenschlogl, Chem. Mater. 27, 1278 (2015).
- [72] S. Kong, T. Wu, M. Yuan, Z. Huang, Q.-L. Meng, Q. Jiang, W. Zhuang, P. Jiang, and X. Bao, J. Mater. Chem. A 5, 2004 (2017).
- [73] S. Kong, T. Wu, W. Zhuang, P. Jiang, and X. Bao, J. Phys. Chem. B 122, 713 (2018).
- [74] M.-J. Lee, J.-H. Ahn, J. H. Sung, H. Heo, S. G. Jeon, W. Lee, J. Y. Song, K.-H. Hong, B. Choi, S.-H. Lee *et al.*, Nat. Commun. 7, 12011 (2016).
- [75] E. Guilmeau, Y. Bréard, and A. Maignan, Appl. Phys. Lett. 99, 052107 (2011).
- [76] J. Azema, P. Lombardo, and A.-M. Daré, Phys. Rev. B 90, 205437 (2014).
- [77] A. Manaparambil and I. Weymann, Phys. Rev. B 107, 085404 (2023).