Supplementary Materials for

Quantized thermal transport in single-atom junctions
Longji Cui,* Wonho Jeong,* Sunghoon Hur, Manuel Matt, Jan C. Klöckner, Fabian Pauly, Peter Nielaba, Juan Carlos Cuevas,† Edgar Meyhofer,† Pramod Reddy†

*These authors contributed equally to this work.
†Corresponding authors. Email: juancarlos.cuevas@uam.es (J.C.C.); meyhofer@umich.edu (E.M.); pramodr@umich.edu (P.R.)

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This PDF file includes:
Materials and Methods
Figs. S1 to S10
Captions for Movies S1 to S6
References

Other Supplementary Material for this manuscript includes the following:
(available at www.sciencemag.org/cgi/content/full/science.aam6622/DC1)
Movies S1 to S6
Materials and Methods

1. Nanofabrication process for C-SThM probes

The steps involved in the nanofabrication of the C-SThM probes are shown in Fig. S1A. Briefly, the fabrication process proceeds as follows. The fabrication began with a silicon (Si) wafer. T-shaped beams were realized by making a trench on the Si wafer followed by wet oxidation and deposition of 600 nm of LPCVD SiN$_x$. Subsequently, the backside of the Si wafer was patterned to facilitate KOH-based etching to release the devices in the last step of fabrication. Then a platinum (Pt) serpentine line was defined which forms a very sensitive temperature sensor. Further, 50 nm of PECVD SiN$_x$ was deposited on the serpentine line to electrically insulate it. Subsequently, the probe was released by a KOH etch. After successfully releasing the probes, each of the probes was individually flipped and aligned on a shadow mask to deposit 500 nm of the desired metal (Au or Pt) on the tip and the side walls.

The structure of the fabricated probe is shown in Figs. 1B and C. The beams of the probe are 200 µm long and the rib height is 18 µm. Other relevant dimensions are also highlighted in the figure.

![Fig. S1 Nanofabrication steps for thermal probes](image)

(A) (Step 1) Definition of T-shaped beams and backside patterning. (Step 2) Fabrication of the Pt serpentine resistance thermometer (30 nm thick). (Step 3) Deposition of the SiN$_x$ insulation layer, Pt tip (100 nm thick) definition and front side patterning. (Step 4) Release of the probe. (Step 5) Aligning the probe’s tip with respect to a shadow mask. (Step 6) Sputtering of Au or Pt (500 nm thick) on the tip and side walls. (Step 7) Detaching the probe from the shadow mask. (B, C) Drawings show the geometry of the fabricated probe and relevant dimensions.

2. Characterization of the thermal conductance and thermal time constant of the C-SThM probes

The thermal conductance of the probe was characterized using an approach similar to that described in our previous works (38). Briefly, a known amount of heat was supplied into the suspended region of the probe via the integrated Pt serpentine line and the corresponding temperature rise was measured. The relationship between the power input ($Q_{in}$) and the measured temperature rise ($\Delta T_p$) is shown in Fig. S2A. This information can be used to readily estimate the
thermal resistance of the C-SThM probe \((R_P)\) via \(R_P = \Delta T_P/Q_{in}\), which was estimated to be 1.34 MK/W.

**Fig. S2.** Measured thermal resistance and frequency response of the C-SThM probe. (A) Temperature rise of the Pt resistance thermometer as a function of the heat input. (B) Normalized temperature rise of the probe as a function of frequency of heat input. The -3dB point is marked by a red square.

In order to evaluate the thermal time constant of the C-SThM probe we input sinusoidal heat currents of constant amplitude and varying frequency into the suspended region of the probe. This was accomplished by supplying a sinusoidal current of amplitude \((I_f = 5 \mu A)\) and at frequency \(f\) through the Pt heater-thermometer. This current produced sinusoidal Joule heating \((Q_{2f})\) in the device at frequency \(2f\), with corresponding temperature fluctuations at an amplitude \(\Delta T_{2f}\). A voltage component across the Pt heater-thermometer at \(3f\), \(V_{3f}\), is related to these temperature fluctuations by the relationship \(V_{3f} = \frac{\Delta T_{2f} \alpha I_f R}{2}\), where \(R\) is the nominal resistance of the Pt thermometer. Figure S2B presents the measured amplitude of these temperature oscillations (normalized by the amplitude at the lowest frequency). Note that the -3dB point \((f_{-3dB})\) is at ~7 Hz. Therefore, the thermal time constant \((\tau)\) of the C-SThM probe, which to an excellent approximation is a first order system, is given by \(\tau = (2\pi f_{-3dB})^{-1} \sim 25\) ms.

### 3. Evaluation of the stiffness of the C-SThM probes

In order to estimate the stiffness of the C-SThM probes, we performed finite element analysis (FEA) simulations using COMSOL™ (Solid Mechanics Module), which accurately predicts device stiffnesses (38). In performing these calculations, we applied “fixed” boundary conditions to the distal ends of the beams of the C-SThM probe as shown in Fig. S3A. To estimate the stiffness of the probe, a 100 nN force was applied either in the normal or transverse directions at the end of the probe tip (see Figs. S3B, C, D). The resultant displacement field, as computed by the FEA, enabled us to estimate the stiffness of the probe. From the computed deflections, the
stiffness of the probe was estimated to be ~12,500 N/m in the normal direction and ~250 N/m and 9.1 N/m for the two transverse directions, respectively (see Figs. S3B, C, D). The lower stiffness in (D) arises partly due to the fact that the beam (stiffener) underneath the tip region does not fully extend to the end of the suspended region. From our experiments, we found that these stiffness values were sufficiently large to ensure stable atomic junction formation. We note that substantially lower stiffnesses can severely compromise the junction stability due to thermal fluctuation induced deflections of the probes and due to elastic instabilities. In these simulations the values of Young’s modulus and Poisson’s ratio of SiNx were taken to be 290 GPa and 0.20, respectively (39).

Fig. S3. Finite element analysis of the stiffness of a C-SThM probe. (A) The mesh used in our FEM scheme for the computation of the stiffness. A 100 nN force was applied in normal and transverse directions of the beams and the deflection for each of the cases was computed. (B–D) From the calculations the stiffness of the probe was estimated be 12,500 N/m (B), 250 N/m (C) and 9.1 N/m (D), respectively.

4. Analysis of the temperature distribution and thermal expansion of the probe

We employed a COMSOL-based FEA to analyze the temperature distribution within the C-SThM probe when a heat flux is applied at the tip. The results of our calculations show that the temperature drop occurs primarily along the beams (Fig. S4A). This ensures that the temperature reported by the Pt resistance thermometer can be used to accurately estimate the heat flow into the probe.
A second question of importance is whether the sinusoidal electric current supplied to the Pt resistance thermometer causes deflections of the C-SThM probe due to bimaterial effects. To answer this question we first employed the FEA to compute the deflection of the C-SThM probe when a DC electric current is supplied into the Pt thermometer resulting in a 1 K temperature rise of the suspended region. Our results (Fig. S4B) show that the tip deflection is 1.06 nm/K. In order to estimate the perturbations due to our sinusoidal electric currents (10 µA, f = 1 kHz) supplied into the Pt line, we estimate the temperature oscillations of the probe at 2 kHz (note that Joule heating occurs at twice the excitation frequency, 2f) by noting that our probe behaves as a first order system (see Fig. S2B). Specifically, to estimate ΔT(2f) we use the expression ΔT(2f) ≈ ΔT_{DC} × f_{3dB} / (2f), where ΔT_{DC} (= 3.25 K) is the temperature increase of the suspended device when a DC current of 10 µA is supplied to the probe, f_{3dB} is the cut-off frequency of our scanning probe (~7 Hz). From this analysis we estimate the temperature rise at 2 kHz to be ~11 mK. Thus the amplitude of fluctuations of the probe due to bimaterial effects is ~12 pm (11 mK×1.06 nm/K). Since this amplitude is much smaller than the lengths over which the atomic junctions are stretched they do not have any adverse effects on our measurements.

Fig. S4. Finite element analysis of the temperature distribution and thermal expansion of the probes. (A) Computed results for the temperature increase of the probe when a power input of 10 µW was applied to the Au tip end. It can be seen that the majority of the temperature drops along the beams. (B) Deflection of the C-SThM probe, due to bimaterial effects, when the suspended region of the C-SThM probe was heated by 1 K (DC heating).

5. Ultra-low noise measurement environment

All measurements in this experiment were performed in ultra-high vacuum (~10^{-9} Torr) scanning probe microscope (RHK UHV 750). The instrument was housed inside an ultra-low noise facility where the ground vibrations were attenuated to meet the NIST-A standard. Temperature drift in the room where the scanning probe microscope is located was actively controlled to be within <100 mK around the set-point temperature (295 K).
6. Electrical circuitry

As shown in Fig. 1A of the manuscript the electrical conductance of atomic junctions is measured by supplying a small sinusoidal electric voltage of 1 mV at 10 kHz across the scanning probe and the substrate, and monitoring the amplitude of the resultant current by using a current amplifier and a lock-in amplifier (SR 810). The small amplitude of the applied bias gives rise to very small amounts of Joule heating in single atom junctions (~25 pW), which is negligible in comparison to the 10 nW heat flow that occurs in Au single atomic junctions in response to a 20 K temperature differential (as is applied in our measurements).

The thermal conductance is measured by recording the temperature change of the scanning probe. This is accomplished by monitoring the changes in the electrical resistance of the Pt serpentine line (Pt thermometer). To achieve this goal the Pt sensor forms part of a Wheatstone bridge whose output signal was amplified by an instrumentation amplifier with a gain of 100. The amplified signal was measured using a lock-in amplifier (SR 830).

7. Noise characterization of the Pt resistance thermometer

The temperature resolution of the integrated Pt resistance thermometer was evaluated following the protocols developed by us in the past (21). Briefly, our temperature measurement employs a modulated electrical current at 1 kHz to measure unmodulated temperature changes in a bandwidth of 10 Hz. Given this scheme, the noise in the measurement has contributions from electronics (amplifiers), Johnson noise, shot noise and ambient temperature drift. We quantified these components following the detailed protocols established in (21) and estimated the noise equivalent temperature (NET) of our current thermometry scheme to be <1 mK (~0.6 mK) RMS in a 10 Hz bandwidth.

8. Sample preparation and surface cleaning protocols

Employing proper surface cleaning protocols is essential for successfully minimizing any surface contaminations that compromise the desired thermal measurements. Towards this goal, we developed protocols for sample preparation and for cleaning the surfaces of the scanning probe and the substrate sample.

Planar Au and Pt samples were prepared by employing a template stripping approach. Briefly, a 150 nm thick layer of Au or Pt was deposited using E-beam evaporation on a pristine Si wafer. Subsequently, a low-viscosity epoxy (Epotek 377) was applied uniformly on the metal-coated Si wafer to glue a clean 7 mm × 7 mm Pyrex piece to the top surface of the wafer. The wafer was cured at ~150 °C for two hours. Right before the experiment the Pyrex substrate was peeled off to successfully expose a pristine metallic sample, which is protected from oxidation by the Si substrate. The peeling off process was conducted in a pure N₂ filled glove box, minimizing the exposure of the clean surface to the ambient environment.

Since the above-described approach cannot be applied to the metal tip of the C-SThM probe we employed the following protocol to eliminate any contamination that may have accumulated on the surfaces due to exposure to the ambient. The probes were first sonicated in acetone, IPA and then DI water for ~10 minutes in each step. Subsequently, the probe was dried in N₂ and subjected to multiple oxygen plasma cleaning cycles (300 W, 5 mins). For Pt-coated scanning probes, additional hydrogen plasma cleaning cycles (50 W, 20 mins) were applied after oxygen
plasma treatment. All cleaned probes and samples were placed in a N\textsubscript{2} gas environment to avoid direct contact with the ambient. Successful experiments were accomplished when the apparent tunneling barrier heights (40, 29) measured in the experiments were large (>2 eV).

9. Details of histogram construction and histograms obtained from the measured electrical and thermal conductance traces for Pt atomic junctions

The 2D histogram in Fig. 2B was constructed by collecting the electrical conductance ($G_e$) and the corresponding Lorenz number ($L / L_0$) of the four measured electrical and thermal conductance traces shown in Fig. 2A and counting the number of data falling into the joint bins of $[(G_e)_i, (L / L_0)_j]$, where $i, j = 1, 2, \ldots, N$. In constructing our histograms $N$ was chosen to be sufficiently large (>100, as large as 1000 in some cases) to give results that were invariant with further increasing the value of N. The same procedure was applied to obtain the joint plot of electrical and thermal conductances in Fig. 2E, where we used ~2000 traces of concurrently measured $G_e$ and $G_{Th}$, without any data selection. These measured traces were also used to obtain 1D histograms of electrical conductance (Fig. 2C) and thermal conductance (Fig. 2D) and the corresponding Lorenz number (Fig. 2F). Histograms in Figs. 3C and 3D were constructed using the same approach (with a $N = 50$) as outlined for the data analysis in Fig. 2 but by using 100 computed electrical and thermal conductance traces. We note that these results are independent of probes and could be successfully repeated with multiple probes and samples.

The histograms obtained from the measured electrical and thermal conductance traces for Pt junction are shown in Fig. S5. As explained in the manuscript, the histograms for Pt atomic junction, in contrast to histograms for Au atomic junctions, do not show any clear peaks at integral multiples of $G_0$, $G_{0,Th}$, suggesting that there is no observable thermal conductance quantization for Pt junctions at room temperature.

**Fig. S5. Histograms for Pt atomic junctions.** (A, B) Electrical and thermal conductance histograms for Pt atomic junctions (obtained from experimental data). The histograms are relatively featureless and do not display any distinct conductance quantization.
10. Theoretical modelling

As explained in the manuscript, we computed the thermal and electrical conductance of Au and Pt atomic-size contacts within the framework of the Landauer-Büttiker formalism for coherent transport. For this purpose, we combined non-equilibrium Green’s function (NEGF) techniques, various electronic structure methods, and classical molecular dynamics (MD) simulations. In this section, we present a description of these different theoretical techniques as well as some additional results. To be precise, we first summarize the basic formulas of the Landauer-Büttiker approach to compute the thermal conductance of a nanoscale system. Then, we describe the transport approach based on density functional theory (DFT) and finally, we discuss how we performed MD simulations to determine the geometries of the atomic contacts and how they were combined with a tight-binding model to compute the transport properties of these atomic-scale contacts.

10.1 Thermal conductance within the Landauer-Büttiker approach

There are two basic contributions to the thermal conductance, namely due to electrons and phonons. Within the Landauer-Büttiker approach for coherent transport these contributions are determined by the corresponding electronic, $\tau_{el}$, and phononic, $\tau_{ph}$, transmission functions. The electronic contribution to the linear thermal conductance, $G_{Th,e}$, is given by (5)

$$G_{Th,e} = \frac{2}{hT} \left( K_2 - \frac{K_1^2}{K_0} \right),$$  \hspace{1cm} (S1)

where $T$ is the absolute temperature and the coefficients $K_n$ are defined as

$$K_n = \int_{-\infty}^{\infty} (E - \mu)^n \tau_{el}(E) \left( -\frac{\partial f(E)}{\partial E} \right) dE,$$  \hspace{1cm} (S2)

where $f(E,\mu,T) = \{\exp[(E - \mu)/k_B T] + 1\}^{-1}$ is the Fermi function. Here, the chemical potential $\mu = E_F$ is approximately given by the Fermi energy $E_F$. Let us point out that, if the electronic transmission does not strongly depend on energy around $E_F$, it is easy to show that the electronic thermal conductance is approximated by the Wiedemann-Franz law, i.e., $G_{Th,e} \approx L_0 T G_e$, where $L_0 = (k_B / e)^2 \pi^2 / 3$ is the Lorenz number and $G_e = (2e^2 / h)\tau_{el}(E_F)$ is the zero-temperature electrical conductance.

The phonon thermal conductance in the linear response regime is given by (5)

$$G_{Th,ph} = \frac{1}{h} \int_0^{\infty} E \tau_{ph}(E) \frac{\partial n(E,T)}{\partial T} dE,$$  \hspace{1cm} (S3)

where $n(E,T) = [\exp(E / k_B T) - 1]^{-1}$ is the Bose function.

On the other hand, the electrical conductance for arbitrary temperature is given by (5)

$$G_e = \frac{2e^2}{h} \int_{-\infty}^{\infty} \tau_{el}(E) \left( -\frac{\partial f(E)}{\partial E} \right) dE.$$  \hspace{1cm} (S4)

Thus, the description of the different transport properties investigated in this work requires the calculation of the electronic and phononic transmission functions. In the following subsections we show how we computed these functions with the help of NEGF techniques and different electronic structure methods.
10.2 First principles transport calculations

We combined density functional theory (DFT) with non-equilibrium Green’s function techniques (NEGF) to compute the transport properties of Au atomic-size contacts within the Landauer-Büttiker approach. To be precise, we calculated both the electrical and thermal conductance (due to both electrons and phonons) of one-atom thick contacts that describe the situation that takes places in the last stages prior to the rupture of these metallic atomic-size contacts (i.e., in the last conductance plateau). For this purpose, we made use of the first-principles formalism developed by some of us and reported in \( (32, 33) \). In what follows, we briefly describe this formalism.

10.2.1 Contact geometries, electronic structure, and vibrational properties. The first step in our calculations is the construction of the atomic junction geometries. We focused on the analysis of one-atom thick contacts of Au. We used DFT to compute equilibrium geometries through total energy minimization and to describe their electronic structure. Then we obtained the vibrational properties of the optimized contacts in the framework of density functional perturbation theory.

We used both procedures as implemented in the quantum chemistry software package TURBOMOLE 6.5 \( (41-43) \), that employs the PBE exchange-correlation functional \( (44, 45) \), the basis set def2-SV(P) \( (46) \) for Au, and the corresponding Coulomb fitting basis \( (47) \). To make sure that the vibrational properties, i.e., vibrational energies and force constants, are accurately determined, we used very stringent convergence criteria. Thus, total energies were converged to a precision of better than \( 10^{-9} \) atomic units while geometry optimizations were performed until the change of the maximum norm of the Cartesian gradient was below \( 10^{-5} \) atomic units.

The contact geometries for Au one-thick contacts were modeled as shown in Fig. S6A below. Starting from ideal fcc \(<111>\) lattice positions, the two tip atoms and their 3 nearest neighbors in each of the tips on the left and right were relaxed, while the other electrode atoms were kept fixed at their fcc \(<111>\) positions.

10.2.2 Electronic transport. To determine the electronic structure of the atomic junctions and to compute the electronic transmission that determines the different electronic transport properties within the Landauer-Büttiker approach we made use of NEGFs expressed in a local non-orthogonal basis. Briefly, the local basis allows us to partition the basis states into L, C and R ones, where L and R correspond to the left and right electrode, respectively, while C corresponds to a central region including the atomic neck. Thus, the Hamiltonian (or single-particle Fock) matrix \( H \), as well as the overlap matrix \( S \), can be written in the block form as follows

\[
H = \begin{pmatrix}
H_{LL} & H_{LC} & 0 \\
H_{CL} & H_{CC} & H_{CR} \\
0 & H_{RC} & H_{RR}
\end{pmatrix}.
\] (S5)

The energy-dependent electronic transmission \( \tau_{el}(E) \) entering equations (S2) and (S4) can be expressed in terms of the Green’s functions as \( (5) \)

\[
\tau_{el}(E) = \text{Tr} \left[ \Gamma_L G_{CC}^r \Gamma_R G_{CC}^a \right],
\] (S6)

where the retarded Green’s function is given by

\[
G_{cc}^r(E) = \left[ (E + i\eta)S_{cc} - H_{cc} - \Sigma^L(E) - \Sigma^R(E) \right]^{-1},
\] (S7)
where $\eta$ is an infinitesimal positive parameter (that will be omitted hereafter) and $G_{cc}^a = \left[ G_{cc}^T \right]^\dagger$. The self-energies in the previous equation adopt the form

$$\Sigma_X^a(E) = \left( H_{cc}^a - ES_{cc}^a \right) g_{xx}^a(E) \left( H_{cc}^a - ES_{cc}^a \right).$$

(S8)

On the other hand, the scattering rate matrices that enter the expression of the electronic transmission are given by $\Gamma_X(E) = i \left[ \Sigma_X^a(E) - \Sigma_X^a(E) \right]$, and $g_{xx}^a(E) = \left( E S_{xx}^a - H_{xx} \right)^{-1}$ are the electrode Green's functions with $X = L, R$. Finally, it is convenient to decompose the total electronic transmission in terms of individual transmission coefficients. For this purpose, we can write equation (S6) as

$$\tau_{el}(E) = \text{Tr} \left[ t(E) t^\dagger(E) \right] = \sum_i \tau_i(E),$$

(S9)

where $t = \Gamma_L^{1/2} G_{cc}^L \Gamma_R^{1/2}$ is the transmission matrix and $\tau_i$ are the eigenvalues of $tt^\dagger$, known as transmission coefficients, while the corresponding eigenfunctions are known as conduction channels.

In order to describe the transport through the atomic contacts, we first extract $H_{cc}$ and $S_{cc}$ and the matrices $H_{cc}$ and $S_{cc}$ from a DFT calculation of an extended center cluster that includes the central wires and part of the leads. On the other hand, the electrode Green's functions $g_{xx}^a(E)$ are modeled as surface Green's functions of ideal semi-infinite crystals. To obtain these Green's functions, we first compute separately the electronic structure of a large spherical fcc cluster. Then, we extract the bulk Hamiltonian and overlap matrix elements and we use them to model a semi-infinite crystal that is infinitely extended perpendicular to the transport direction. The surface Green’s functions are then calculated from this crystal with the help of a decimation technique (48, 32).

### 10.2.3 Phonon transport

We computed the phonon transmission appearing in equation (S3) by combining DFT and NEGF techniques following our previous work (33). Briefly, the starting point is the description of the phonons or vibrational modes of the junctions within the harmonic approximation. In this approximation, the phonon Hamiltonian for small displacements $\{Q_{\xi}^j\}$ of the atoms around their equilibrium positions $\{ R_{\xi}^{(0)} \}$ adopts the following

$$\hat{H} = \frac{1}{2} \sum_{\xi} \hat{p}_{\xi}^2 + \frac{1}{2\hbar^2} \sum_{\xi \xi} \hat{q}_{\xi} \hat{q}_{\xi}^\dagger K_{\xi\xi},$$

(S10)

where we have introduced mass-weighted displacement operators $\hat{q}_{\xi} = \sqrt{M_{\xi}} \hat{Q}_{\xi}$ and mass-scaled momentum operators $\hat{p}_{\xi} = \hat{P}_{\xi} / \sqrt{M_{\xi}}$ as conjugate variables. These variables obey bosonic commutation relations: $[\hat{q}_{\xi}, \hat{p}_{\chi}] = i\hbar \delta_{\xi\chi}$ and $[\hat{q}_{\xi}, \hat{q}_{\chi}] = [\hat{p}_{\xi}, \hat{p}_{\chi}] = 0$, where $\xi = (j,c)$ denotes a Cartesian component $c = x,y,z$ of atom $j$ at position $\vec{R}_j = \vec{R}_j^{(0)} + \vec{Q}_j$. The phonon system is characterized by its dynamical matrix $K_{\xi\chi} = \hbar^2 \delta_{\xi\chi} E_{\text{Total}} / \sqrt{M_{\xi} M_{\chi}}$, which is the mass-weighted Hessian of the DFT total ground state energy $E_{\text{Total}}$ with respect to the Cartesian atomic
coordinates. These harmonic force constants are computed within density functional perturbation theory.

In analogy with the electronic system above, the use of a local displacement basis enables the portioning of the dynamical matrix into three parts, a central scattering region $C$, and the two semi-infinite $L$ and $R$ electrodes

$$ K = \begin{pmatrix} K_{LL} & K_{LC} & 0 \\ K_{CL} & K_{CC} & K_{CR} \\ 0 & K_{RC} & K_{RR} \end{pmatrix}. $$ (S11)

The energy-dependent phononic transmission $\tau_{\text{ph}}(E)$ can be expressed as (49, 33)

$$ \tau_{\text{ph}}(E) = \text{Tr}[\Lambda_L D_{CC}^r \Lambda_R D_{CC}^a], $$

where $D_{CC}^r(E)$ are the retarded and advance phonon Green’s functions of the central region that can be computed by solving the following Dyson equation

$$ D_{CC}^r(E) = \left((E + i\eta)^2 1 - K_{CC} - \Pi_L^r(E) - \Pi_R^r(E)\right)^{-1}, $$

where $\eta > 0$ is an infinitesimal parameter and $D_{CC}^a = [D_{CC}^r]^\dagger$. On the other hand, the scattering rate matrices

$$ \Lambda_X(E) = i\left[\Pi_X^r(E) - \Pi_X^a(E)\right] $$ (S14)

are related to the corresponding contact self-energies

$$ \Pi_X^r(E) = K_{CX} d_{XX}^r(E) K_{XC}, $$

(S15)

describing the coupling between the central region $C$ and the electrode $X$. In the previous expression, $d_{XX}^r(E)$ is the surface Green’s function of the lead $X = L, R$ and $\Pi_{CC}^r(E) = [\Pi_{CC}^r(E)]^\dagger$.

To compute the different parts of the dynamical matrix in equation (S11) we followed the same strategy as in the electronic case described above. We first compute the dynamical matrix for an extended central cluster including the central part of the atomic wire and parts of the leads. Subsequently, we extract from there the matrices $K_{CC}$ and $K_{XC}$. On the other hand, the surface Green’s functions of the electrodes $d_{XX}^r(E)$ are obtained by extracting bulk force constant from a separate calculation of a big cluster and then using these extracted parameters in combination with a decimation technique (48, 32) to describe the surface of a semi-infinite perfect crystal, exactly like in the electronic case.

10.2.4 Results. The ballistic phonon thermal conductance (eqn. (S3)) is determined from the phonon transmission function given in equation (S12). The phonon transmission for the Au single-atom contact of Fig. S6A is shown in Fig. S6B as a function of energy. Here, we have decomposed the total phonon transmission $\tau_{\text{ph}} = \sum_i \tau_i$ into its contributions from the individual transmission channels $\tau_i$, like in the electronic case. Notice that the transmission at low energies is mainly determined by two almost degenerate channels, while for higher energies the transmission is dominated by a single channel. The temperature dependence of the phononic
thermal conductance computed from equation (S3) for this contact is shown in Figs. 3A of the manuscript. At room temperature, we find a phononic thermal conductance of 24.3 pW/K for this geometry.

Fig. S6. Phonon transmission of an Au single-atom contacts. (A) Geometry of the gold single-atom contact considered in Fig. 3A and 3B of the manuscript. (B) Total phonon transmission function $\tau_{ph}$ and the three largest contributions from the individual transmission channels $\tau_i$ for the contact of panel A.

10.3 Molecular dynamics (MD) simulations

To perform a thorough statistical analysis of the thermal conductance of our Au and Pt atomic-size contacts, we carried out classical molecular (MD) dynamics simulations to determine the geometry of these contacts following our previous work (11). These geometries were then employed to compute the thermal conductance as we explain below. The MD simulations were carried out using the open source program package LAMMPS (50, 51). Within LAMMPS, we use the embedded atom method with the semi-empirical potentials from Ackland et al. (52) for Au and from Sheng et al. (53) for Pt to describe the interactions between atoms. Let us emphasize that these potentials account for the possibility to have an atomic coordination different from bulk. To determine the geometry of the atomic contacts, we start with an ideal fcc lattice, where the crystal direction $<100>$ lies parallel to the $z$ axis, which corresponds to the transport and elongation direction. In these simulations we first divide the geometry into three parts: Two electrodes and a central wire bridging the gap between them (see Fig. S7). The electrodes consist of 661 atoms each that are kept fixed during the MD simulations. The central wire is made up of 563 atoms whose motion is described with Newtonian equations of motion. We assume a canonical ensemble and use the velocity Verlet integration scheme (54). The simulated wires have an initial length of 0.82 nm for gold and 0.78 nm for platinum. The starting velocities of the atoms in the wire were chosen randomly with a Gaussian distribution to yield an average temperature of $T = 300$ K. Because of this randomness, every elongation calculation evolves differently, while a Nosé-Hoover thermostat keeps the temperature fixed (54). To relax the system, the wire is equilibrated for 0.1 ns. Finally, the elongation process is simulated by separating the electrodes at a constant velocity of 0.4 m/s. During this process, every 10 ps the geometry is recorded. A stretching process needs a total simulation time of about 4.5 ns, until the contact breaks.
**Fig. S7. Contact geometries in the molecular dynamics simulations.** (A) Ideal fcc starting structure of the atomic contacts. (B) Example of atomic contact of gold at an elongation of 1.5 nm. In both panels we have indicated the partitioning of the contacts into the upper and lower electrodes and the central wire, as used for the MD and transport calculations.

10.3.1 **Tight-binding-based transport calculations.** We used the geometries of the atomic contacts that were determined with the MD simulations to compute the electronic contribution to the transport properties within the Landauer-Büttiker formalism. In this case, the electronic transmission that determines both the electrical conductance and the electronic contribution to the thermal conductance is computed with the help of a tight-binding model. To be precise, we employed a non-orthogonal Slater-Koster tight-binding parameterization (55), which has been quite successful in determining a variety of properties of these atomic wires (30, 56, 31, 11). In this parameterization we take into account the relevant valence orbitals of Au and Pt, which include the 5d, 6s, and 6p orbitals. Moreover, the hopping and overlap matrix elements in this tight-binding model are functions of the distance between the atoms, which allows us to combine this model with our MD simulations.

To compute the transmission in the framework of our tight-binding model we made use of NEGF techniques and the formulas detailed in section 10.1, very much like in the DFT-based calculations. The corresponding details can be found in (28, 53). Briefly, as in the MD simulations, the system is divided into three regions for the transport calculations, i.e., the two electrodes and the central wire (see Fig. S7). Because the local environment of the atoms in the central part is very different from that in the bulk, we enforce the charge neutrality for all the atoms of the wire (28, 53). Such a neutrality condition is typically a good approximation for metallic systems. As in the DFT case, the electrodes are considered to be semi-infinite perfect crystals and their surface Green's functions are computed with the help of a decimation technique (48, 32). Again, as in the DFT-based calculations, the Green’s function techniques also allow us to compute the individual transmission coefficients, $\tau_i$. 
Fig. S8. Individual electrical and thermal conductance traces in the molecular dynamics simulations. (A-B) Individual traces of the electrical conductance and the electronic thermal conductance for Au (A) and Pt (B) computed with the combination of MD simulations and the tight-binding model. The solid lines correspond to the electrical conductance (left scales) and the symbols to the electronic thermal conductance (right scales). In order to test the validity of the Wiedemann-Franz law, the electrical conductance, $G_e$, has been normalized by the quantum of conductance, $G_0 = 2e^2 / h$, while the thermal conductance has been normalized by $L_0 T G_0$, where $L_0$ is the Lorenz number and $T$ is the temperature. As one can see, there is an excellent correlation between both conductances, with only small deviations in the case of the Pt wires. All the results were obtained at $T = 300$ K.

10.3.2 Results. With the combination of the classical MD simulations, the tight-binding model, and the NEGF techniques we carried out a systematic analysis of the electrical conductance and the electronic thermal conductance of Au and Pt atomic contacts. Let us remark that with these theoretical techniques we focus on the electronic contribution to the thermal conductance because our DFT-based calculations have shown that phonons play a marginal role. We carried out 100 simulations of the stretching of the contacts at room temperature. In Fig. S8 we show different examples of the evolution of the electrical and thermal conductance during the stretching of the Au and Pt contacts. We normalize the electrical conductance, $G_e$, by the quantum of conductance, $G_0 = 2e^2 / h$, while the thermal conductance is normalized by $L_0 T G_0$, where $L_0$ is the Lorenz number and $T$ is the temperature. This normalization is convenient to test the validity of the Wiedemann-Franz law. As one can see, this law is very precisely fulfilled in the case of the Au contacts, while there are small deviations (of a few per cent) in the case of the Pt wires. These deviations are due to the fact that the electronic transmission in the Pt case exhibits a stronger energy dependence around the Fermi energy than in the Au case. This is due to the fact that in this transition metal the Fermi energy lies close to the edge of the 5d band (11).
Fig. S9. Evolution of the electrical and the thermal conductance in the MD simulations. (A, B) Two-dimensional density plots showing the evolution of the electrical conductance (A) and electronic thermal conductance (B) during the elongation of 100 different Au contacts as obtained from our MD simulations combined with the tight-binding model. (C, D) The same as in (A) and (B) but for Pt wires. The electrical conductance, $G_e$, has been normalized by the quantum of conductance, $G_0 = 2e^2/h$, while the thermal conductance has been normalized by $L_0TG_0$, where $L_0$ is the Lorenz number and $T$ is the temperature. The insets in the different panels show a blow-up of the last stages of the breaking of the wires. All the results were obtained at $T = 300$ K.

In Fig. S9 we show 2D density plots of the evolution of the electrical and thermal conductance for 100 MD simulations of the breaking of Au and Pt wires. In particular, the insets show the corresponding results for the last stages of the breaking of these wires. As one can see, in the case of Au there is a statistical tendency to see quantized values of both the electrical and thermal conductance. On the contrary, there is no such a conductance quantization in the Pt wires and the last plateau exhibits values largely spread. Again, the fundamental difference between these two materials lies in their different electronic structure, as explained in (11). While in the Au case the transport properties are dominated by the $6s$ with a single orbital per atom, in the Pt case the $5d$ band also plays a fundamental role and several $d$-orbitals contribute to the electronic and thermal transport (apart from the $6s$ orbital). This implies in practice that the transport properties of Au few-atom contacts are determined by fully open conduction channels (with transmission coefficients $\sim 1$), which naturally explains the tendency to observe quantized conductance values (both for the electrical and for the thermal conductance). On the other hand, in the Pt case the transport properties are determined by partially open conduction channels with transmission somewhere in between 0 and 1, which explains the absence of quantization in this material (11).

For completeness we show in Fig. S10A the conductance histograms for the Pt junctions as obtained from the MD simulations of the junction formation. The corresponding histograms for Au are shown in Fig. 3C of the manuscript. As one can see, the Pt junctions only exhibit a very broad peak related to one-atom thick contacts, but the conductance values are largely spread and
there are no signs of conductance quantization. As explained above, this is due to the fact that in the Pt case the $5d$ orbitals play a crucial role in the transport properties and give rise to partially open channels, even in the case of single-atom contacts. This is a well-known behaviour of transition metals (5,11). We note that these computational results broadly agree with our experimental observation of discrete steps in conductance traces but the histograms do not reveal pronounced quantization. On the other hand, these histograms allow us to systematically study the validity of the Wiedemann-Franz law for contacts of arbitrary size. This validity is conveniently studied in terms of the Lorenz ratio defined as $L/L_0 = G_{Th,e}/(L_0 T G_e)$ which we show in Fig. S10B for the Pt contacts as a function of the electrical conductance (see Fig. 3D for the corresponding results for Au). As for the individual traces discussed above (Fig. S8), the Wiedemann-Franz law is fulfilled with deviations below 5% irrespective of the contact size. As mentioned above, these deviations are slightly larger than those in the Au case due to the more pronounced energy dependence of the electronic transmission around the Fermi energy.

Fig. S10. Pt conductance histograms computed with the MD simulations. (A) Electrical and electronic thermal conductance histograms obtained from 100 MD simulations of the formation of Pt atomic contacts at room temperature. (B) Lorenz ratio $L/L_0 = G_{Th,e}/(L_0 T G_e)$ for the Pt contacts as a function of the electrical conductance $G_e$ as obtained from the histograms of panel A. Notice that the ratio is very close to one with deviations below 5%, which shows that the Wiedemann-Franz law is obeyed with good accuracy, irrespective of the contact size.
Captions for Movies:

**Movie S1.** Representative example of the molecular dynamics simulations of the stretching of an Au contact where one can see the atomic rearrangements during the elongation process (right panel). Only the last stages before the rupture of the atomic wire are shown for clarity. The left panel shows both the electrical conductance and (left vertical axis, $G = G_e$) and the electronic contribution to the thermal conductance (right vertical axis, $\kappa_{el} = G_{Th,e}$) during the elongation of the contact. In the lower part of this panel we show the individual transmission coefficients that give a significant contribution to the total electronic transport.

**Movie S2.** Second example of the stretching of an Au contact as obtained from our molecular dynamics simulations. See caption of movie S1 for details.

**Movie S3.** Third example of the stretching of an Au contact as obtained from our molecular dynamics simulations. See caption of movie S1 for details.

**Movie S4.** First example of the stretching of a Pt contact as obtained from our molecular dynamics simulations. See caption of movie S1 for details.

**Movie S5.** Second example of the stretching of a Pt contact as obtained from our molecular dynamics simulations. See caption of movie S1 for details.

**Movie S6.** Third example of the stretching of a Pt contact as obtained from our molecular dynamics simulations. See caption of movie S1 for details.
References and Notes


20. Materials and methods are available as supplementary materials.


