Imaging resonant dissipation from individual atomic defects in graphene

Dorri Halbertal,1,4 Moshe Ben Shalom,2,4 Aviram Uri,1 Kousik Bagani,1 Alexander Y. Meltzer,1 Ido Marcus,1 Yuri Myasoedov,1 John Birkebeck,2 Leonid S. Levitov,3 Andre K. Geim,2 Eli Zeldov1,5

Conversion of electric current into heat involves microscopic processes that operate on nanometer length scales and release minute amounts of power. Although central to our understanding of the electrical properties of materials, individual mediators of energy dissipation have so far eluded direct observation. Using scanning nanothermometry with submicron Kelvin sensitivity, we visualized and controlled phonon emission from individual atomic-scale defects in graphene. The inferred electron-phonon "cooling power spectrum" exhibits sharp peaks when the Fermi level comes into resonance with electronic quasi-bound states at such defects. Rare in the bulk but abundant at graphene's edges, switchable atomic-scale phonon emitters provide the dominant dissipation mechanism. Our work offers insights for addressing key materials challenges in modern electronics and enables control of dissipation at the nanoscale.

Understanding the microscopic mechanisms of momentum and energy dissipation is a central problem in fields ranging from condensed matter to particle physics. It is also of keen interest to researchers designing new approaches to handle, convert, and use energy. Dissipation pathways are particularly intriguing in ultrapure materials, such as graphene (1), because of tight restrictions on the phase space for electron-phonon scattering (2–4). Furthermore, in condensed matter physics, we are interested in processes concealed within materials. This lack of access, along with the fact that the power released in such processes is very small, poses a key challenge for experimentally probing dissipation at the nanoscale. We used a recently developed ultrasensitive scanning nanothermometer with submicron Kelvin sensitivity (5), achieved with a superconducting quantum interference device (SQUID) placed on an extremely sharp tip (SQUID-on-tip, or SOT), to probe these subtle effects in high-mobility graphene. Owing to its exceptional cleanliness and the two-dimensional nature of its electrons and phonons (1), graphene is an excellent platform to study electron-phonon relaxation.

Our measurements were performed on exfoliated graphene encapsulated between hexagonal boron nitride (hBN). Charge carriers were injected into a micrometer-scale "electron chamber" by applying electrical current through narrow constrictions [Fig. 1, A and B, and section 1 of (6)]. Transport measurements in such samples routinely show ballistic signatures over a wide range of temperatures and carrier densities (7–9). Our SQUID-on-tip (10) acts as an extremely sensitive thermometer (SOT) (5) with an effective diameter of 33 nm and thermal sensitivity of 510 nK/Hz1/2 at 4.2 K, and it provides a map of the local temperature variations δT(x, y) upon scanning at a height h of 10 to 40 nm above the sample surface (as specified for each measurement). The tip is mounted on a quartz tuning fork (11), which allows the tSOT to vibrate parallel to the sample surface with a controlled amplitude xac = 2.7 nm at a frequency of ~37 kHz [sections 2 and 3 of (6)]. The resulting ac signal, Tact(x, y) = xac•67TX(x, y)/ΔT, renders higher-sensitivity imaging (Fig. 1C) by avoiding the low-frequency 1/f noise of the tSOT. We control the carrier density in graphene globally by a back-gate bias VBB to the Si/SiO2 substrate and locally by applying a tip potential VT to the tSOT (Fig. 1A). Description of sample fabrication and thermal imaging is provided in (6).

Figure 1C shows the thermal signal Tact(x, y) measured while applying a fixed current Iac = 3 μA through two of the constrictions, as shown in Fig. 1B. The image reveals a complex array of fine rings along the edges of the heterostructure (5). In addition, three isolated rings are observed in the bulk of graphene, labeled A, B, and C. The bulk rings are rare and have comparable diameters, in sharp contrast to the rings at the edges, which are dense and display widely varying sizes (movies S1 and S2). We show below that the rings mark dissipation from single atomic defects positioned at their centers. Electron-phonon cooling pathways in graphene are particularly interesting for several reasons. Owing to the exceptional stiffness of the carbon bonds, scattering by optical phonons in graphene is inefficient below room temperature. Moreover, the small size of the electron's Fermi surface restricts the phase volume for scattering by acoustic phonons, blocking the intrinsic electron-lattice relaxation pathway (2–4). However, theory predicts that disorder can substantially ease the electron-phonon scattering (4). Our key finding is that hot electrons, generated by the applied current, dissipate their energy through a very specific disorder-induced mechanism: resonant inelastic scattering by local electronic resonances caused by individual defects. Each such localized state (LS) mediates cooling through resonant electron scattering, creating an atomic-scale thermal link between the electronic bath, at an effective hot-electron temperature Tep, and the phonon bath, at a base temperature T0 [section 4 of (6)]. To characterize this thermal link, we define the electron-phonon heat conductivity of a defect, κep(ep), which describes the power transferred between the baths, P0(ep) = κep(ep)ΔT (where ΔT = Tep - T0 and ε is the energy relative to the Dirac point). The resulting "cooling power spectrum" P0(ep) (CPS)—the fundamental quantity accessed in our experiment through local temperature increase δT(ep) < P0(ep)—is found to peak sharply when the Fermi level EF is aligned with the quasi-bound LS resonant energy Ehp.

Our analysis [section 4 of (6)] of the observed resonances suggests that they originate from quasi-bound states arising at a carbon vacancy or adatom bonded to a single C atom when its sp2 orbital transforms to an sp3 state (12–15). Such defects are known to produce sharp electronic resonances at energies near the Dirac point (16, 17). Although these defects have been extensively investigated by means of ab initio calculations and scanning tunneling microscopy (STM) (12–19), their prominent role in dissipation has not been anticipated by previous work. The defect-induced CPS originates from the part of the local density of electronic states that mediates electron-phonon coupling [EP-LDOS, D0(ep)]—a hitherto inaccessible quantity—convoluted with the electron and phonon Fermi and Bose energy distribution functions, respectively [section 4 of (6)]. Our measurements and analysis indicate that the spectral width of D0(ep) is much greater than the thermal broadening, in which case the CPS can be approximated as P0(ep) ~ D0(ep) [section 4 of (6)]. This quantity can be probed experimentally, as illustrated schematically in Fig. 2, A to C. By parking the tSOT above the defect and varying VBB, we can induce local band bending that shifts D0(ep) with respect to EF [Fig. 3A and section 6 of (6)]. The resulting variation in the measured temperature, δT(VBB), provides a spectroscopic measurement of P0(ep) ~ D0(ep) (Fig. 2B). Additional information can be obtained by tuning EP by the back-gate VBB, yielding resonant peaks in P0(ep) aligned as diagonal lines in the δT(VBB, VBB) map (Fig. 2C). Importantly, in this configuration, phonon emission can be turned on and off by applying a potential on the tSOT tip, demonstrating control of nonequilibrium dynamics and probing them at the nanoscale.

The experimental δT(VBB, VBB) map of defect C (Fig. 2D) displays, in agreement with the discussion above, a sharp resonance (Fig. 2E) along a single diagonal line, which passes close

*Corresponding author. Email: dorri.halbertal@weizmann.ac.il (D.H.); moshebs@tauex.tau.ac.il (M.B.S.); eli.zeldov@weizmann.ac.il (E.Z.)
single peak in is caused by the presence of a LS with a narrow energy [section 8 of (]). The sharp thermal rings observed in Fig. 1C as heterostructure.

Fig. 1. Observing individual dissipation sources in a graphene nanothermometer (tSOT). (A) Schematic side view of the measurement setup with the hBN-graphene-hBN heterostructure and SQUID-on-tip nanothermometry (tSOT). (B) Optical image of the device patterned into a square chamber (bright; 4 µm × 4 µm). A fixed current \( I_{dc} = 3 \) µA is driven through the connecting constrictions (arrows). (C) Scanning ac nanothermometry \( T_{ac}(x,y) \) of the area outlined in (B) at \( V_{bg} = -2 \) V, \( V_{tg} = 9 \) V, and 4.2 K. The tSOT scans the sample while oscillating with amplitude \( x_{ac} = 27 \) nm at 12 Hz to the x axis. Scan area, 5.5 µm × 5 µm; pixel size, 18 nm; scan speed, 20 ms per pixel; height \( h = 20 \) nm; \( I_{dc} = 3 \) µA. The sharp rings (marked A, B, and C) uncover three isolated sources of dissipation in the bulk of graphene, in addition to a dense array of resonances along the graphene edges. (D) Zoomed-in view of defect C at \( V_{tg} = 5 \) V. Scan area, 140 nm × 150 nm; pixel size, 1.9 nm; scan speed, 20 ms per pixel; \( h = 20 \) nm; \( I_{dc} = 3 \) µA. (E) Illustration of an atomic defect in graphene that creates a localized resonant dissipative state at the center of the ring (D), which in turn mediates inelastic scattering of an impinging electron (red) into a phonon (orange) and a lower-energy electron (blue). The defect, forming an sp³ orbital (green), can arise from a carbon vacancy, adatom, or admolecule.

to the origin in the \( V_{tg}-V_{bg} \) plane. This resonance is caused by the presence of a LS with a narrow single peak in \( D_{ep}(e) \) (Fig. 2F) close to the Dirac energy [section 2 of (6)]. Such LSs give rise to the sharp thermal rings observed in Fig. 1C as follows. For the LS to cause inelastic electron scattering, its energy level \( E_{ls} \) has to be aligned with the energy of the impinging electrons, \( E_{p} \) (the global Fermi energy). For a given tip potential \( V_{tg} \), this resonant condition occurs when

\[
E_{p} = E_{ls} \Rightarrow V_{tg} = V_{bg} + 2V \quad \text{(1)}
\]

experimental \( \delta T(V_{tg}, V_{bg}) \), measured by the tSOT at \( h = 10 \) nm above the center of defect C in the presence of \( I_{dc} = 3 \) µA, revealing a single resonance dissipation line (data were not taken for the white portion of the plane in this measurement). The signal was obtained through integration of \( T_{ac}(x,y) \) over \( V_{tg} \) [section 2 of (6)]. (E) A zoomed-in line cut of \( \delta T(V_{tg}) \) along the dashed line in (D) at \( V_{tg} = V_{bg} + 2V = 0.2 \) V. (F) The cooling power spectrum \( P_{ep}(\epsilon) \), derived from the measurement of the resonant dissipation ring [section 9 of (6)], showing a single sharp peak near the Dirac point at \( \epsilon_{ls} = -22 \) meV.
monovalent adatoms are known to form LSs at energies comparable to our measured values (14, 16) [section 4 of (6)] and thus are strong candidates for the observed bulk defects. (vii) The bulk defects are extremely rare (we found only seven such defects in total in 13 samples with a total area of 3500 μm²), corresponding to an estimated average areal density of 2 × 10⁶ cm⁻² or volume concentration of 5 × 10⁻⁵ parts per million if originating from the parent graphite. Their spectral properties appear to be the same within our experimental resolution (section 8 of (6)), pointing to a common chemical or structural origin.

These conclusions are reinforced by examining the LSs along the edges of graphene, which display spectroscopic features very similar to those of the bulk defects, but with some notable differences. Shown in Fig. 4, D and E, are tSOT line scans along the bottom edge of the sample that cross through numerous LSs, taken while increasing \( V_{bg} \) (movies S6 and S7). Each LS is visible as a bell-shaped trace, similar to the ones in Fig. 4, A to C, indicating the same microscopic origin of different LSs. In contrast to LSs in the bulk, the edge LSs are extremely dense, with some adjacent states only about 1 nm apart (fig. S15E). This puts an additional bound on their spatial extent [section 10 of (6)]. We ascribe their origin to the carbon dangling bonds near the edge with high affinity to adatoms and molecules, giving rise to resonance states formed by the resulting sp³ vacancies (12–15).

Notably, unlike the LSs in the bulk, the edge LSs display large variations in \( E_{LS} \) values, manifested in Fig. 4, D and E, by the vertical spread of the bell-shaped traces over the entire \( V_{bg} \) range of 20 V. This translates into a 260–meV spread in \( E_{LS} \) limited by our bias range. We are able to resolve states that are less than 2 nm apart but differ in their \( E_{LS} \) by as much as 160 meV [section 10 of (6)]. Such large energy-level variation may arise from the atomic defects at graphene edges having more diverse chemical origins than the native bulk defects. An alternative explanation is Coulomb interaction between the charged defects. Charging a LS by one electron would shift the energy of a neighboring LS at a distance of 2 nm by ~240 meV [section 7 of (6)], consistent with our observations.

The above results suggest that hot electrons lose most of their energy to phonons at the edges of graphene. To verify this conjecture, we measured the bare \( \delta T(x, y) \) in the absence of tSOT electrostatic influences [\( V_{bg} \) = \( V_{ac} \)] at a flat-band condition; section 5 of (6)]. Measurement of sample 2 (Fig. 4, F and G) revealed a higher temperature along the sample edges relative to the temperature in the sample bulk. Together with numerical simulations [section 5 of (6)], this finding implies that the LSs along the graphene edges are the dominant source of dissipation at all doping levels reachable in our experiment. Therefore, the excess phonons, corresponding to the overall temperature rise, are not generated locally in the graphene bulk. Instead, the phonons are predominantly emitted through inelastic electron scattering by those LSs at graphene edges that are at resonance at a given \( V_{bg} \) value [section 5 of (6)].
of (6)). The observed atomic-scale resonant LSs thus emerge as the leading mechanism of dissipation in clean graphene, each acting as a pointlike source emitting phonons that then propagate ballistically throughout the entire sample.

The observation of sharply localized resonant states and their role in dissipation should have considerable implications for understanding the thermal (22), magnetic (12, 16, 23), chemical (24), and transport (25-28) properties of graphene. These states are distinct from the extended edge states anticipated for crystalline graphene edges (23). Further, resonant dissipation is completely different from the conventional nonresonant picture of electron-phonon coupling (2-4), posing interesting questions for future experimental and theoretical work. This dissipation mechanism may affect the edge transport characteristics (29-31) and explain previous observations of the mean free path being limited by the device size in state-of-the-art encapsulated graphene (7-9). The resonance states, localized at the edge and in the bulk, thus emerge as a key factor governing the dissipation and possibly limiting the carrier mobility in pure graphene.

REFERENCES AND NOTES
6. Materials and methods are available as supplementary materials.

ACKNOWLEDGMENTS
We thank M. E. Huber for the SOT readout setup and M. Solody for assistance with data analysis. This work was supported by the Minerva Foundation with funding from the German Federal Ministry of Education and Research; NSF/DMR-BSF Binational Science Foundation (BSF) grant no. 2015653 and NSF grant no. 1609519; the Weizmann–UK Making Connections Programme; and a Rosa and Emilio Segré Research Award. A.K.G. and M.B.S. acknowledge support from the Lloyd’s Register Foundation and the European Research Council ARTIMATTER project (ERC-2012-ADG). L.S.L. and E.Z. acknowledge the support of the MISTI (MIT International Science and Technology Initiatives) MIT–Israel Seed Fund. Data presented in this paper can be obtained from the corresponding authors upon reasonable request. A patent describing the dissipation imaging technique has been submitted (WO 2016/142945).

SUPPLEMENTARY MATERIALS
www.sciencemag.org/content/358/6368/1303/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S15
Movies S1 to S7
9 March 2017; resubmitted 25 July 2017
Accepted 3 November 2017
10.1126/science.aan0877
Imaging resonant dissipation from individual atomic defects in graphene

Dorri Halbertal, Moshe Ben Shalom, Aviram Uri, Kousik Bagani, Alexander Y. Meltzer, Ido Marcus, Yuri Myasoedov, John Birkbeck, Leonid S. Levitov, Andre K. Geim and Eli Zeldov

Science 358 (6368), 1303-1306.
DOI: 10.1126/science.aan0877

Watching electrons lose steam in graphene

Although graphene can be fabricated to be extremely clean, it still has a nonzero electrical resistance. Resistance is associated with turning electrons’ energy into heat, but how exactly does this happen? Halbertal et al. used a tiny scanning temperature probe based on a superconducting quantum interference device to investigate this problem. As the current flowed through a square-shaped sample of graphene, electrons lost energy predominantly in the vicinity of atomic-scale defects, which were few and far between in the bulk but much more common on the edges of the sample. Science, this issue p. 1303