Imaging gate-tunable Tomonaga–Luttinger liquids in 1H-MoSe₂ mirror twin boundaries

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One-dimensional electron systems exhibit fundamentally different properties than higher-dimensional systems. For example, electron–electron interactions in one-dimensional electron systems have been predicted to induce Tomonaga–Luttinger liquid behaviour. Naturally occurring grain boundaries in single-layer transition metal dichalcogenides exhibit one-dimensional conducting channels that have been proposed to host Tomonaga–Luttinger liquids, but charge density wave physics has also been suggested to explain their behaviour. Clear identification of the electronic ground state of this system has been hampered by an inability to electrostatically gate such boundaries and tune their charge carrier concentration. Here we present a scanning tunnelling microscopy and spectroscopy study of gate-tunable mirror twin boundaries in single-layer 1H-MoSe₂ devices. Gating enables scanning tunnelling microscopy and spectroscopy for different mirror twin boundary electron densities, thus allowing precise characterization of electron–electron interaction effects. Visualization of the resulting mirror twin boundary electronic structure allows unambiguous identification of collective density wave excitations having two velocities, in quantitative agreement with the spin–charge separation predicted by finite-length Tomonaga–Luttinger liquid theory.
Fig. 1 | STM characterization of a SL MoSe₂/graphene/hBN/SiO₂/Si device at temperature $T = 5\, K$. a, Large-scale STM topography of a SL MoSe₂/graphene/hBN/SiO₂/Si device (set-point parameters: $V_{st} = -2\, V, I_{st} = 10\, pA$). Here, SLG refers to single-layer graphene, and BLG refers to bilayer graphene. b, Schematic of the experimental device set-up. $V_b$ is the bias voltage applied between the sample and STJ tip. c, A close-up STM derivative image of the MTBs in the area indicated by a red square in a (the derivative plot enhances the MTB image contrast). d, The $dI/dV$ spectrum acquired on the MTB in the yellow rectangle in c at the position marked by a white cross ($V_{st} = 0.3\, V, I_{st} = 100\, pA, V_{mod} = 2\, mV$). $V_{mod}$ is the a.c. modulation voltage in $dI/dV$ spectroscopy measurements.). The energy gap is bracketed by the HOS ($v_0$) and the LUS ($c_0$). Other 1D quantum well states are labelled with black arrows while a charging peak is labelled with a blue arrow. e, Constant-height $dI/dV$ maps of the MTB in c taken at the LUS (top) and the HOS (bottom; $I_{st} = 100\, pA, V_{mod} = 10\, mV$). The HOS map exhibits 13 nodes ($n$) while the LUS map exhibits 14 nodes. f, LDOS line profiles of the MTB at the energies of both the LUS and the HOS, acquired along the orange and green lines in e.

these parameters within a single 1DES provides unusually strong support for identification of the ground state as a TLL.

SL 1H-MoSe₂ was grown via molecular beam epitaxy (MBE) at the surface of epitaxial graphene supported by hexagonal boron nitride (hBN)/SiO₂/Si (Fig. 1a and Supplementary Fig. 1). This heterostructure arrangement allows systematic control of electron filling at the MoSe₂ surface by way of a doped Si bottom gate (Fig. 1b). The device was characterized by STM topographic imaging (Fig. 1a), which shows large SL MoSe₂ islands as well as a moiré superlattice formed by alignment of the graphene and hBN37. Isolated MTBs and MTB networks are seen as double-straight-line features that arise from the particle-in-a-box-like form of the MTB)38. For E₃, the spatial distribution of MTB electronic states at different energies was characterized by performing constant-height $dI/dV$ mappings of the MTB in Fig. 1c. Figure 1e shows the electronic LDOS of both the highest occupied state (HOS) at $V \approx -93\, meV$ ($v_0$) and the lowest unoccupied state (LUS) at $V \approx 33\, meV$ ($c_0$), revealing periodic charge modulations along the MTB, as well as a two-lobe spatial feature perpendicular to the MTB as seen previously14,27,29. The HOS is observed to have 13 nodes, whereas the LUS has 14, as seen from direct comparison of the LDOS line profiles (Fig. 1f) acquired along the orange and green lines in Fig. 1e (nodes here are defined as local minima in the interior of the MTB). A $dI/dV$ map of the $v_1$ peak exhibits 12 nodes, while a map of the $c_0$ peak exhibits 15 nodes (Supplementary Fig. 2a-c), suggesting a particle-in-a-box nodal progression (that is, the number of nodes increases by 1 with each higher energy peak). The peaks $v_i$ and $c_i$ ($i \geq 0$) can thus be interpreted as representing confined quantum levels. Similar nodal structure was observed in all the MTBs studied here (Supplementary Fig. 3 for additional representative data).

To gain insight into the nature of the energy gap at $E_c$, we performed STS measurement of the MTB shown in Fig. 1c for different gate voltages in the range $−60\, V \leq V_g \leq 60\, V$, thus enabling the MTB to be tuned from the hole-doped regime ($V_g = −60\, V$) to the electron-doped regime ($V_g = 60\, V$). Figure 2a shows the gate-dependent $dI/dV$ curves acquired at the position marked in Fig. 1c, while Fig. 2b shows a $dI/dV$ intensity plot for a finer set of gate voltages at the same position. A key observation here is that the gap size changes with gate voltage. The $dI/dV$ spectrum at $V_g = −60\, V$ (Fig. 2a, orange) shows a large gap at $E_F$ of $\Delta_{\text{large}} \approx 121\, meV$ that is similar to the gap $\Delta_n$ observed at $V_g = 0\, V$ (Fig. 2a, red). The $dI/dV$ spectrum at $V_g = 60\, V$ (Fig. 2a, blue), however, shows a substantially smaller gap of $\Delta_{\text{small}} \approx 70\, meV$. The peaks at the gap edge of $\Delta_{\text{small}}$ are also observed to have reduced intensities compared to those bracketing $\Delta_{\text{large}}$. As $V_g$ increases from $−60\, V$, the overall band structure shifts rigidly towards lower energies, consistent with the electronic structure of the bottom gate. For $V_g \approx 10\, V$, a pronounced peak (blue arrow) appears at negative bias voltage and shifts to higher energies with increasing $V_g$, opposite to the overall lowering trend seen for the rest of the band structure. Such behaviour allows us to identify this peak as a tip-induced charging feature of the LUS (Supplementary Fig. 4 shows a representative real-space image of the charging-ring feature associated with this peak in another MTB)29. For $V_g \approx 20\, V$, both the charging peak and the LUS begin to cross $E_F$, resulting in a transition from the large energy gap to the smaller gap. For $V_g > 20\, V$ both the charging peak and the overall band structure continue to shift, as expected for increased electron
filling of the MTB. We note that a second charging peak can be seen (starting at $V_g = 15$ V and $V = -0.3$ V in Fig. 2b) that is possibly due to another MTB nearby. The influence of multiple charging peaks was mitigated by picking MTBs well isolated from others. Similar gate-dependent behaviour was also observed for 19 other MTBs that were similarly measured using a variety of different STM tips (Supplementary Fig. 5 for representative data).

Constant-height $dI/dV$ maps of the HOS and LUS of the MTB in Fig. 1c at $V_g = \pm 60$ V further reveal gate-dependent real-space electronic structure (Fig. 3). The HOS and LUS for the large gap configuration at $V_g = -60$ V ($\Delta_{\text{large}}$) exhibit 13 nodes and 14 nodes, respectively (Fig. 3b), consistent with the real-space electronic structure observed for the undoped ($V_g = 0$ V) case (Fig. 1e,f). The HOS and LUS for the small gap configuration at $V_g = 60$ V ($\Delta_{\text{small}}$), on the other hand, both exhibit 14 nodes (Fig. 3c). The LDOS maps of higher energy peaks are summarized in Supplementary Fig. 2d–i. (Similar gate-dependent nodal structure was observed for nine MTBs). This behaviour is in contrast to a Peierls instability in which out-of-phase spatial patterns are expected at the HOS and LUS\(^{19}\).

In order to characterize the energy- and momentum-resolved MTB electronic structure, we measured $dI/dV$ spectra along an MTB for the large gap case ($V_g = 0$ V; Fig. 4a) and performed Fourier transform (FT) analysis of the resulting density plot (here we chose a longer MTB than that in Figs. 1–3 to achieve better momentum resolution. Figure 4b shows the energy dependence of the STS intensity plot as a function of the MTB axial coordinate ($x$ axis) and the sample bias ($y$ axis). Fast real-space modulations (wavelength $\lambda \approx 1$ nm) create a complex MTB nodal structure that coexists with a longer wavelength modulation that induces a dome-shaped charge density profile (similar real-space modulations in electronic structure have been previously reported both for MTBs\(^{19,21}\) and carbon nanotubes\(^{18,19}\)).

Figure 4c shows the corresponding FT of the STS intensity plot, revealing both the energy dependence and momentum dependence of the electronic structure. Two linear dispersion branches with different slopes are seen to cross $E_F$ at $q/2\pi \approx 1$ nm\(^{-1}\) (which we identify as $q = 2k_F$ where $k_F$ is the Fermi wavevector) and are labelled by blue and red markers in Fig. 4c. These branches correspond to ‘fast’ real-space nodal structure and are dubbed the ‘fast branches’ hereafter. The velocity of the blue branch is $3.5 \times 10^5$ m s\(^{-1}\) (extracted from twice the slope of the dispersion since LDOS$\propto |\psi(x)|^2$, where $\psi(x)$ is the electron wavefunction) and is consistent with the Fermi velocity, $v_F$, of the MTB metallic band structure\(^{22,27}\). The velocity of the red branch, on the other hand, is $6.5 \times 10^4$ m s\(^{-1}\) and is higher than $v_F$. An additional linear branch near the $\Gamma$ point (labelled by orange markers in Fig. 4c) can be resolved that corresponds to the long wavelength modulation mentioned above (and is dubbed the ‘slow branch’ hereafter). The existence of multiple linear dispersion branches causes blurring of the real-space nodal structure at peak energies far from $E_F$ (Supplementary Fig. 3). A static mode (that is, constant wavevector with energy) at $q = 2k_F$ can also be observed, consistent with previous results\(^{24}\). Figure 4d provides a second-derivative plot of the data presented in Fig. 4c, which allows the various dispersive features to be more clearly seen. This type of behaviour was observed in all seven of the MTBs that were characterized in this way (Supplementary Figs. 6 and 7 for additional representative data). All the measured MTBs were well isolated from other MTBs and defects to avoid spatial inhomogeneities in the local electrostatic environment that might obscure the intrinsic MTB behaviour. We also calibrated our STM tip on a material (Au) with a work function close to that of MoSe\(_2\), to minimize tip-induced band bending effects (tip-induced band bending can lead to ‘curving’
of the chemical potential with tip position due to local tip gating (Supplementary Figs. 6a and 8)).

Our experimental results are in excellent agreement with the theoretical predictions for a confined TLL. Our observation of gate-induced modulation of the energy gap size reveals that el-el Coulomb repulsion is a dominant factor in MTB electronic structure, a major characteristic of TLLs (the gate dependence of the gap size cannot be explained by screening effects or electron–photon coupling; Supplementary Note 1 and Supplementary Fig. 9).

Were el-el interactions absent, the Fermi level energy gap would be gate independent and would equal the 1D single-particle level spacing. Since the presence of el-el Coulomb repulsion explains the large and small gap variation seen for different electron fillings, we expect both $\Delta_{\text{large}}$ and $\Delta_{\text{small}}$ to scale as $L^{-1}$. This is confirmed by measurements of the gap size statistics for MTBs of different lengths ranging from 6 nm to 30 nm (Fig. 5a; this provides further evidence against a Peierls instability-induced gap, which should be length independent). The ratio of $E_c/E_{\text{gap}}$ is thus experimentally observed to be universal for MTBs of different lengths. This ratio is related to TLL behaviour through the TLL parameter $K_c$ as:

$$K_c = \left(1 + \frac{2E_c}{E_{\text{gap}}}ight)^{-\frac{1}{2}}$$

(Supplementary Note 2.1). The energy gaps measured in our spectroscopy of MTBs of different lengths yield a universal value of $K_c = 0.54 \pm 0.03$ (Fig. 5b).

Another piece of evidence supporting the TLL interpretation of MTBs is the observation of spin–charge separation. The existence of
two linear fast branches in the FT-STS suggests that a single metallic band picture is insufficient, whereas TLL-based spin–charge separation can explain this behaviour quantitatively. To see this we simulated the expected STM tunnelling LDOS by calculating the electron spectral function for a finite 1D TLL and with all other material-dependent parameters: \( V_m = -0.6 \text{ V}, I_m = 100 \text{ pA} \). The excellent agreement between the \( K_C \) values obtained using these two different experimental techniques provides strong evidence for TLL behaviour in SL MoSe\(_2\) MTBs.

Fig. 5 | Gap size statistics and MTB TLL parameter obtained in two different ways. a, Measured large (green) and small (orange) energy gaps for MTBs of different lengths. Both types of gap scale in size as \( 1/L \) where \( L \) is the MTB length. The dashed lines represent linear fits to the data. b, The TLL parameter obtained from the measured charging energy, \( E_C \) and single-particle level spacing, \( E_s \) for MTBs having different lengths (\( K_C = 0.54 \pm 0.03 \)). c, The TLL parameter obtained from the ratio of the measured spin and charge velocities for MTBs having different lengths (\( K_C = 0.53 \pm 0.05 \)).
parameters constrained by experimental values (Supplementary Note 2.2). Both the fast and slow modulations can be seen in the resulting theoretical energy-dependent LDOS (Fig. 4c), which closely resembles the experimental features seen in Fig. 4b. Clear spin–charge separation can be observed in the FT of the simulated LDOS, as seen in Fig. 4f, where two linear branches show LDOS modulations induced by spin (blue arrow) and charge (red arrow) density excitations that have distinct velocities (Supplementary Note 2.1). This technique yields a value of $K_c = 0.53 \pm 0.05$ (Fig. 5c), in excellent agreement with the value of $K_c = 0.54 \pm 0.03$ determined from the energy gap ratio $E_c/E_0$ (Fig. 5b). The TLL picture is thus confirmed through self-consistent measurements of both energy-level alignment (Fig. 2) and spatial LDOS modulations (Fig. 4). We also note that the static modulation, previously interpreted as a Peierls instability, can also be explained by a pure TLL model (Fig. 4f) without invoking the Peierls physics.

In conclusion, our observation of gate-dependent energy gaps via STS allows precise measurement of the el-el Coulomb interaction energy in 1D MTBs. The Luttinger parameter values determined separately from the el-el interaction energy and spin and charge velocities are in excellent agreement with each other. Our device thus provides an ideal platform to study the response of 1D TLL systems to magnetic scatterers, external magnetic field, and tuned dielectric environments. Since the width of MTBs in transition metal dichalcogenides is only ~1 nm, such studies are a critical step towards understanding the behaviour of conducting wires at the ultimate level of miniaturization.

Online content
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References
1. Kim, B. J. et al. Distinct spinon and holon dispersions in photoemission spectral functions from one-dimensional SrCuO2. Nat. Phys. 2, 397–401 (2006).
2. Greiner, G. The dynamics of charge-density waves. Rev. Mod. Phys. 60, 1129–1181 (1988).
3. Bockrath, M. et al. Single-electron transport in ropes of carbon nanotubes. Nature 397, 598–601 (1999).
4. Yao, Z., Postma, H. W. C., Balents, L. & Dekker, C. Carbon nanotube intramolecular junctions. Nature 402, 273–276 (1999).
5. Ishii, H. et al. Direct observation of Tomonaga–Luttinger liquid state in carbon nanotubes at low temperatures. Nature 426, 540–544 (2003).
6. Yang, W. et al. Observation of a Luttinger-liquid plasmon in metallic single-walled carbon nanotubes. Nat. Photon. 9, 515–519 (2015).
7. Chang, A. M. Chiral Luttinger liquids at the fractional quantum Hall edge. Rev. Mod. Phys. 75, 1449–1505 (2003).
8. Stuhlér, R. et al. Tomonaga–Luttinger liquid in the edge channels of a quantum spin Hall insulator. Nat. Phys. 16, 47–51 (2019).
9. Auslaender, O. M. et al. Tunneling spectroscopy of the elementary excitations in a one-dimensional wire. Science 295, 825–828 (2002).
10. Auslaender, O. M. et al. Spin-charge separation and localization in one dimension. Science 308, 88–92 (2005).
11. Ilijin, A. et al. Probing spin-charge separation in a Tomonaga-Luttinger liquid. Science 325, 597–601 (2009).
12. Auslaender, O. M. et al. Experimental evidence for resonant tunneling in a Luttinger liquid. Phys. Rev. Lett. 84, 1764–1767 (2000).
13. Batzill, M. Mirror twin grain boundaries in molybdenum dichalcogenides. J. Phys. Condens. Matter 30, 493001 (2018).
14. Barja, S. et al. Charge density wave order in 1D mirror twin boundaries of MoSe2. Nat. Phys. 12, 751–756 (2016).
15. Ma, Y. et al. Metalic twin grain boundaries embedded in MoSe2, monolayers grown by molecular beam epitaxy. ACS Nano 11, 5130–5139 (2017).
16. Ma, Y. et al. Angle resolved photoemission spectroscopy reveals spin charge separation in metallic MoSe2, grain boundary. Nat. Commun. 8, 14231 (2017).
17. Jolie, W. et al. Tomonaga-Luttinger liquid in a box: electrons confined within MoS2 mirror-twin boundaries. Phys. Rev. X 9, 011055 (2019).
18. Wang, L. et al. Direct observation of one-dimensional Peierls-type charge density wave in boundaries of monolayer MoTe2. ACS Nano 14, 8299–8306 (2020).
19. Xia, Y. et al. Charge density modulation and the Luttinger liquid state in MoSe2 twin mirror boundaries. ACS Nano 14, 10716–10722 (2020).
20. Yang, X. et al. Manipulating Hubbard-type Coulomb blockade effect of metallic wires embedded in an insulator. Preprint at https://arxiv.org/abs/2104.08577 (2021).
21. Fabrizio, M. & Gogolin, A. O. Interacting one-dimensional electron gas with open boundaries. Phys. Rev. B 51, 17827–17841 (1995).
22. Eggert, S., Johannesson, H. & Mattsson, A. Boundary effects on spectral properties of interacting electrons in one dimension. Phys. Rev. Lett. 76, 1505–1508 (1996).
23. Mattsson, A. E., Eggert, S. & Johannesson, H. Properties of a Luttinger liquid with boundaries at finite temperature and size. Phys. Rev. B 56, 15615–15628 (1997).
24. Kane, C., Balents, L. & Fisher, M. P. A. Coulomb interactions and mesoscopic effects in carbon nanotubes. Phys. Rev. Lett. 79, 5086–5089 (1997).
25. Anfuso, F. & Eggert, S. Luttinger liquid in a finite one-dimensional wire with box-like boundary conditions. Phys. Rev. B 68, 241301 (2003).
26. Kakashvili, P., Johannesson, H. & Eggert, S. Local spectral weight of a Luttinger liquid: effects from edges and impurities. Phys. Rev. B 74, 085114 (2006).
27. Yang, W. et al. Epitaxial growth of single-domain graphene on hexagonal boron nitride. Nat. Mater. 12, 792–797 (2013).
28. Brar, G. S. et al. Gate-controlled ionization and screening of cobalt adatoms on a graphene surface. Nat. Phys. 7, 43–47 (2011).
29. Mallet, P., Sacks, W., Roditchev, D., Défourneau, D. & Klein, J. Spatial and energy variation of the local density of states in the charge density wave phase of 2H-NbSe2. J. Vac. Sci. Technol. B 14, 1070–1074 (1996).
30. Miranda, E. Introduction to bosonization. Braz. J. Phys. 33, 3–35 (2003).
31. Lee, D. H. & Toner, J. Kondo effect in a Luttinger liquid. Phys. Rev. Lett. 69, 3378–3381 (1992).
32. Furusaki, A. & Nagaosa, N. Kondo effect in a Tomonaga-Luttinger liquid. Phys. Rev. Lett. 72, 892–895 (1994).
33. Hikihara, T., Furusaki, A. & Matveev, K. A. Renormalization of impurity scattering in one-dimensional interacting electron systems in magnetic field. Phys. Rev. B 72, 035301 (2005).
Methods

Sample fabrication. The preparation of the epitaxial graphene/hBN heterostructure supported on a SiO2/Si substrate is described in ref. 37. Single-layer 1H-MoSe₂ films with MTBs were grown directly on epitaxial graphene/hBN heterostructures using MBE. Mo and Se were evaporated from an electron-beam evaporator and a home-built Knudsen cell, respectively. The flux ratio between Mo and Se was ~1:100 and the sample was kept at 450 °C during the growth. After growth the sample was heated to ~600 °C and annealed under Se for 30 min. The sample was capped with ~20 nm of amorphous Se before being taken out of the ultra-high-vacuum growth chamber. Electrical contacts were made by depositing Cr and Au (3 nm and 30 nm) through a shadow mask.

STM/STS measurements. STM/STS measurements were performed in a low-temperature ultra-high-vacuum STM system (CreaTec) at T = 5 K. Prior to measurement, the samples were annealed in ultra-high vacuum at ~200 °C for 1 hour to remove the Se capping layers and then immediately transferred in situ to the STM stage at T = 5 K. Electrochemically etched tungsten tips were calibrated on a Au(111) surface before other measurements. The dI/dV spectra were collected using standard lock-in techniques (frequency f = 401 Hz). The dI/dV mapping was performed in constant-height mode (that is, with the feedback loop open).

Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request. Source data are provided with this paper.

Code availability

The codes used in this study are available from the corresponding authors upon reasonable request.

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Author contributions

T.Z., W.R., F.W. and M.F.C. initiated and conceived this project. W.R., T.Z. and C.Z. carried out STM/STS measurements under the supervision of M.F.C.; Y.-Q.W. and W.R. performed theoretical analysis and numerical calculation under the supervision of J.E.M.; T.Z. and T.W. performed MBE growth under the supervision of Z.Q.Q.; H.-Z.T. and F.L. performed device fabrication under the supervision of M.F.C. and A.Z.; S.W. prepared epitaxial graphene under the supervision of G.Z.; and K.W. and T.T. synthesized hBN crystals. T.Z., W.R., J.B.N., A.W.-B., F.W. and M.F.C. analysed the experimental data. T.Z., W.R., Y.-Q.W. and M.F.C. wrote the manuscript with help from all the authors. All authors contributed to the scientific discussion.

Competing interests

The authors declare no competing interests.

Additional information

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