there is 'a particle in a box', except that the 'potentials of the box' are provided by the superconductors. It follows that discrete Andreev bound states emerge at the junction and their spectrum is a function of the phase difference  $\phi$  across the junction (Fig. 1b). It turns out that the bound states at E=0 are Majoranas. Since  $I \sim \mathrm{d}E/\mathrm{d}\phi$ , the presence of Majoranas gives rise to a  $4\pi$  periodic current–phase relation (green lines in Fig. 1c). Under a d.c. bias voltage  $V_{\mathrm{dc}}$  across the junction, while charge-2e Cooper pairs tunnel at a frequency of  $2eV_{\mathrm{dc}}/h$ , Majoranamediated charge-e quasiparticles tunnel at half the frequency,  $eV_{\mathrm{dc}}/h$  (ref.  $^7$ ).

Experimentally observing this  $4\pi$ periodic fractional Josephson effect is complicated by the existence of multiple channels along the junction and by scattering from thermally excited bulk quasiparticles<sup>7</sup>. Both relaxation processes might gap out the Majoranas (red dashed lines in Fig. 1b), lift the ground-state degeneracy, and thus restore the  $2\pi$  periodic supercurrent (red dashed lines in Fig. 1c). The fast high-frequency experiment performed by Li and colleagues has the advantage of avoiding these relaxation processes. When a Josephson junction is irradiated with microwaves the d.c. currentvoltage characteristic exhibits a Shapiro step8 when the frequency of tunnelling current is an integer multiple of the microwave frequency (Fig. 1d). All integer Shapiro steps should be present for the usual Josephson effect, whereas only the even steps should be visible for a  $4\pi$  periodic fractional Josephson effect9. Now, Li and colleagues clearly find that the  $N = \pm 1$  steps are missing in their experiments.

To achieve this result, the researchers, by doping Bi with Sb, first fine-tuned their

material to the transition point between topological and trivial band insulator. This produces an accidental bulk Dirac point neither protected by any symmetry nor connected to any surface Fermi arc. They used angle-resolved photoemission spectroscopy and magnetotransport to quantify the contributions to transport from unwanted surface states and the bulk Dirac cone, respectively. Next, they fabricated Josephson junctions of varying width and Nb-electrode separation on the surfaces of such accidental Dirac semimetals. Each junction shows a supercurrent as a clear manifestation of proximity-induced superconductivity, and moreover the  $N = \pm 1$ Shapiro steps are missing for the shorter junctions. The researchers estimate that the  $4\pi$  periodic contribution characteristic of Majoranas accounts for up to 20% of the total critical current. In addition, they show that a small perpendicular orbital magnetic field decreases the total critical current, whereas a small in-plane Zeeman magnetic field suppresses only the  $4\pi$ periodic component.

The disappearance of odd Shapiro steps has been observed before in a Josephson effect mediated by helical edge states10, but all experiments on the surfaces of topological insulators<sup>11,12</sup> or Dirac semimetals<sup>2,13</sup> only find the  $N = \pm 1$ steps missing. This might be due to competing capacitive effects or relaxation processes. While the fractional Josephson effect in a topological Dirac semimetal Cd<sub>3</sub>As<sub>2</sub> was attributed to surface-arc superconductivity13, Li and co-authors consider the bulk Dirac cone responsible for the same effect in their accidental Dirac semimetal. Notably, 3D topological Josephson junctions can exist14, and this

fact might support the explanation by Li and co-authors. Going forward, it will be of paramount importance to solve these puzzles, to examine Josephson effects in other topological materials such as  $(Bi_{1-x}In_x)_2Se_3$  (ref. <sup>15</sup>) and 1T' WTe<sub>2</sub> (ref. <sup>16</sup>), and to explore the interaction-driven  $8\pi$  periodic Josephson effect that has been predicted as a signature of 'fractional Majoranas'<sup>7</sup>. The missing Shapiro steps identified by Li and colleagues and other teams represent an important step in realizing topological superconductivity and fractional Josephson effects. Their results are truly desired and inspiring.

## Fan Zhang<sup>1\*</sup> and Wei Pan<sup>2\*</sup>

<sup>1</sup>Department of Physics, University of Texas at Dallas, Richardson, TX, USA. <sup>2</sup>Sandia National Laboratories, Albuquerque, NM, and, Livermore, CA, USA.

\*e-mail: zhang@utdallas.edu; wpan@sandia.gov

Published online: 17 September 2018 https://doi.org/10.1038/s41563-018-0179-1

#### References

- 1. Josephson, B. D. Phys. Lett. 1, 251-253 (1962).
- Li, C. et al. Nat. Mater. https://doi.org/10.1038/s41563-018-0158-6 (2018).
- 3. Kitaev, A. Y. Phys. Usp. 44, 131-136 (2001).
- 4. Fu, L. & Kane, C. L. Phys. Rev. Lett. 100, 096407 (2008).
- Sau, J. D., Lutchyn, R. M., Tewari, S. & Das Sarma, S. Phys. Rev. Lett. 104, 040502 (2010).
- Alicea, J., Oreg, Y., Refael, G., von Oppen, F. & Fisher, M. P. A. Nat. Phys. 7, 412–417 (2011).
- 7. Zhang, F. & Kane, C. L. Phys. Rev. Lett. 113, 036401 (2014).
- 8. Shapiro, S. Phys. Rev. Lett. 11, 80-82 (1963)
- 9. Jiang, L. et al. Phys. Rev. Lett. 107, 236401 (2011).
- 10. Bocquillon, E. et al. Nat. Nanotech. 12, 137-143 (2017).
- 11. Rokhinson, L. P., Liu, X. & Furdyna, J. K. *Nat. Phys.* **8**, 795–799 (2012).
- 12. Wiedenmann, J. et al. Nat. Commun. 7, 10303 (2016).
- 13. Yu, W. et al. Phys. Rev. Lett. 120, 177704 (2018).
- 14. Zhang, F. & Kane, C. L. Phys. Rev. B 90, 020501(R) (2014).
- 15. Wu, L. et al. Nat. Phys. 9, 410-414 (2013).
- 16. Wu, S. et al. Science 359, 76-79 (2018).

## **SUPERLUBRICITY**

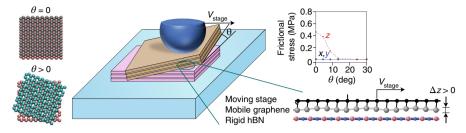
# Slippery in every direction

A graphite and hexagonal boron nitride heterojunction enables superlubric sliding, almost independent of alignment orientation, in micrometre-sized contacts under 'real-life' working conditions.

## J. G. Vilhena and Rubén Pérez

nergy is dissipated when two macroscopic bodies slide in contact. This ubiquitous phenomenon, known as friction, has important economic and social implications. To pick a familiar example, almost one-third of a vehicle's fuel

is spent in overcoming friction between the different moving parts of the engine, transmission and tyres<sup>1</sup>. Additionally, one must also consider the indirect costs associated with friction such as the failure of different parts as a result of wear occurring in poorly lubricated contacts. Given the importance of sustainable development, the quest for mitigating friction is a topic of vibrant research<sup>1</sup>. Now, writing in *Nature Materials*, Yiming Song and colleagues<sup>2</sup> combine atomic



**Fig. 1** Schematic representation of the superlubric sliding at constant velocity ( $V_{\text{stage}}$ ) in hBN-graphite heterojunctions. The left insets show a homojunction (a graphene-graphene junction) and the misalignment (with angle  $\theta$ ) between the planes leading to an incommensurable contact. Contrary to this case, the hBN-graphite heterojunction (represented in pink/grey in the central panel) preserves superlubricity even when the crystalline planes are aligned ( $\theta$  = 0). This stems from differential out-of-plane stiffnesses in the hBN-graphite junctions, which, in turn, give rise to a less dissipative out-of-plane motion when sliding, as compared to the standard centre-of-mass stick-slip motion. As nicely evidenced by the Cartesian components of the calculated frictional stress versus misalignment angles, shown in the upper right inset, the energy dissipation is mainly through the out-of-plane motion (red line, in z direction) rather than lateral motion (black and blue lines, in x and y directions). This process is what ultimately allows for superlubric sliding even when the contacts are aligned, thus showing an alternative route to the original Hirano's structural superlubricity. Top and bottom right insets are adapted from ref. z, Springer Nature Ltd.

force microscope (AFM) experiments and atomistic simulations to demonstrate the possibility of achieving superlubricity, an almost frictionless motion, in micrometresized contacts under ambient conditions. The simplicity of the set-up, the ability to work at variable humidity conditions, its durability over many 'rubbing' cycles, and different superlubric mechanisms revealed by the atomistic simulations endow this finding with both practical and fundamental relevance.

The term superlubricity was first coined in the early 1990s by Motohisa Hirano to describe a theoretically conjectured frictionless sliding state between two incommensurate crystal surfaces<sup>3,4</sup>. Such incommensurable contact, provided either by different lattices or by a rotation between two identical crystal surfaces, ensures that there is no energetically preferred pinning position and, thus, the surfaces may slide effortlessly. Due to the strict requirement of misalignment or incommensurability, this process is often called 'structural superlubricitythis'4. Soon after the theoretical prediction, the first experimental demonstration of superlubricity was provided by sliding misaligned MoSe, atomically thin sheets<sup>5</sup>. Over a decade later<sup>6</sup>, it was shown experimentally that friction between two identical crystal graphite surfaces is strongly dependent on the rotation angle between them. Misalignment resulted in superlubric sliding<sup>3</sup> whereas, when aligned, a much higher friction regime was found6.

Those milestone experiments were performed under high-vacuum and

low-temperature conditions, which is far from the conditions of most real-life applications. Interestingly, the subsequent realization of technologically relevant dry superlubrication was achieved through many different routes<sup>4,7</sup>, namely: the original Hirano's single crystalline incommensurate counterfaces<sup>8,9</sup>, miniature multi-contact ball bearings<sup>10</sup>, and the surface chemistry of amorphous carbon contacts<sup>11,12</sup>. Despite the undisputed merit of these achievements, there are still several issues that hamper a widespread use of superlubrication, including the self-realignment of crystalline homojunctions, the ability to operate under variable humidity conditions, and wear avoidance over multiple rubbing cycles.

Song and co-workers<sup>2</sup> conclusively demonstrate that, in crystalline micrometresized contacts, all the aforementioned limitations may be circumvented. This achievement arises in an ideally simple set-up where by intercalating a hexagonal boron nitride (hBN)-graphite heterojunction between the surface and the slider (Fig. 1), they are able to achieve superlubric sliding. More strikingly, they show that superlubricity endures even when the crystalline contacts are aligned, which is in direct contrast with the homogeneous graphene-graphene counterpart. In the latter, the aligned sliding proceeds in a process known as stick-slip. This process consists of a stick phase where a large sliding force is increasingly applied without resulting in a relative motion of the sliders, followed by a slip phase where enough energy has been accumulated to overcome the energy barrier and the system is able

to slip to the next low energy pinned state. The mechanical energy stored in the contact during the stick phase is released in the sudden centre-of-mass motion during the slip, converted into atomic vibrations, and, finally, dissipated as heat. Misalignment in the contact allows this regime to be avoided as there is no pinning stage, and thus it follows Hirano's structural superlubrication.

Song and co-workers<sup>2</sup> have shown that, in hBN-graphite heterojunctions, where the interface remains incommensurate even for the aligned contact due to the intrinsic lattice vector misfit, the dissipation mechanism seems to be fundamentally different. As shown in Fig. 1, the dissipation associated with the in-plane motion is almost independent of alignment angle, while, interestingly, most energy is dissipated via the out-of-plane motion of the softest contact (graphite), which is simply a smooth buckling of the carbon atoms in the graphite layers close to the contact. This superstructure of out-of-plane deformations, known as moiré patterns, is naturally present in heterogeneous contacts and allows the system to accommodate the lattice mismatch. In the aligned regime, instead of having two equal atoms going against each other until enough energy is accumulated to force them to pass one over the other in an uncontrolled way, the moiré pattern imposes how this dynamic will proceed—that is, through deformation of the weakest material, avoiding the stick-slip instability and, thus, dissipating much less energy. Undoubtedly, the general interest of this work is further enhanced as Song et al. carefully demonstrate that, in these micrometre-sized contacts, superlubricity endures not only the spontaneous reorientation of misaligned to aligned configuration that usually occurs in these contacts<sup>6</sup>, but also variable humidity conditions, large scanning speeds and high normal loads. Furthermore, they showed no evidence of wear during repeated rubbing cycles.

These heterojunctions provide an elegant alternative detour to the strict requirements of Hirano's structural superlubricity, via a differential out-of-plane stiffness of the two materials composing the contact. Though the arguments presented by Song and co-workers are sound and fully supported by the experimental data, further evidence is still essential to demonstrate the generality of these results. One obvious way to do this would be to perform a systematic study of heterojunctions with other two-dimensional materials. This research line would not only provide critical information on how to tune friction between crystalline contacts but

also how it couples with other materials' features (including adhesion, optical and electric properties, and so on). Additionally, the potential interest of this finding at larger scales remains to be addressed, as it is unclear how the lattice defects, grain boundaries or other crystal imperfections, which would naturally arise in macroscale contacts, would affect the tribology performance of this heterojunction. Nevertheless, the potential technological implications of the findings from Song and co-workers establish an important step. At the micrometre-scale alone, translational and rotational superlubric motion would certainly benefit the

over US\$18 billion market of the microelectromechanical systems.

### J. G. Vilhena<sup>1\*</sup> and Rubén Pérez<sup>2\*</sup>

<sup>1</sup>Physics Department, University of Basel, Basel, Switzerland. <sup>2</sup>Department of Theoretical Physics of Condensed Matter and Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, Madrid, Spain.

\*e-mail: guilherme.vilhena@unibas.ch; ruben.perez@uam.es

Published online: 24 September 2018 https://doi.org/10.1038/s41563-018-0172-8

#### References

- Holmberg, K., Andersson, K. & Erdemir, A. Tribol. Int. 47, 221–234 (2012)
- Song, Y. et al. Nat. Mater. https://doi.org/10.1038/s41563-018-0144-z (2018).
- 3. Hirano, M. & Shinjo, K. Wear 168, 121-125 (1993).
- Erdemir, A. & Martin, J. M. Superlubricity (Elsevier, Amsterdam, 2007).
- Martin, J. M., Donnet, C. Le Mogne, Th. & Epicier, Th. Phys. Rev. B. 48, 10583–10586 (1993).
- Dienwiebel, M. et al. Phys. Rev. Lett. 92, 126101 (2004).
- . Martin, J. M. & Erdemir, A. Phys. Today 71, 40-46 (April, 2018).
- 8. Liu, Z. et al. Phys. Rev. Lett. 108, 205503 (2012).
- Koren, E., Lörtscher, E., Rawlings, C., Knoll, A. W. & Duerig, U. Science 348, 679–683 (2015).
- Berman, D., Deshmukh, S. A., Sankaranarayanan, S. K. R. S., Erdemir, A. & Sumant, A. V. Science 348, 1118–1122 (2015).
- Eryilmaz, O. L. & Erdemir, A. Surf. Coat. Technol. 203, 750–755 (2008).
- Fontaine, J., Donnet, C., Grill, A. & Le Mogne, T. Surf. Coat. Technol. 286, 146–147 (2001).

# Moonage daydreams of space rock

he moon landing by Apollo 11, which will be widely celebrated on its 50th anniversary next year, seemed at least to settle that hoary old question of what material the moon is made of. In all, the Apollo astronauts brought back around 380 kg of the satellite — rocks and regolith — for chemical and mineralogical analysis: one of the few (literally) tangible scientific benefits of the Apollo programme. (NASA, however, had to admit several years ago that many 'astromaterials' had been lost from its collection, including many of the Apollo lunar rock samples, mostly misplaced following loans to researchers and educators.)

Surprisingly, though, these materials have still not produced a consensus about the composition of the moon. Even now, half a century later, studies of physical samples and remote measurements from spacecraft are yielding conflicting conclusions about the lunar fabric. Just last year, Milliken and Li reported1 that spectra of lunar pyroclastic (volcanicderived) deposits, widespread on the lunar surface, taken by the Indian Space Research Organisation's Chandrayaan-1 lunar probe suggest that these materials, which originated deep within the moon's interior, have a high water content. That was consistent with water-rich volcanic glassy grains found in Apollo samples<sup>2</sup>, and implied that those materials weren't anomalies but may

reflect the general composition of the lunar interior. This in turn cast doubt on the common view that the moon's geological fabric is depleted in volatile substances such as water.

The implications of water-rich moon rocks are profound. Media reports spoke excitedly of potential sources of water for future moon bases, but the more immediate issue concerns the moon's formation. If, as was widely suspected, it was created from material torn off the young Earth in a collision with a planet-sized object dubbed Theia in the early solar system, then the violence of that event might have been expected to deplete the debris of volatiles. So whence the water? Did it somehow remain with the terrestrial material that formed to moon? Or was it delivered soon after by comets? Or is the impact hypothesis wrong?

Modern analyses of moon rocks, benefitting from the precision of today's techniques, are still informing and changing this story. Wang and Jacobsen, for example, recently showed<sup>3</sup> that the lunar samples are enriched in heavy isotopes of potassium relative to the Earth, which they explain by invoking a much more catastrophic impact than previously considered, more or less vaporizing the colliding bodies.

As for that water: the jury is not in yet. A new analysis<sup>4</sup> of one of the Apollo 16 samples brought back in 1972 — which has plenty



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of volatiles — shows that its zincisotope composition is what one would expect from a material that had been boiled dry by volcanism. The authors suggest that the interior of the moon is dry after all, while surface materials like the Apollo volcanic glasses became hydrated by condensation of expelled volatiles.

It seems unlikely that we have heard the last word. The stories we tell about the moon seem acutely dependent on how sensitively we can probe the materials that, nearly 50 years ago, we began to bring back from it.

Published online: 24 September 2018 https://doi.org/10.1038/s41563-018-0181-7

### References

- Milliken, R. E. & Li, S. Nat. Geosci. 10, 561–565 (2017).
- 2. Saal, A. E. et al. Nature 454, 192-195 (2008).
- 3. Wang, K. & Jacobsen, S. B. *Nature* **538**, 487–490 (2016).
- Day, J. M. D., Moynier, F. & Shearer, C. K. Proc. Natl Acad. Sci. USA 114, 9547–9551 (2017).