

## VALLEYTRONICS

## Could use a break

Electric fields can controllably break the inversion symmetry of bilayer graphene, which can be harnessed to generate pure valley currents.

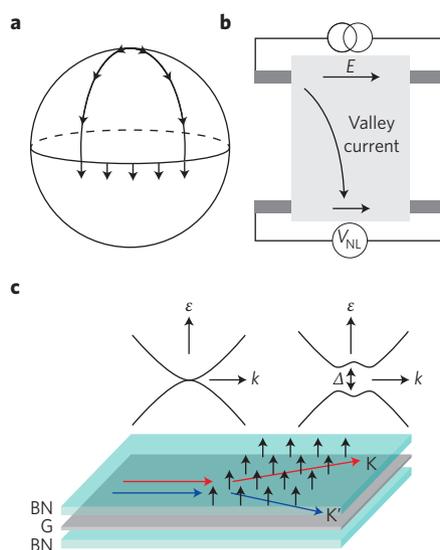
François Amet and Gleb Finkelstein

In quantum mechanics, the time evolution of an electronic state is determined by its Hamiltonian. If the Hamiltonian itself slowly varies in time, an electron initially in an eigenstate will remain so throughout the time evolution, but will acquire an additional phase that is related to the geometrical properties of the Fermi surface — and in particular to its curvature<sup>1</sup> (Fig. 1a). This is the so-called Berry phase, which endows charge carriers with an anomalous velocity<sup>1</sup>.

It is well known that the group velocity of a wave packet is caused by the momentum dispersion of the phase. Similarly, the momentum dispersion of the Berry phase contributes to a drift velocity of the wave packet perpendicular to the electric field. This yields a transverse current comparable to the Hall effect, but arising from the topological properties of the band structure. As they report in *Nature Physics*, two groups demonstrate unprecedented control over the Berry curvature of bilayer graphene, which allows the electrical generation and control of pure valley currents in this material<sup>2,3</sup>.

What makes this anomalous drift velocity particularly interesting is that it depends on the electrons' internal degrees of freedom. In materials with a hexagonal lattice structure, such as graphene, the conduction band has multiple local minima called valleys. Charge carriers therefore have two degrees of freedom: the spin and valley. The main paradigm of spin or valleytronics is then the following: if the Berry curvature causes the two flavours of valley K and K' to drift in opposite directions, a net flavour current will propagate in the sample without dissipation, because the net charge current vanishes<sup>4</sup>. Dissipation-free devices can then rely on the propagation and control of such flavour currents, in analogy to the spin field-effect transistor<sup>5</sup>.

Yet, this anomalous drift velocity is relevant only in materials with a non-zero Berry curvature, which requires either time-reversal or inversion symmetry to be broken. Certain transition metal dichalcogenides, such as molybdenum disulphide, break inversion symmetry and have shown the first signatures of a valley Hall effect<sup>6</sup>. In graphene, the very small



**Figure 1** | Valley Hall effect. **a**, The Berry phase can be compared to the parallel transport of a vector along a curved surface, causing it to rotate after completion of a loop. **b**, A longitudinal electric field,  $E$ , causes a transverse valley current. This results in a sizable non-local voltage,  $V_{NL}$ . **c**, Bilayer graphene (G) is encapsulated in boron-nitride (BN). A perpendicular electric field breaks inversion symmetry and opens an energy gap,  $\Delta$ , in the band-structure,  $\epsilon(k)$ , of bilayer graphene. The resulting Berry curvature causes the two valleys K and K' to drift in opposite transverse directions.

intervalley scattering rate and remarkable electronic mean free path are particularly appealing for valleytronics applications. However valley-dependent transport signatures are scarce at zero field because of the inversion symmetry of its lattice. As a result, only trajectories in momentum space enclosing the Dirac point have a finite Berry phase, which gives rise to a half-integer quantum Hall effect<sup>7</sup>.

To solve this problem, the inversion symmetry of graphene must be broken. This can be caused by the substrate, and in particular boron nitride, which creates a superlattice moiré pattern that breaks inversion symmetry and opens a gap at charge neutrality. The resulting massive Dirac band structure has a non-zero

Berry curvature with opposite signs for each valley, which causes them to drift in opposite directions when an electric field is applied to the electrons<sup>8</sup>. In this scenario, an in-plane electric field induces a transverse valley current but no charge current<sup>9</sup>. This is the valley Hall effect, akin to the spin Hall effect, where valley currents and polarization can be controlled electrically.

To detect the small contribution of this valley Hall effect, a non-local geometry is required (Fig. 1b). With that design, the ohmic contribution of a current flowing on one end of the strip will yield only an exponentially small voltage on the other end. However, in the presence of a valley Hall effect, the electric field creates transverse valley currents propagating to the other end of the strip, then inducing a sizeable voltage by the reverse valley Hall effect<sup>10</sup>. The resulting non-local voltage can be orders of magnitude larger than the ohmic contribution and indicates that valley currents propagate.

For monolayer graphene, the inversion symmetry breaking relies on the precise alignment of the graphene and boron nitride lattices and is not electrostatically tunable. Sui *et al.*<sup>2</sup> and Shimazaki *et al.*<sup>3</sup> showed that bilayer graphene solves this issue, with top and back gates to provide separate control of the Fermi energy and the displacement field. Applying a perpendicular electric field breaks the inversion symmetry and opens an electrically tunable bandgap<sup>11</sup>. The resulting band structure has a Berry curvature that depends on the bandgap and therefore on the displacement field. This means that the valley Hall conductivity can be tuned experimentally (Fig. 1c).

Although valley currents do not dissipate power, they still suffer from intervalley scattering, which smears the accumulated valley polarization. In encapsulated graphene devices, intervalley scattering occurs only at rare atomic scale defects and at the edges, which are highly disordered on the atomic scale. As a result, valley currents were found to decay exponentially on the micrometre scale<sup>2,3,9</sup>, setting geometric constraints on future valleytronics device designs.

Electronic applications of these valley currents require them to survive room-temperature operation. The valley Hall conductivity depends inversely on the energy outside of the gap, which will cause it to decay with inverse temperature if thermal fluctuations are larger than the bandgap. Monolayer graphene on boron nitride offers a gap of the order of only a few meV, far too small for room-temperature operation. However, the bandgap can be an order of magnitude greater in bilayer graphene, and

so hints of valley Hall effect were observed close to room temperature. Practical applications to electronic devices will require even greater gaps: an upcoming challenge for graphene-based valleytronics. □

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## THERMOELECTRIC MATERIALS

# The anharmonicity blacksmith

Anharmonicity is a property of lattice vibrations governing how they interact and how well they conduct heat. Experiments on tin selenide, the most efficient thermoelectric material known, now provide a link between anharmonicity and electronic orbitals.

Joseph P. Heremans

Almost three centuries after Georg Friedrich Händel composed *The Harmonious Blacksmith*<sup>1</sup>, scientists are still uncovering new properties of sound waves. Writing in *Nature Physics*, Chen Li and colleagues<sup>2</sup> clarified the origin of the anharmonic properties of sound waves in tin selenide (SnSe) — limiting the amount of heat they can carry and resulting in a record thermoelectric performance. Not only does this discovery deepen our understanding of the physics at play, it also provides new opportunities for developing ‘anharmonicity smithing’ — engineering heat conduction in materials used for thermal energy conversion.

In the quantum-mechanical picture, sound waves are quasiparticles called phonons. They originate from the vibrations of atoms and propagate through matter, whether solid, liquid or gas. Vibrations constitute degrees of freedom for atoms, and thus harbour entropy and heat. In solids that are not electrically conducting and not magnetic, heat conduction through the medium is the propagation of this entropy through the propagation of phonons. In semiconductors like SnSe, the phonon thermal conductivity dominates over the electronic thermal conductivity, which is the propagation of entropy by electrons.

In crystals, phonons are vibrations of the periodic lattice of atoms. They form a spectrum of allowed frequencies,  $\{f\}$ , for the vibrations of the atoms that are harmonics of each other. The highest frequency, typically of the order of many THz, corresponds to

the rapid vibrational motion where two neighbouring atoms move towards and away from each other. The lowest frequency, typically tens or hundreds of Hz, is that of the sound wave that is the fundamental resonant mode of the macroscopic crystal. If we represent the interatomic forces by springs (with spring constant  $K$ ) and the atoms by balls (of mass  $m$ ), a perfect crystal can be pictured as a 3D ball-and-spring lattice. Figure 1 depicts a transverse phonon involving three atoms in a 1D ball-and-spring chain (for a transverse phonon, the atomic displacement is normal to the direction of propagation). If we further assume that the springs are perfect — that is,  $K$  does not depend on the displacement,  $\delta$ , of the atoms from their average position — then the force on each atom is  $F(\delta) = K\delta$ . The spectrum of frequencies,  $\{f\}$ , of the vibrations involving atoms in such a lattice is only a function of  $K$ ,  $m$  and the propagation velocity,  $v$ , and not of  $\delta$ .

Anharmonicity is a measure of the departure of a real system from this assumption: in an anharmonic solid, the force is not proportional to the displacement, so that  $K$  and the spectrum of resonant frequencies become functions of  $\delta$ , and also of the distance between atoms and the volume,  $V$ , of the unit cell of the crystal. Anharmonicity is characterized by the so-called Grüneisen parameter,  $\gamma(f) \equiv d(\ln f)/d(\ln V)$ , which is defined separately for each frequency  $f$ . The Grüneisen parameter has a strong influence on the probability that a phonon

of frequency  $f$  interacts with other phonons: anharmonic phonons scatter off each other much more frequently than harmonic phonons (Fig. 1). The probability of phonon–phonon interactions is proportional to  $\gamma^2$ . When they scatter, phonons take their momentum and entropy in a direction that is different from their initial direction (in the 1D example this is exactly the opposite direction, but in 3D scattering is less extreme), so this decreases the thermal conductivity. Therefore, the high-temperature phonon conductivity,  $\kappa$ , where phonon–phonon scattering is the dominant phonon scattering mechanism, is proportional to the average of  $\gamma^{-2}$  taken over all the phonon frequencies. The question is, do we know enough about the exact chemical bonds between the atoms, which determine  $K$ , to be able to understand and quantify  $\gamma$ ? Li and colleagues<sup>2</sup> give experimental evidence that we do — and their work holds promise for designing compounds with tuned values of  $\gamma$ , that is, engineering anharmonicity.

The ability to design materials with low thermal conductivity is technologically important. Parasitic heat conduction by phonons is a dominant loss mechanism in all solid-state thermal energy conversion devices, such as thermoelectric generators or Peltier coolers. Low- $\kappa$  solids constitute a whole industry for energy-related applications, such as thermal barrier coatings, and anharmonicity engineering is a powerful tool in that context. Since 2008, researchers have been selecting