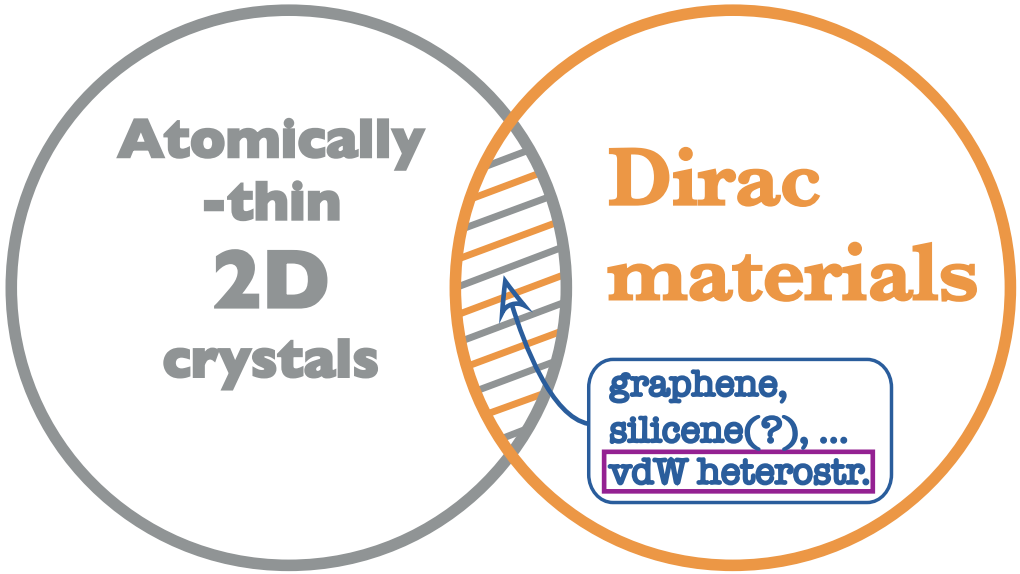
Low-temperature thermoelectric properties of bilayer graphene

Adam Rycerz, Dominik Suszalski, and Grzegorz Rut
Marian Smoluchowski Institute of Physics, Jagiellonian University, Kraków, Poland

StoCP 2018, Zakopane, Poland, September 16–21, 2018

Why graphene?



- h-BN, h-AlN(?)
- MoS_2, $HfSe_2$, ...
- Black-P
- $TiSe_2$ (CWD+SC!)

- Artificial graphenes & analogs
- Topolog. insulators: HgTe/CdTe, $Bi_{1-x}Sb_x$, Bi_2Se_3, Bi_2Te_3, ...
- *d*-wave superconductors
- Weyl semimetals

For a review of the topic, see: Wehling et al., Adv. Phys. 76, 1 (2014).

Theory of SC in $TiSe_2$: Chen et al., arXiv:1806.08064.

Emergent Dirac fermions in graphene

4 August 1972, Volume 177, Number 4047

SCIENCE

More Is Different

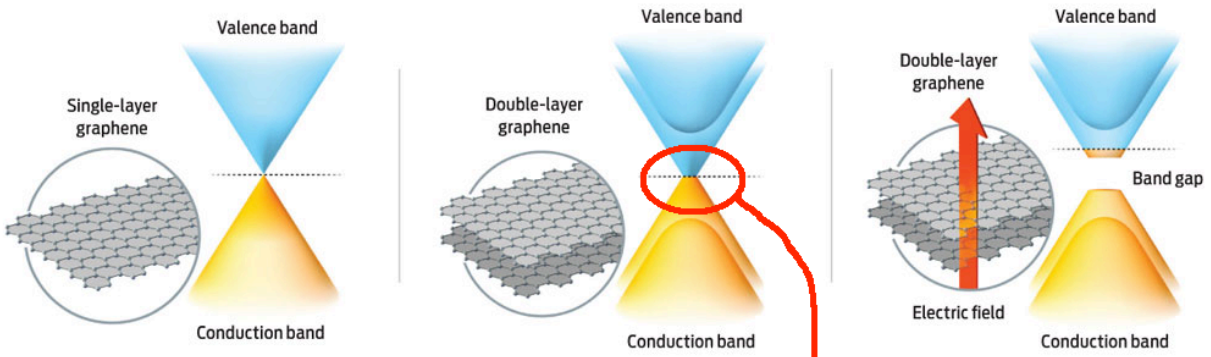
Broken symmetry and the nature of the hierarchical structure of science.

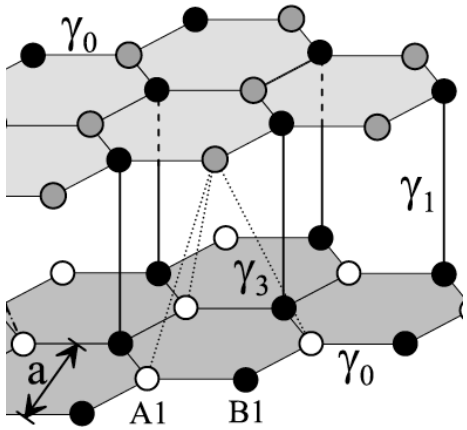
P. W. Anderson

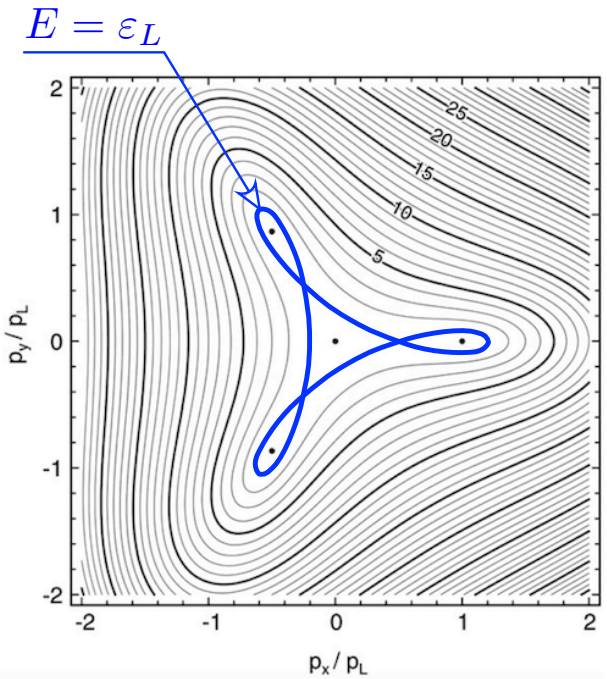
What differs graphene from a collection of carbon atoms?

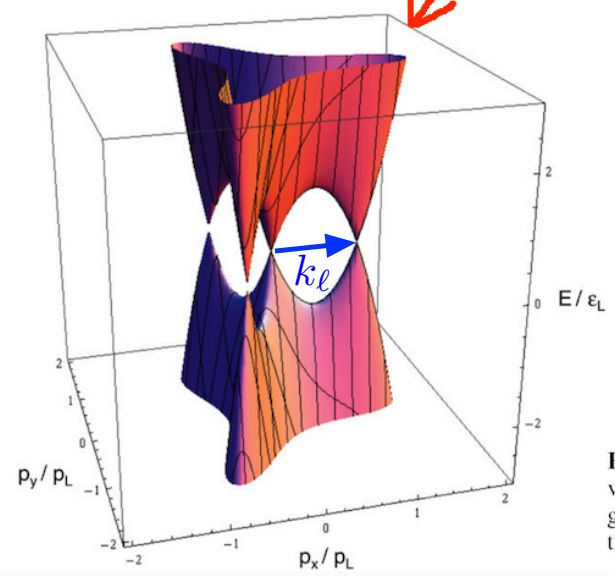
- The **valley pseudospin** ($\Rightarrow$ *fermion doubling*)
- Time-reversal symmetry breaking at zero magnetic field
- Pseudodiffusive charge transport, . . . , SC in twisted-BLG (!)

Tunable band gap and trigonal warping









$$\varepsilon_L = \frac{\gamma_1}{4}\left(\frac{\gamma_3}{\gamma_0}\right)^2 \approx 1\,\text{meV}$$

$$k_\ell = \frac{2}{\sqrt{3}}\frac{\gamma_1\gamma_3}{a\gamma_0^2} \approx 0.05\,\text{nm}^{-1}$$

Figure 4. (*a*) Trigonal warping of the equi-energy lines in the vicinity of each K point, and the Lifshitz transition in bilayer graphene. The energy is in units of ε_L. (*b*) Corresponding three-dimensional plot of the low-energy dispersion.

[*Top:* IEEE Spectrum, 2009; *bottom:* McCann & Koshino, 2013]

Rep. Prog. Phys. **76** (2013) 056503 E McCann and M Koshino

Table 1. Values (in eV) of the SWM model parameters [64–67] determined experimentally. Numbers in parentheses indicate estimated accuracy of the final digit(s). The energy difference between dimer and non-dimer sites in the bilayer is $\Delta' = \Delta - \gamma_2 + \gamma_5$. Note that next-nearest layer parameters γ_2 and γ_5 are not present in bilayer graphene.

Parameter	Graphite [67]	Bilayer [76]	Bilayer [55]	Bilayer [56]	Bilayer [80]	Trilayer [82]
γ_0	3.16(5)	2.9	3.0[a]	—	3.16(3)	3.1[a]
γ_1	0.39(1)	0.30	0.40(1)	0.404(10)	0.381(3)	0.39[a]
γ_2	−0.020(2)	—	—	—	—	−0.028(4)
γ_3	0.315(15)	0.10	0.3[a]	—	0.38(6)	0.315[a]
γ_4	0.044(24)	0.12	0.15(4)	—	0.14(3)	0.041(10)
γ_5	0.038(5)	—	—	—	—	0.05(2)
Δ	−0.008(2)	—	0.018(3)	0.018(2)	0.022(3)	−0.03(2)
Δ'	0.050(6)	—	0.018(3)	0.018(2)	0.022(3)	0.046(10)

[a] This parameter was not determined by the given experiment, the value quoted was taken from previous literature.

[55] Zhang *et al.*, Phys. Rev. B **78**, 235408 (2008).
[56] Li *et al.*, Phys. Rev. Lett. **102**, 037403 (2009).
[67] Dresselhaus & Dresselhaus, Adv. Phys. **51**, 1 (2002).
[76] Malard *et al.*, Phys. Rev. B **76**, 201401(R) (2007).
[80] Kuzmenko *et al.*, Phys. Rev. B **80**, 165406 (2009).
[82] Taychatanapat *et al.*, Nature Phys. **7**, 621 (2011).

$$\varepsilon_L = \frac{\gamma_1}{4}\left(\frac{v_3}{v}\right)^2 \approx 1\,\mathrm{meV}$$

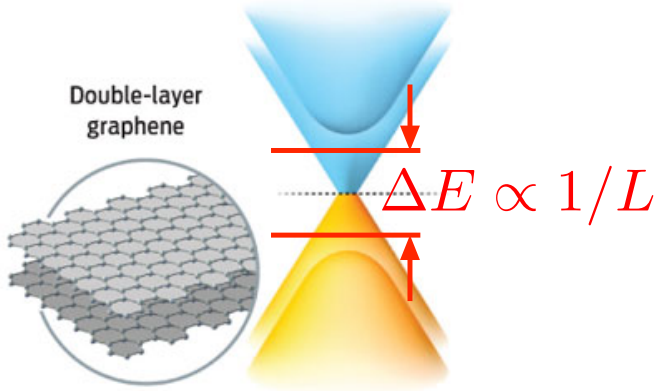
Yankowitz et al., (2014): $\gamma_1 = 0.39\,\mathrm{eV}$, $\gamma_4 = 0.22\,\mathrm{eV}$, but γ_3 not determined ...

$\Rightarrow$ **Novel phenomena governed solely by γ_3 desired!**

Where to expect TW effects on transport?

Time-energy uncertainty relation **limits the energy resolution**:

$$\Delta E \geqslant \frac{\hbar}{\Delta t} \sim \frac{\hbar v_F}{L},$$



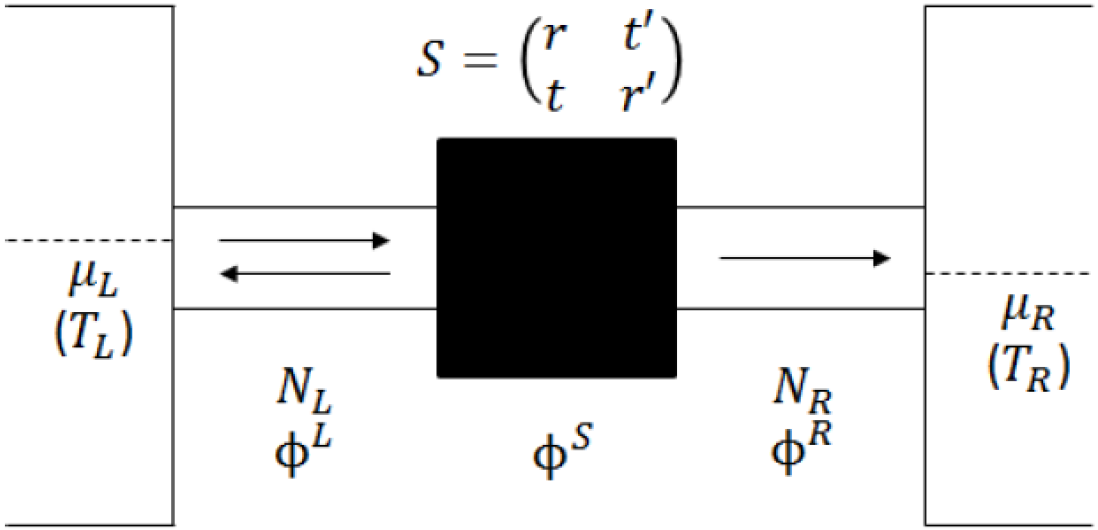
where we set $\Delta t \sim t_{\text{flight}} \approx L/v_F$.

The condition $\Delta E \lesssim 2\varepsilon_L$ leads to

$$\boxed{L \gtrsim \frac{\hbar v_F}{2\varepsilon_L} = \sqrt{3}\,\frac{\gamma_0^3}{\gamma_1\gamma_3^2}\,a \approx 400\,\text{nm},}$$

where $\gamma_0 = 3.16\,\text{eV}$, $\gamma_1 = 0.38\,\text{eV}$, $\gamma_3 = 0.3\,\text{eV}$, $a = 0.246\,\text{nm}$.

$\Rightarrow$ **Effects of $\gamma_3 \neq 0$ on transport prop-s may depend on the system size; the crossover range: $100\,\text{nm} < L < 1\,\mu\text{m}$.**



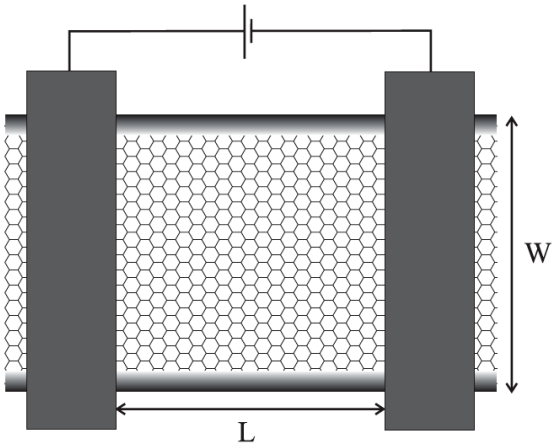
Electric and thermal currents

$$I = -\frac{g_s g_v e}{h} \int dE\, T(E)\, [f_L(E) - f_R(E)]\,,$$

$$I_Q = \frac{g_s g_v}{h} \int dE\, T(E)\, [f_L(E) - f_R(E)]\, (E - \mu),$$

where $g_s = g_v = 2$ denote spin and valley degeneracies, $T(E) \equiv Tr(\mathbf{t}\mathbf{t}^\dagger)$, and f_L, f_R are Fermi-Dirac distributions.

Monolayer at the charge-neutrality point



$$G = \frac{2e^2}{h} \sum_{n=-\infty}^{\infty} \frac{1}{\cosh^2[\pi(n+\alpha)L/W]}$$

$$\underset{\simeq}{W \gg L} \quad \frac{4e^2}{\pi h}\frac{W}{L},$$

where $\alpha = \frac{1}{2}$ for the *mass confinement* ($\Psi_A|_{y=0} = \Psi_B|_{y=0}$, $\Psi_A|_{y=W} = -\Psi_B|_{y=W}$).

The conductivity: $\boxed{\sigma = GL/W = 4e^2/(\pi h) \equiv \sigma_0}$.

Theory: Katsnelson (2006); Tworzydło et al. (2006)
Experiment: Miao et al., (2007); Danneau et al., (2008).

Emergent conductivity of BLG

- Landauer conductivity [Snyman & Beenakker, 2007], $\gamma_3 = \gamma_4 = 0$:

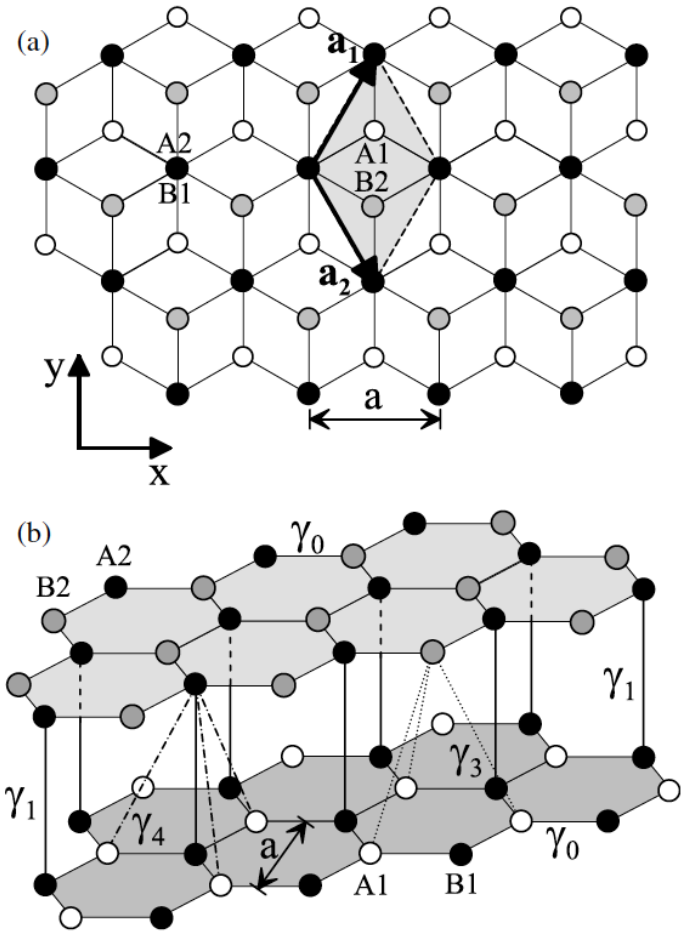
$$\sigma_{\text{bilayer}} = GL/W = 2\sigma_0$$

- Kubo conductivity [Cserti et al., 2007], $\gamma_3 \neq 0$:

$$\sigma_{\text{bilayer}} = 6\sigma_0 \quad (!)$$

- *Experiment:* [Mayorov et al., 2011] $\sigma_{\text{bilayer}} \simeq 5\sigma_0$.

[*with* $\sigma_0 \equiv (4/\pi)e^2/h$ – **universal conductivity of a monolayer**.]



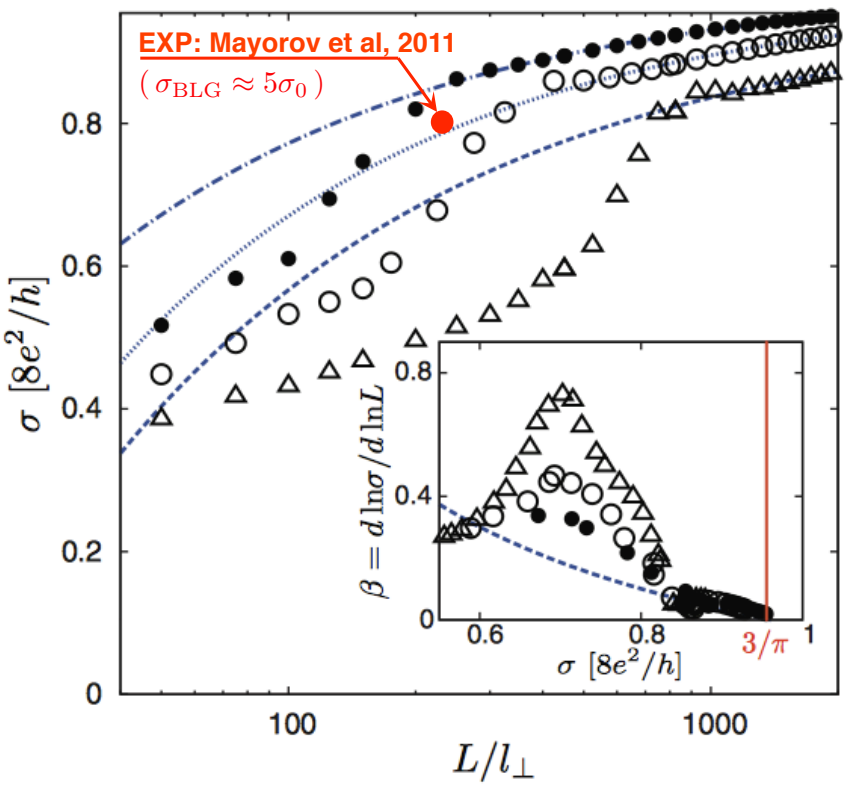


Fig. 3: (Colour on-line) Minimal conductivity of an unbiased graphene bilayer as a function of the sample length L (specified in units of $l_\perp = \hbar v_F/t_\perp \simeq 1.60\,\text{nm}$). Different datapoints correspond to different values of the next-nearest neighbor interlayer hopping: $t' = 0.1\,\text{eV}$ (△), $0.2\,\text{eV}$ (◯), and $0.3\,\text{eV}$ (●).

[Notation: $t_\perp \equiv \gamma_1$, $t' \equiv \gamma_3$ **]**

Non-cummuting limits:

$$\lim_{L\to\infty}\lim_{d\to\infty} \sigma_{\rm BLG} = 2\sigma_0$$

$$\lim_{d\to\infty}\lim_{L\to\infty} \sigma_{\rm BLG} = 6\sigma_0\ (!)$$

[$\gamma_1 \sim \gamma_3 \sim e^{-Bd/d_0}$, $\epsilon_L \sim \left(e^{-Bd/d_0}\right)^3$, and thus $\epsilon_L/\gamma_1 \to 0$ with $d \to \infty$ (*the interlayer distance*)]

Surprising analogy with systems showing spontaneous symmetry breaking !

Grzegorz Rut & AR:
⇒ PRB **89**, 045421 (2014)
⇒ EPL **107**, 47005 (2014)

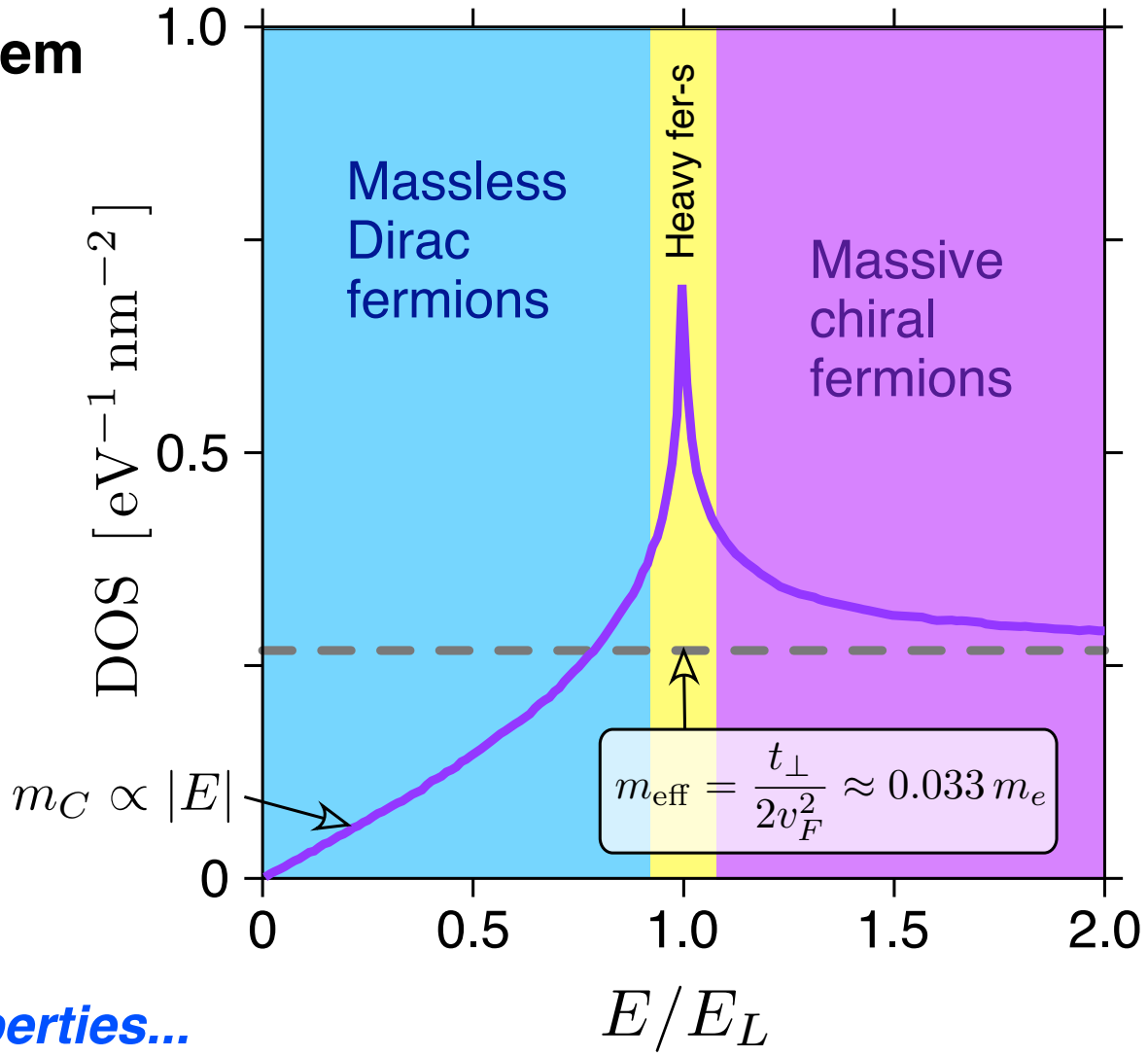
Quasiparticles in *doped* BLG

In a generic 2D system

the *cyclotronic mass*:

$$m_C(E) = \frac{\pi\hbar^2}{2}\mathrm{DOS}(E)$$

Transitions between different populations of quasiparticles should have signatures in thermoelectric properties...



Why thermoelectrics?

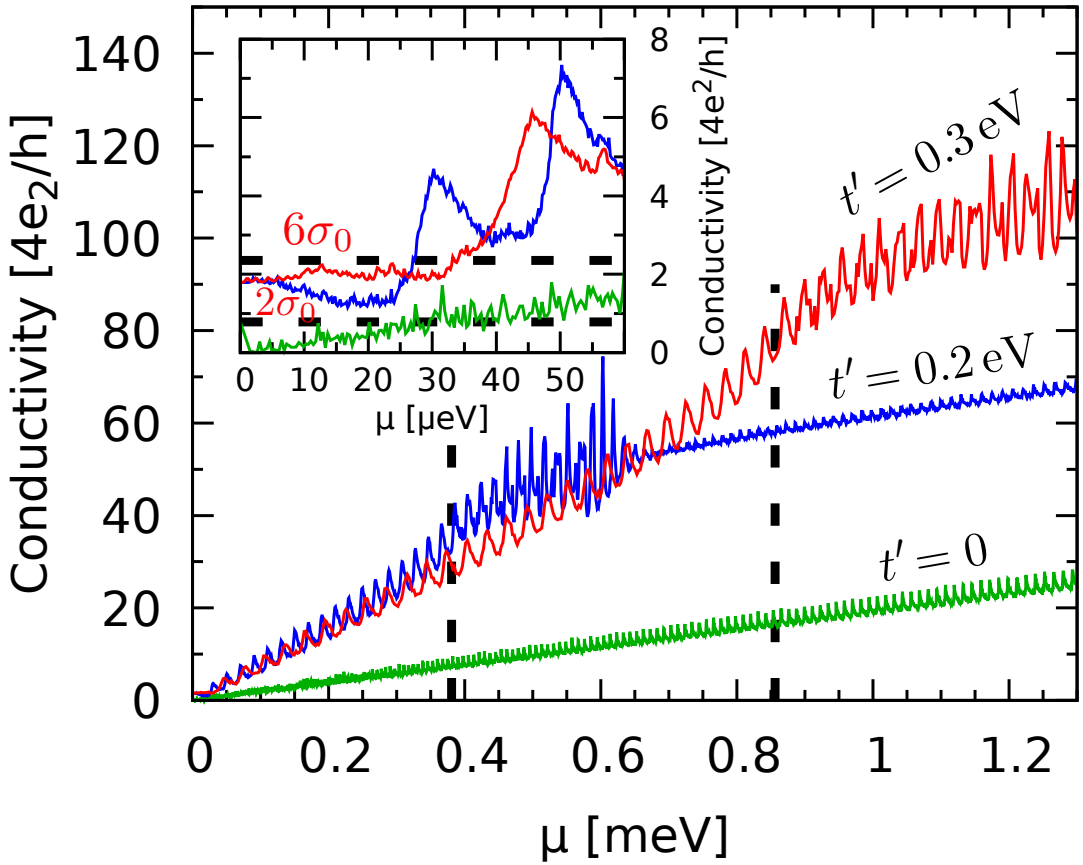
The Mott formula for metals [Cutler & Mott, Phys. Rev. (1969)]

$$S \approx \frac{\pi^2 k_B^2 T}{3e} \left[\frac{\partial \ln \sigma(E)}{\partial E} \right]_{E=E_F},$$

The Drude conductivity: $\sigma = ne^2\tau/m_{\text{eff}} \sim \text{DOS}(E_F) \times k_B T$ (provided that the mobility $\tilde{\mu}(E) \sim \tau/m_{\text{eff}} \approx$ const.).
$\Rightarrow$ Any *abrupt* change in DOS(E) should has some signature in S.

The Goldsmid-Sharp energy gap in semiconductors $|S|_{\max} \approx E_g/(2eT_{\max})$ allows the thermoelectric-based band-gap (E_g) determination, instead of employing the familiar activation formula $\sigma \sim exp(-E_g/2k_B T)$.
[Goldsmid & Sharp, J. Electron. Mater. (1999)] .

Zero-temperature conductivity ($\mu \neq 0$)



Fabry-Perrot resonances: $\Delta E \approx 2\pi(\hbar v_F/L)\sqrt{|E|/t_\perp}$ for $t' = 0$, or $\Delta E \sim \pi\hbar v_3/L = 2\pi(\hbar v_F/L)\sqrt{E_L/t_\perp}$ for $t' \neq 0$.

Above: $L = 10^4 l_\perp = 17.7\,\mu$m. [*Suszalski, Rut, AR, PRB (2018)*]

In the linear-responce regime:

$$G = \left.\frac{I}{V}\right|_{\Delta T=0} = e^2 L_0,$$

$$S = -\left.\frac{V}{\Delta T}\right|_{I=0} = \frac{L_1}{eTL_0},$$

$$K_{\rm el} = \left.\frac{I_Q}{\Delta T}\right|_{I=0} = \frac{L_0 L_2 - L_1^2}{TL_0},$$

with L_n given by

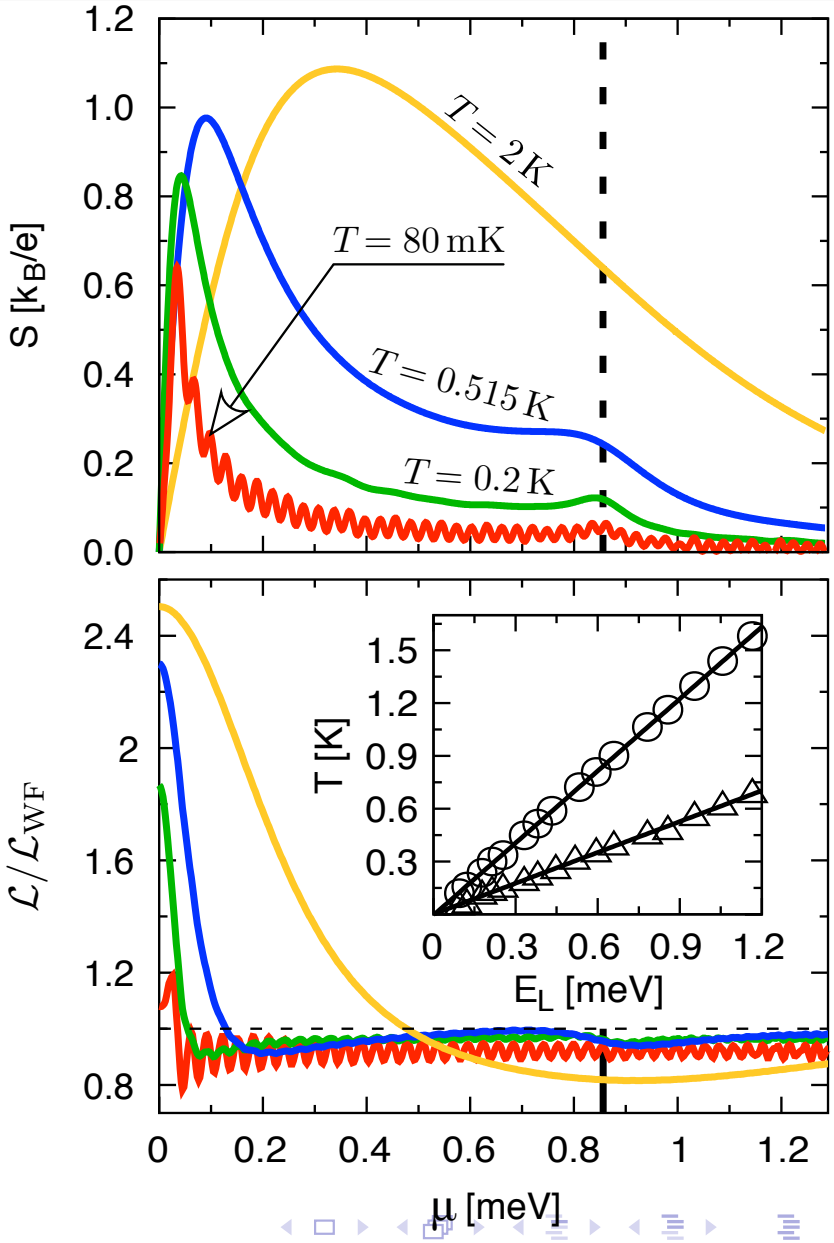
$$L_n = \frac{g_s g_v}{h}\int dE\, T(E)\left(-\frac{\partial f_{\rm FD}}{\partial E}\right)(E-\mu)^n$$

The Lorentz number

$$\mathcal{L} = \frac{K_{\rm el}}{TG} = \frac{L_0 L_2 - L_1^2}{e^2 T^2 L_0^2}$$

[$\mathcal{L}_{\rm WF} \equiv \frac{1}{3}\pi^2 (k_B/e)^2 \Leftrightarrow T(E) =$const;
a model $T(E) \propto |E| \Leftrightarrow \mathcal{L}_{\rm max} \approx 2.37\mathcal{L}_{\rm WF}$.]

[*Suszalski, Rut, AR, PRB (2018)*]



⇒ One does not necessarily need to include interactions to understand some experimental data!

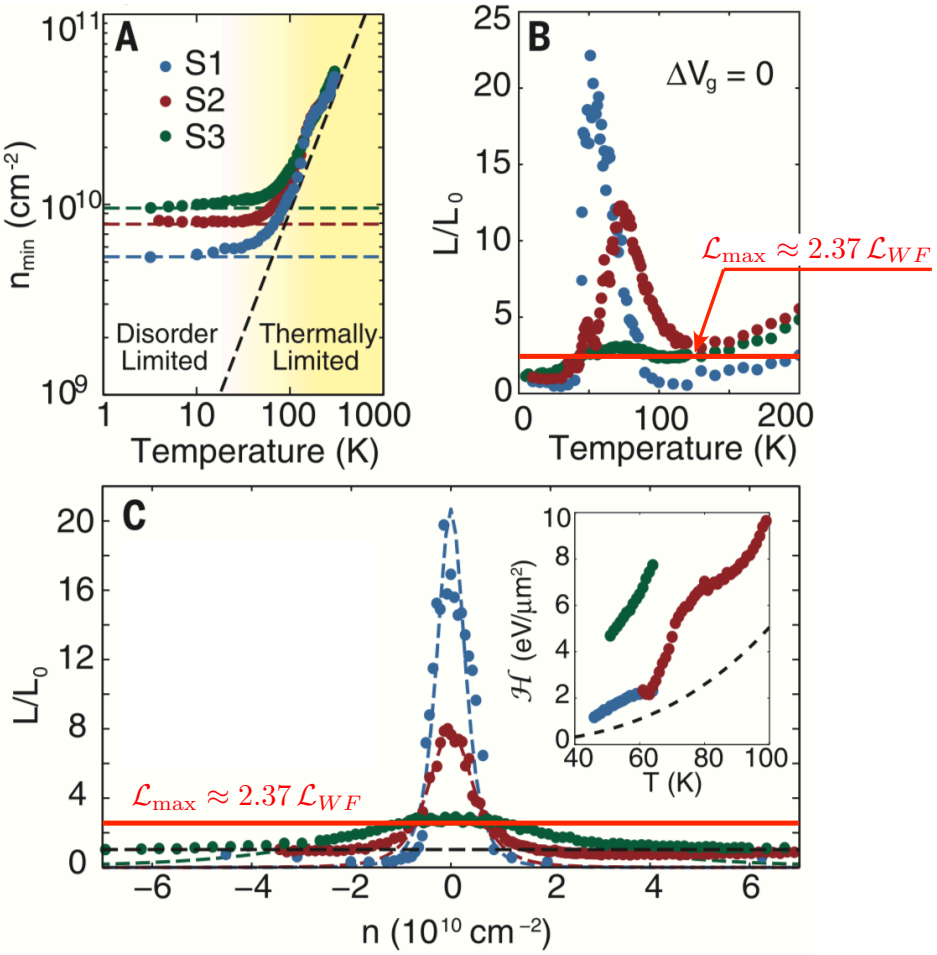


Fig. 3. Disorder in the DF. (**A**) Minimum carrier density as a function of temperature for all three samples. At low temperatures, each sample is limited by disorder. At high temperatures, all samples become limited by thermal excitations. Dashed lines are a guide for the eye. (**B**) Lorentz ratio of all three samples as a function of bath temperature. The largest WF violation is seen in the cleanest sample. (**C**) The gate dependence of the Lorentz ratio is well fit to the hydrodynamic theory of (*5*, *6*). Fits of all three samples are shown at 60 K. All samples return to the FL value (black dashed line) at high density. The inset graph shows the fitted enthalpy density as a function of temperature and the theoretical value in clean graphene (black dashed line). The schematic inset illustrates the difference between heat and charge current in the neutral Dirac plasma.

[**EXP**: Crossno et al, Science (2016)]

Chemical potential μ is not a directly-measurable quantity, but it is monotonically-dependent on the carrier density n.

Characteristic temperatures, at which the secondary maximum of S (minimum of $\mathcal{L}$) vanishes are:

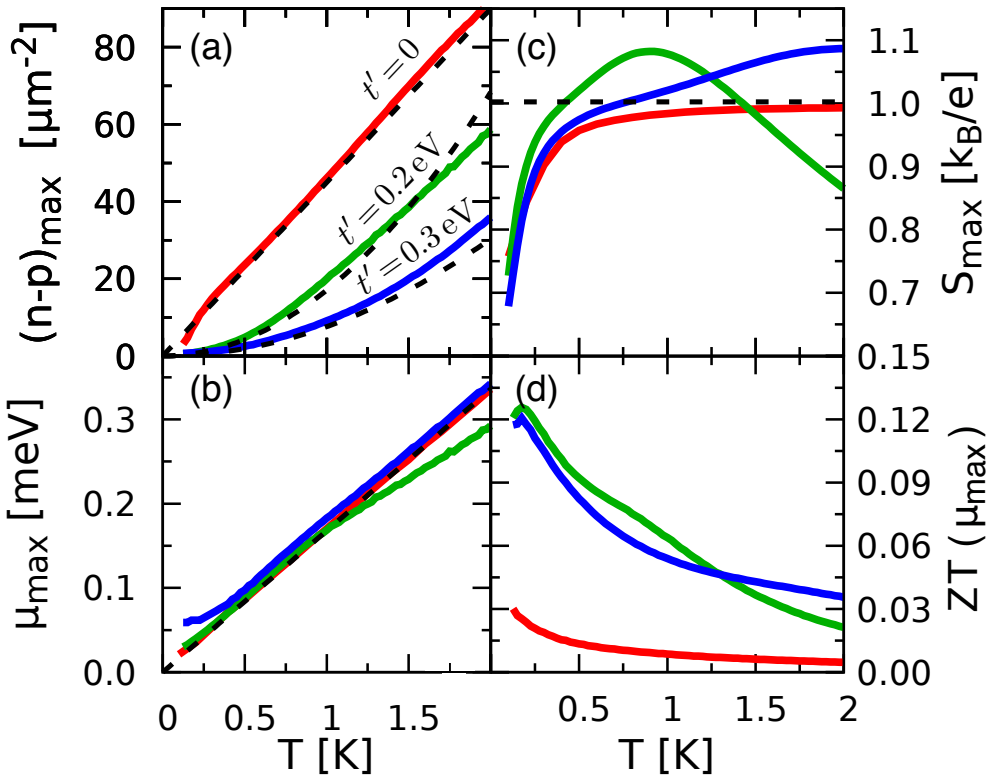
$$T_\star^S = 0.050 \times E_L/k_B,$$
$$T_\star^{\mathcal{L}} = 0.118 \times E_L/k_B.$$

(For $t' = 0.3\,\mathrm{eV}$, $E_L/k_B \approx 10\,\mathrm{K}$.)

Also, a **global maximum of** S corresponds to

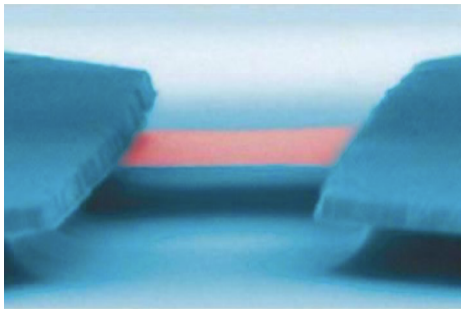
$$T_{\mathrm{max}}^S = 0.20 \times E_L/k_B.$$

[*Suszalski, Rut, AR, PRB (2018)*]



Remarks on *intrinsic* gap in BLG (1)

Free-standing (suspended) BLG:



[*Credit*: Lau lab, UC Riverside]

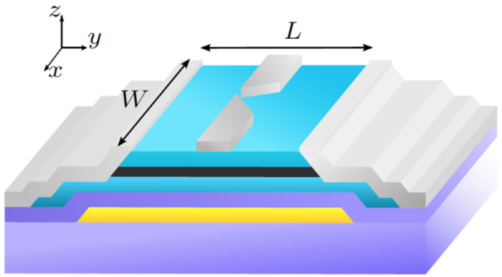
Width of resistivity peak matches the self-consistent (*mean-field*) gap:

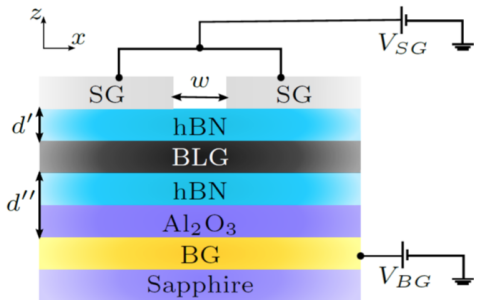
$$\Delta_i(T) = \Delta_i(0)\tanh\left(1.74\sqrt{\frac{T_c}{T}-1}\right) \text{ for } T \leq T_c,$$

with $\Delta_i(0) \approx 1.5\,\text{meV}$, $T_c \approx 12\,\text{K}$ ($\Delta_i(0)/k_B T_c \approx 1.5$).

[Nam et al., 2D Mater 2016; Morpurgo, Graph. Week 2018]

BLG in v.d. Walls heterostructures (vdWH):





No signatures of $\Delta_i > 0$ found as yet (!)

[Kraft et al., Nat. Comm 2018]

Remarks on *intrinsic* gap in BLG (2)

Possible explanations of the presentce/absence of Δ_i in free-standing BLG / vdWH containing BLG:

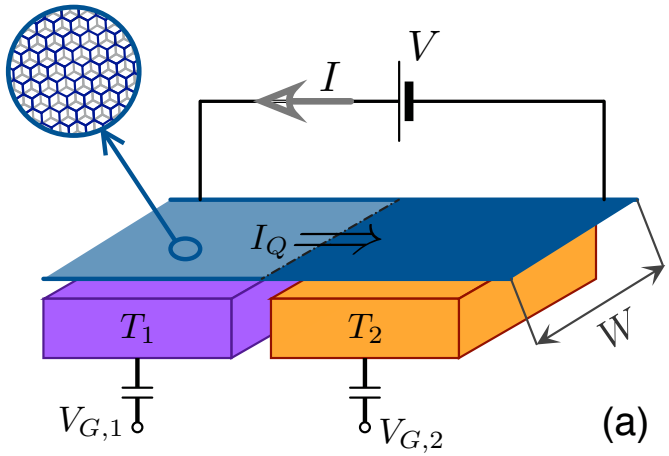
- Self-consistent gap strongly depends on effective Hubbard-U: $\boxed{\Delta_i \sim t_0 \exp(-const/U_{\text{eff}})}$ [Hirsch, 1985].

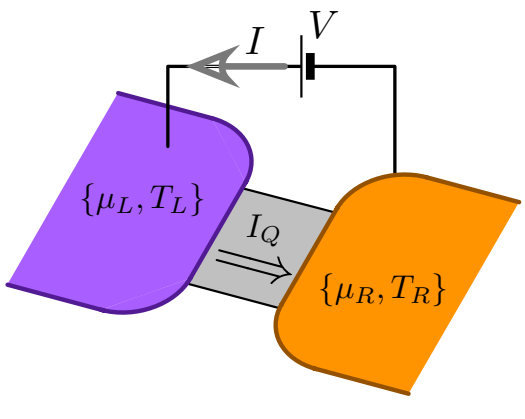
  Supression of U_{eff} due to dielectric constant may dramatically reduce Δ_i and T_c.

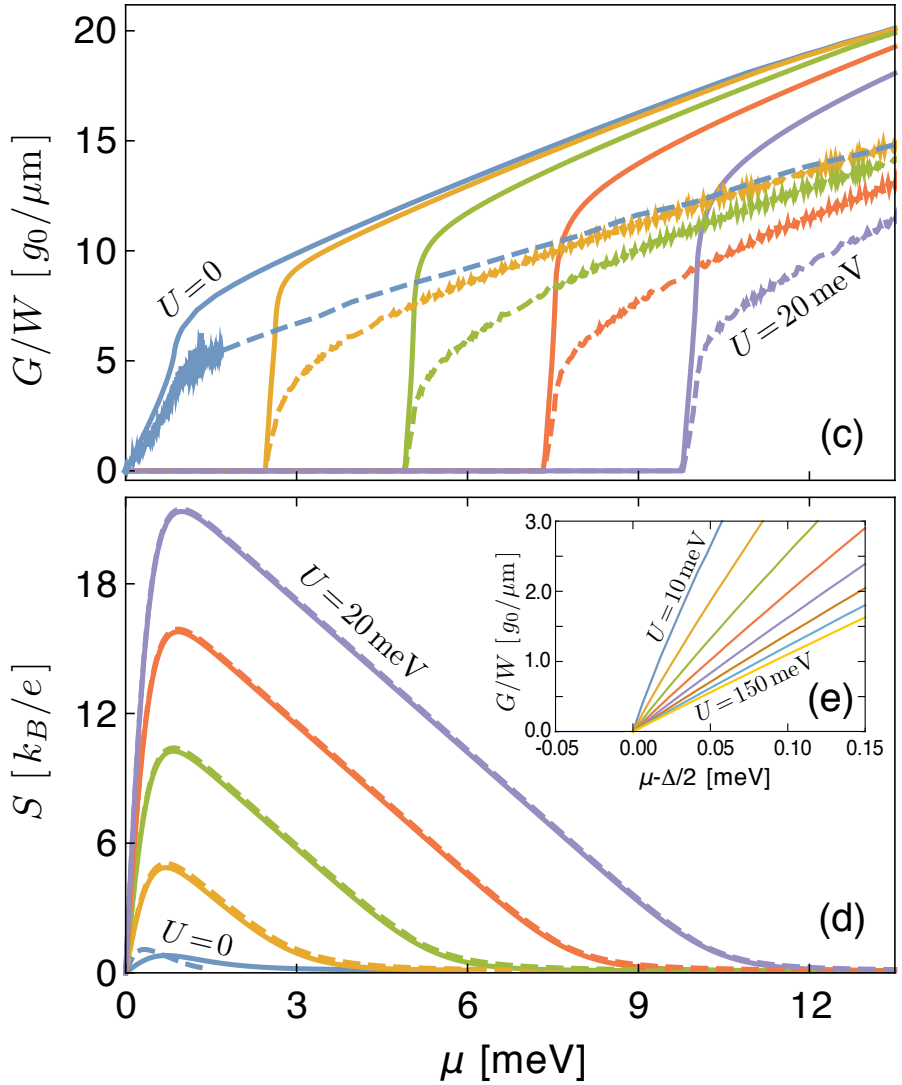
- Lattice mismatch between BLG and h-BN induces an effective potential (*Moiré pattern*) destabilizing *quasi*-long range order (?)

- . . . ?

The nonzero gap case ($\Delta > 0$)



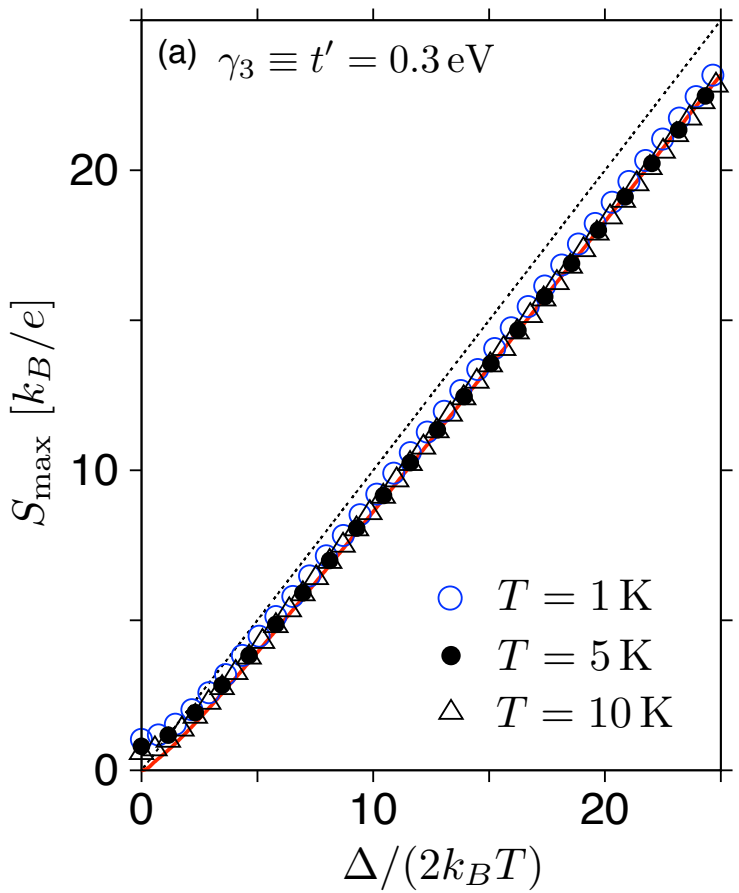


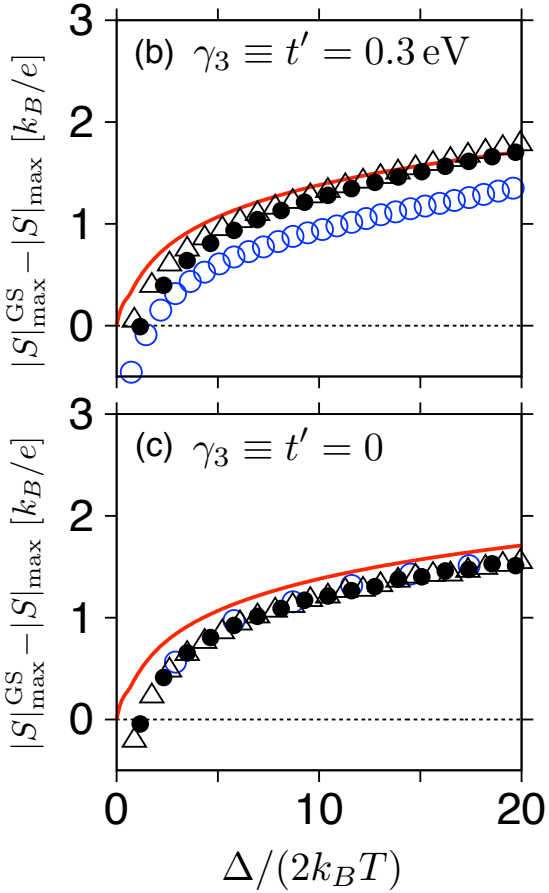


[*Rut, Suszalski, AR, in preparation*]

Dotted line:
The reference (**Goldsmid-Sharp**) value:

$$|S|^{\mathrm{GS}}_{\mathrm{max}} = \frac{\Delta}{2eT}$$





Red solid line:
Approx/asymptotic expression $[\Leftrightarrow T(E) \propto \Theta(|E| - \frac{1}{2}\Delta)]$

$$|S|_{\mathrm{max}} = |S|^{\mathrm{GS}}_{\mathrm{max}} - (k_B/e) \times \left[\tfrac{1}{2}\ln x + \ln 2 - \tfrac{1}{2} + \mathcal{O}(x^{-1})\right], \text{ with } x = \Delta/2k_BT \gg 1.$$

[*Rut, Suszalski, AR, in preparation*]

Thermoelectric figure of merit

$$ZT = \frac{\sigma S^2 T}{\kappa_{\rm el} + \kappa_{\rm ph}},$$

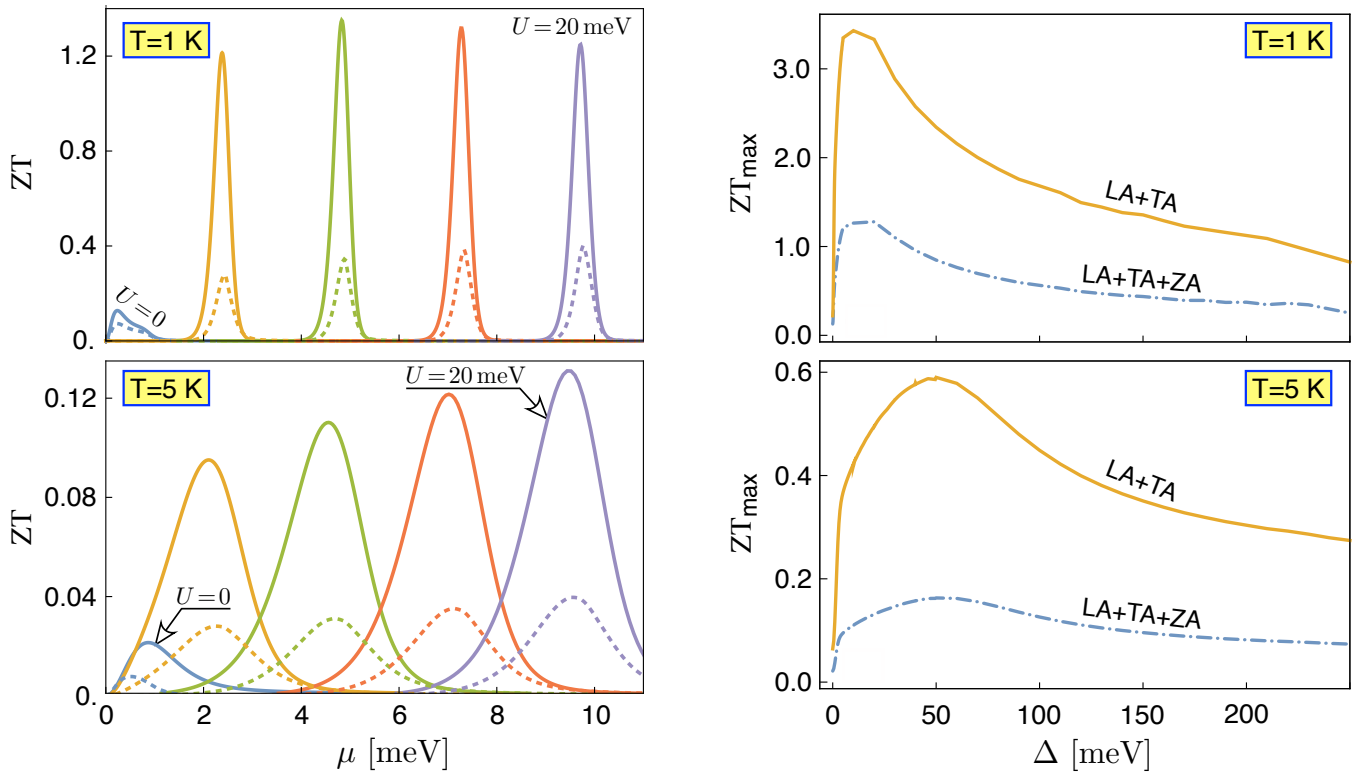
where σ is the electrical conductivity, S-the Seebeck coefficient, $\kappa_{\rm el}$ ($\kappa_{\rm ph}$) - electronic (phononic) part of the thermal conductivity.

In the linear-responce regime, one can roughly approximate the maximal **energy conversion efficiency**

$$\eta = \frac{P_{\rm el}}{I_Q} \approx \frac{1}{4} ZT \frac{\Delta T}{T} \left(= \frac{ZT}{4} \eta_\star \right)$$

(for $\Delta T \ll T$), with $P_{\rm el}$ – the maximal (*usefull*) electric power and I_Q – the thermal current [*see*: Kim et al., PNAS **112**, 8205 (2015)].

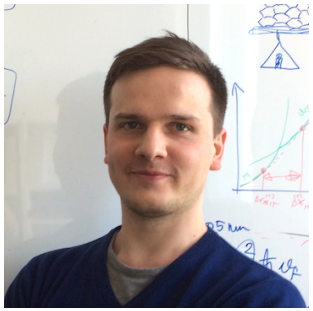
For instance, $ZT = 3$, $\Delta T = 100\,\mathrm{K}$ and $T = 300\,\mathrm{K}$ gives $\eta \approx 0.25$, comparable with $\eta_\star = 0.33$ for a perfect Carnot engine.



$\boxed{ZT = S^2\sigma T/\kappa}$, with $\kappa = \kappa_{\rm el} + \kappa_{\rm ph}$. We have $\mu^{ZT}_{\rm max} \approx \Delta/2$; in contrast: $\mu^{S}_{\rm max} \approx \frac{1}{2}k_BT\ln(2\Delta/k_BT) \ll \Delta/2$. In effect, $ZT_{\rm max}$ is sensitive to $T(E)$ details near the band boundary and **does not grow monotonically with Δ** (like $|S|_{\rm max}$). Instead, **ZT reaches a global maximum** for $\Delta_{\rm max} \sim 10^2 k_BT$. [*Rut, Suszalski, AR, in preparation*]

Acknowlegments

The group:



Grzegorz Rut Dominik Suszalski

Former collaboration: Anton Akhmerov, Jens Bardarson, Carlo Beenakker, Patrik Recher, Klaus Richter, Björn Trauzettel, Jakub Tworzydło, Michael Wimmer, . . .

Funding:

Project web site: http://th.if.uj.edu.pl/∼adamr/sonata.html

See also: Suszalski et al., **POSTER NO. 15**

Rut et al., **POSTER NO. 13**

THANK YOU!