Detection of topological phase transitions through entropy measurements

Valeriy Gusynin

Bogolyubov Institute for Theoretical Physics, Kyiv, Ukraine
of the National Academy of Sciences of Ukraine

Conference on Modern Concepts and New Materials for Thermoelectricity
ICTP, Italy, March 14, 2019

In collaboration with: Y. Galperin, D. Grassano, A. Kavokin, A. Varlamov, O. Pulci, S. Sharapov, V. Shubnyi

Table of contents

Entropy per particle

Internal energy for a varying particle number:

$$d\mathcal{E}(S, V, N) = TdS - PdV + \mu dN,$$

where the entropy, $dS = \frac{\delta Q}{T}$ with δQ being the heat.
Entropy is important not only for describing thermodynamical experiments, but also in interpreting heat transport experiments, e.g. Seebeck and Nernst - Ettingshausen effects are characterized by the entropy per particle:

$$s = \left(\frac{\partial S}{\partial N}\right)_T = \frac{1}{V}\left(\frac{\partial S}{\partial n}\right)_T,$$

set $V = 1$ and use instead of carrier number N the carrier density n.

Entropy per particle via Maxwell relation

System in the thermostat described by the Gibbs free energy: $dG(T,P,N) = d(\mathcal{E} - TS + PV) = -SdT + VdP + \mu dN$, so that

$$\left(\frac{\partial G}{\partial T}\right)_{p,n} = -S, \qquad \left(\frac{\partial G}{\partial n}\right)_{T,p} = \mu$$

Maxwell relation,

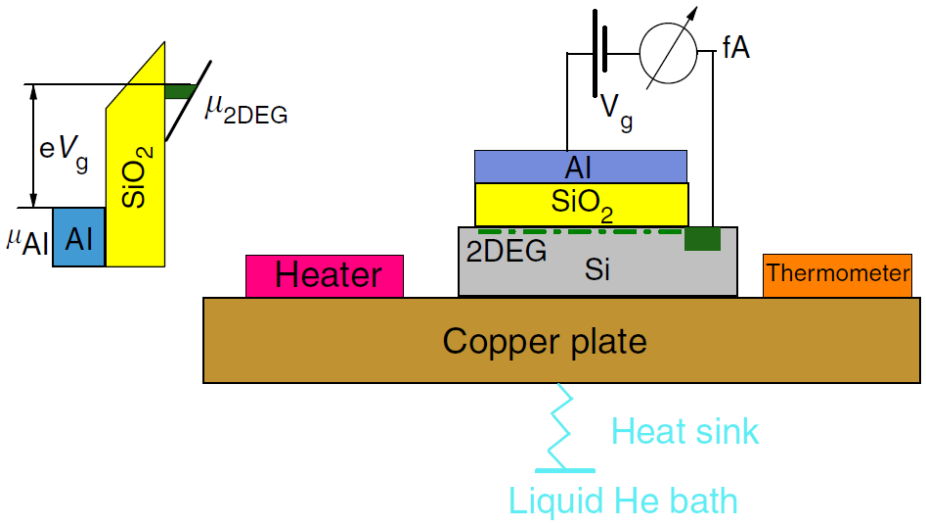
$$s = \left(\frac{\partial S}{\partial n}\right)_{T} = -\left(\frac{\partial \mu}{\partial T}\right)_{n}$$

makes entropy per particle measurable quantity.

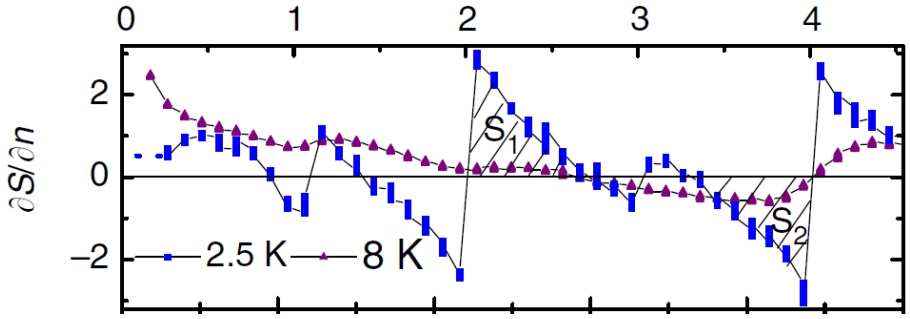
A.Y. Kuntsevich, Y.V. Tupikov, V.M. Pudalov, I.S. Burmistrov, "Strongly correlated two-dimensional plasma explored from entropy measurements", Nature Commun. **6**, 7298 (15).

Thermodynamic method to measure the entropy per electron in gated structures. Technique appears to be three orders of magnitude superior in sensitivity to a.c. calorimetry, allowing entropy measurements with only 10^8 electrons.

Measuring entropy per particle



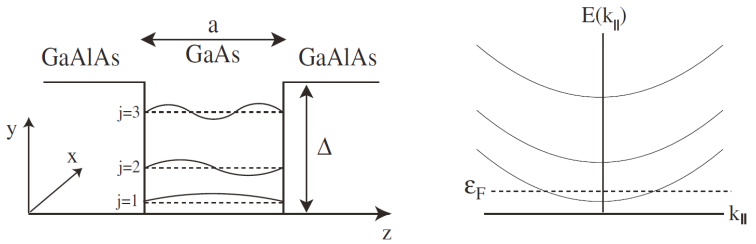
Example of the measurements in Si-MOS structures. Magnetic field applied $\perp$ to the structure $B = 9T$

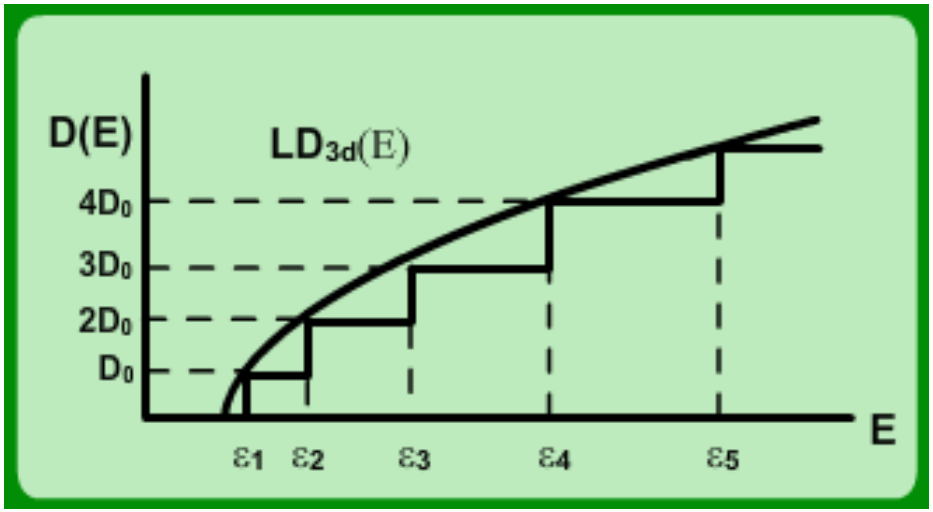


$\partial S/\partial n$ versus electron density ($10^{11}\mathrm{cm}^{-2}$).

Modulation of the sample temperature $T(t) = T_0 + \Delta T \cos(\omega t)$ changes the chemical potential and causes recharging of the gated structure. The derivative $\partial\mu/\partial T$ is directly determined in the experiment from the measured recharging current: $i(T) = \frac{\partial\mu}{\partial T}\Delta T \omega C \sin(\omega t)$. Here, C stands for the capacitance between the gate electrode and 2D electron layer, $\Delta T \sim 0.1K$, $\omega/(2\pi) \sim 0.5Hz$.

Quasi-two-dimensional electron gas





Electron subbands in the quasi-2D electron gas: $\varepsilon_j(\mathbf{k}) = E_j + \frac{\hbar^2 k_\parallel^2}{2m^*}$.
In the absence of scattering, the density of electronic states in a non-interacting 2DEG has a staircase-like shape

$$D(\varepsilon) = \frac{m^*}{\pi\hbar^2} \sum_{j=1}^{\infty} \theta\left(\varepsilon - E_j\right).$$

Electronic topological transition or Lifshitz transition in quasi-2DEG, $\delta D(\varepsilon) = C\theta(E - E_c)$.
The presence of impurities results in the level broadening:

$$\theta'(\varepsilon) = \delta(\varepsilon) \to \delta_\gamma(\varepsilon) \equiv \frac{\gamma}{\pi(\varepsilon^2 + \gamma^2)},$$

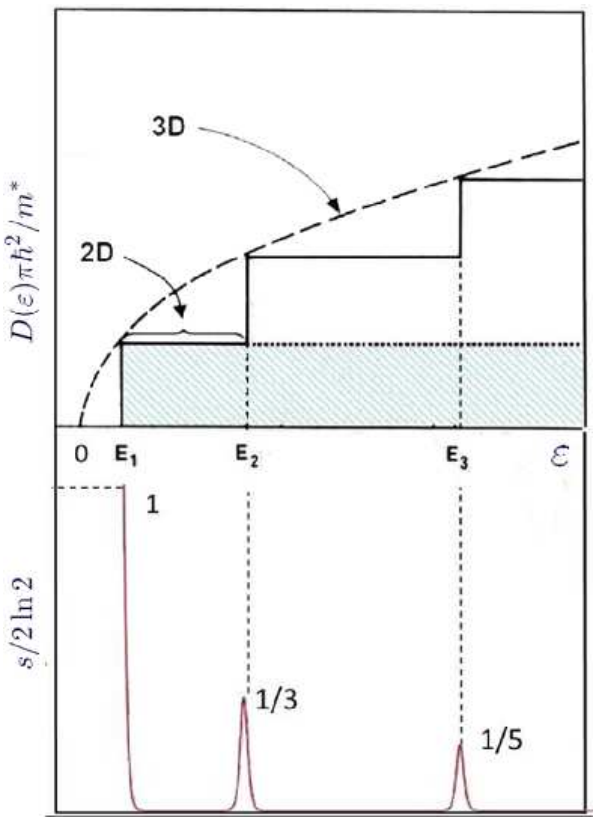
where $\hbar/\gamma$ is a finite life-time. The steps of the DOS are smeared $\theta_\gamma(\varepsilon) = \frac{1}{2} + \frac{1}{\pi}\arctan\left(\frac{\varepsilon}{\gamma}\right)$.

Quantization of entropy per particle

Formal matters :

$$s = -\left(\frac{\partial \mu}{\partial T}\right)_n = \left(\frac{\partial n}{\partial T}\right)_\mu \left(\frac{\partial n}{\partial \mu}\right)_T^{-1}, \quad n(\mu, T) = \int_{-\infty}^{+\infty} \frac{D(\varepsilon)}{\exp\left(\frac{\varepsilon-\mu}{T}\right)+1}\, d\varepsilon.$$

A. Varlamov, A. Kavokin, and Y. Galperin, PRB **93**, 155404 (16).



The value of the entropy per particle in the N-th maximum depends *only* on the size-quantization quantum number N:

$$s(T \to 0)|_{\mu=E_n} = \frac{\ln 2}{N - 1/2} \qquad k_B = 1.$$

In the absence of scattering this result is independent of the shape of the transversal potential that confines 2DEG and of the material parameters including the electron effective mass and dielectric constant.

Exact formulas for 2DEG at finite temperature and scattering rate

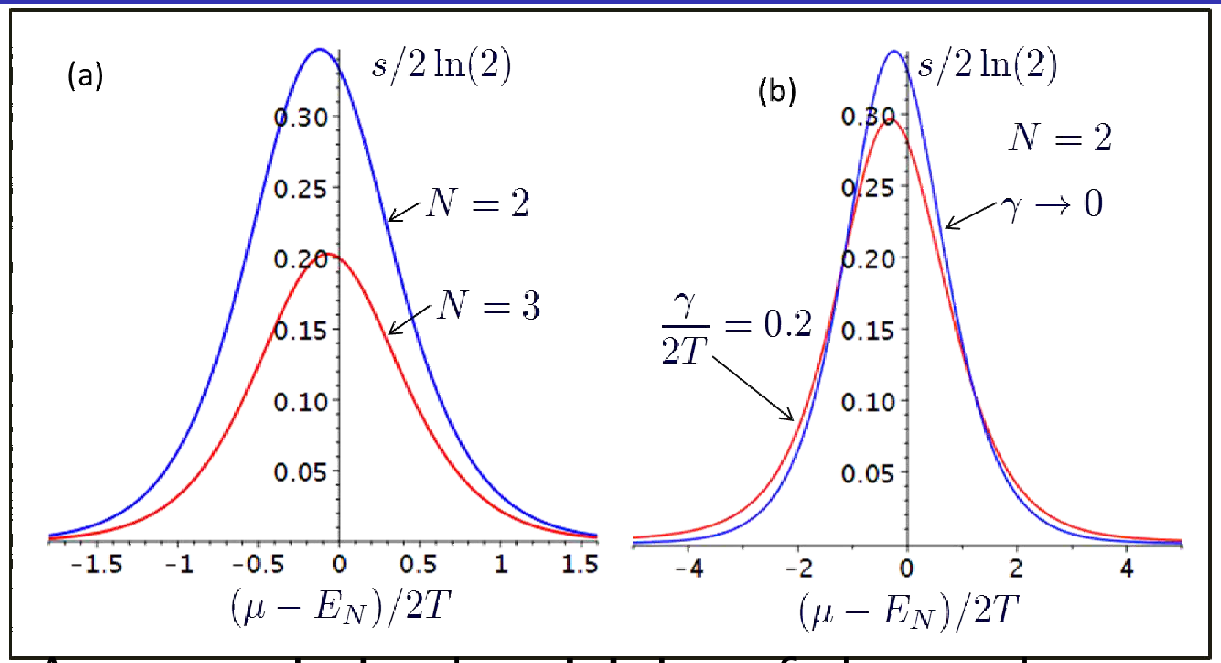
$$\left(\frac{\partial n}{\partial T}\right)_{\mu} = \frac{2m^*}{\pi\hbar^2}\sum_{j=1}\mathrm{Re}\left[\frac{\gamma+i(\mu-E_j)}{2T}\Psi\left(\frac{1}{2}+\frac{\gamma+i(\mu-E_j)}{2\pi T}\right)\right.$$

$$\left. - \frac{\gamma}{2T} - \pi\ln\left\{\Gamma\left(\frac{1}{2}+\frac{\gamma+i(\mu-E_j)}{2\pi T}\right)\right\} + \frac{\pi}{2}\ln(2\pi)\right],$$

$$\left(\frac{\partial n}{\partial \mu}\right)_{T} = \frac{m^*}{2\pi\hbar^2}\sum_{j=1}\left\{1+\frac{2}{\pi}\mathrm{Im}\Psi\left(\frac{1}{2}+\frac{\gamma+i(\mu-E_j)}{2\pi T}\right)\right\},$$

where $\Psi(z)$ is the digamma function. We have taken into account that $\mu \gg T$. The general expression for entropy per particle in the quasi-2DEG can be calculated from the above expressions.

Role of temperature and disorder



Dependence of the entropy per particle, s, on $(\mu - E_N)/2T \equiv \delta_N/2T$ for (a) $N = 2, 3$; $\gamma \to 0$; (b) $N = 2$; $\gamma/2T = 0, 0.2$.

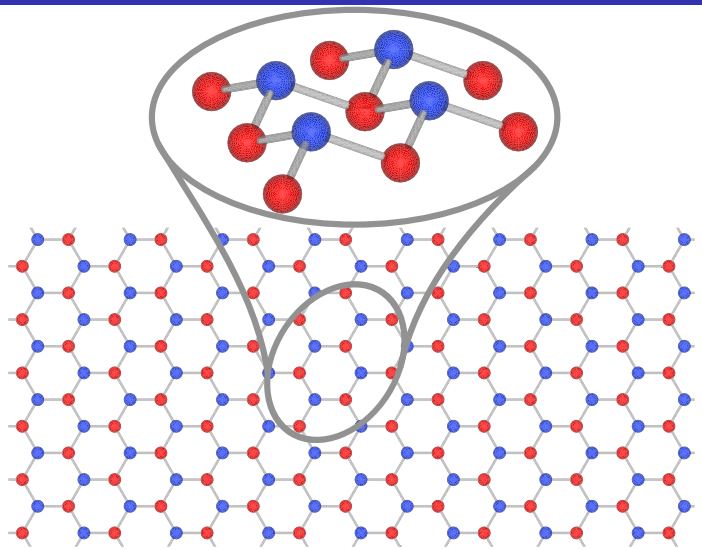
Asymptotic in the vicinity of the peak:

$$s(\mu = E_N + \delta_N) = \begin{cases} \frac{|\delta_N|}{T} \frac{\exp\left(-\frac{|\delta_N|}{T}\right)}{N-1+\exp\left(-\frac{|\delta_N|}{T}\right)}, & \delta_N \ll -T, \\ \frac{\ln 2}{N-1/2}, & 0 < \delta_N \ll T, \\ \frac{\delta_N}{TN} \exp(-\delta_N/T), & \delta_N \gg T. \end{cases}$$

The peak is suppressed by the elastic scattering of electrons:

$$s|_{\mu=E_N} = \frac{\ln 2 - (\gamma/\pi T)}{N - 1/2}.$$

Low-buckled Dirac materials

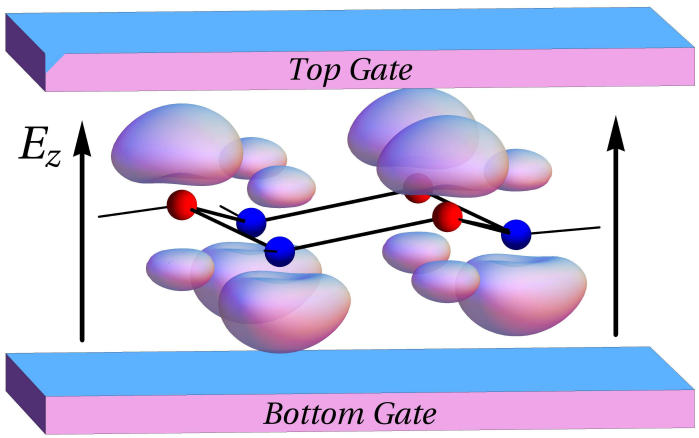


Silicene: vertical distance between sublattices $2d \approx 0.46$Å. Lattice constant $a = 3.87$Å. So far grown on metallic substrates Ag, Au, Pt, Al, as well as less interactive substrates such as MoS_2 (gap $\sim 1.23 - 1.8$eV). 2D sheets of Ge, Sn and P atoms (germanene, stanene and phosphorene). No transport measurements yet.

The same hexagonal lattice as in graphene, but due to buckling there is also a strong intrinsic spin-orbit interaction

$$H_{SO} = i\frac{\Delta_{SO}}{3\sqrt{3}} \sum_{\substack{\langle\langle i,j\rangle\rangle \\ \sigma\sigma'}} c^{\dagger}_{i\sigma}(\boldsymbol{\nu}_{ij}\cdot\boldsymbol{\sigma})_{\sigma\sigma'} c_{j\sigma'},$$

$\nu^z_{ij} = \pm 1$, $\Delta_{SO} \approx 4.2meV$ in silicene, $\Delta_{SO} \approx 11.8meV$ in germanene.



Perpendicular to the plane electric field E_z opens the tunable gap $\Delta_{el} = E_z d$. Interplay of two gaps: Δ_{SO} and Δ_{el}.

Low-energy Hamiltonian of silicene

$$\mathcal{H}_\eta = \sigma_0 \otimes [\hbar v_F(\eta k_x \tau_1 + k_y \tau_2) + \Delta_{el}\tau_3] - \eta \Delta_{SO} \sigma_3 \otimes \tau_3,$$

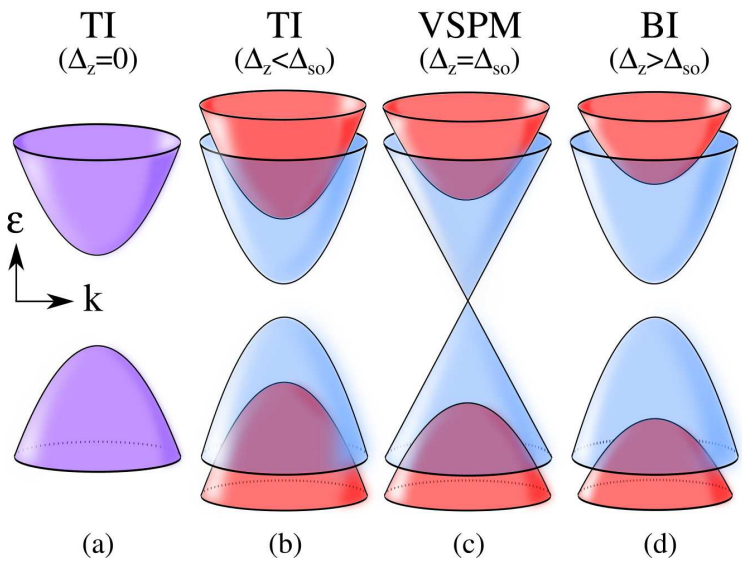
$\boldsymbol{\tau}$ and $\boldsymbol{\sigma}$ – sublattice and spin; $\mathbf{k}$ is measured from the $\mathbf{K}_\eta$ points.
There is a spin $\sigma = \pm$, and valley $\eta = \pm$ dependent gap (or mass $\Delta_{\eta\sigma}/v_F^2$)

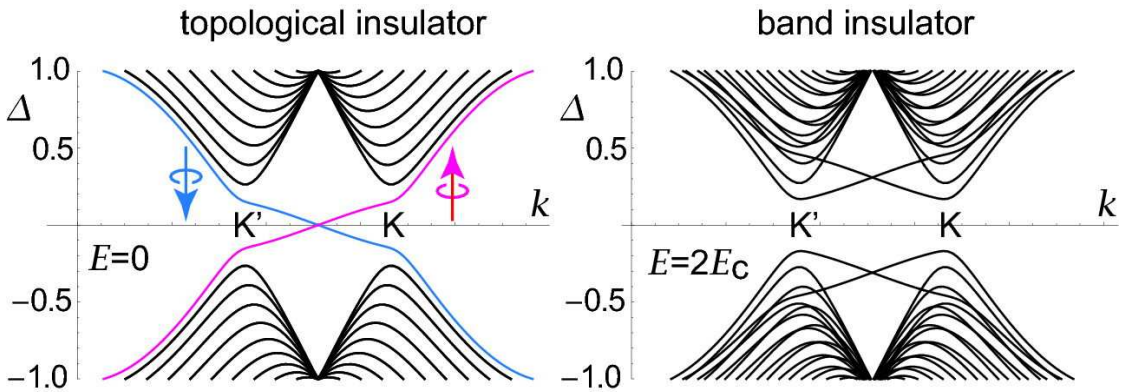
$$\Delta_{\eta\sigma} = \Delta_{el} - \eta\sigma\Delta_{SO}, \qquad \varepsilon_{\eta\sigma}(k) = \pm\sqrt{\hbar^2 v^2 k^2 + \Delta_{\eta\sigma}^2}.$$

C. Liu, W. Feng, and Y. Yao, PRL **107**, 076802 (11); N. Drummond, V. Zólyomi, and V. Fal'ko, PRB **85**, 075423 (12);

M. Ezawa, New J. Phys. **14**, 033003 (12), J. Phys. Soc. Jpn. **81**, 064705 (12).

Time-reversal symmetry (TRS) is unbroken.





The band structure: bulk and edge states in nanoribbons for varying Δ_{el}.

DOS of the Dirac materials

Generic form of the DOS: $D(\varepsilon) = f(\varepsilon) \sum_{i=1}^{M} \theta\left(\varepsilon^2 - \Delta_i^2\right).$

$M = 1$: gapped graphene $\varepsilon(k) = \pm\sqrt{\hbar^2 v_F^2 k^2 + \Delta^2}$ and $f(\varepsilon) = 2|\varepsilon|/(\pi\hbar^2 v_F^2)$ (spin-valley degeneracy is included).

$M = 2$: silicene, germanene, etc. $\varepsilon_{\eta\sigma}(k) = \pm\sqrt{\hbar^2 v_F^2 k^2 + \Delta_{\eta\sigma}^2}$ and $f(\varepsilon) = |\varepsilon|/(\pi\hbar^2 v_F^2)$. $i = 1$ corresponds to $\eta = \sigma = \pm$ with $\Delta_1 = |\Delta_{SO} - \Delta_z|$ and $i = 2$ corresponds to $\eta = -\sigma = \pm$ with $\Delta_2 = |\Delta_z + \Delta_{SO}|$.

Since $D(\varepsilon) = D(-\varepsilon)$, instead of the total density of electrons one operates with the difference between the densities of electrons and holes ($\gamma = 0$):

$$n(T, \mu, \Delta_1, \Delta_2, \ldots, \Delta_M) = \frac{1}{4}\int_{-\infty}^{\infty} d\varepsilon\, D(\varepsilon)\left[\tanh\frac{\varepsilon+\mu}{2T} - \tanh\frac{\varepsilon-\mu}{2T}\right].$$

Clearly, $n(T, \mu) = n(T, -\mu)$, so that $n(T, \mu = 0) = 0$. V. Tsaran, A. Kavokin, S. Sharapov, A. Varlamov, and V.G., Sci. Rep. **7**, 10271 (2017).

Quantization of entropy in Dirac materials

We need $\partial n/\partial T$ and $\partial n/\partial \mu$. For $\Delta_i < |\mu| < \Delta_{i+1}$ and $T \to 0$:

$$\frac{\partial n(T,\mu)}{\partial T} = D'(|\mu|)\frac{\pi^2 T}{3}\,\mathrm{sign}(\mu), \quad \Delta_i > 0.$$

and at the discontinuity points $\mu = \pm\Delta_N$ at $T \to 0$,

$$\left.\frac{\partial n(T,\mu)}{\partial T}\right|_{\mu=\pm\Delta_N} = \pm\left[D(\Delta_N + 0) - D(\Delta_N - 0)\right]\int_0^\infty \frac{x\,dx}{\cosh^2 x} = \pm f(\Delta_N)\ln 2.$$

If $\mu = \pm\Delta_N$ with $N < M$ and $T \to 0$, one obtains

$$\left.\frac{\partial n(T,\mu)}{\partial \mu}\right|_{\mu=\pm\Delta_N} = f(\Delta_N)\sum_{i=1}^{M}\theta(\Delta_N^2 - \Delta_i^2) = f(\Delta_N)(N - 1/2),$$

The entropy per particle in Dirac materials is

$$s(T \to 0, \mu = \pm\Delta_N) = \pm\frac{\ln 2}{N - 1/2}, \quad N = 1, 2, \ldots M.$$

Gapped graphene and silicene: analytics

Carrier imbalance in gapped graphene:

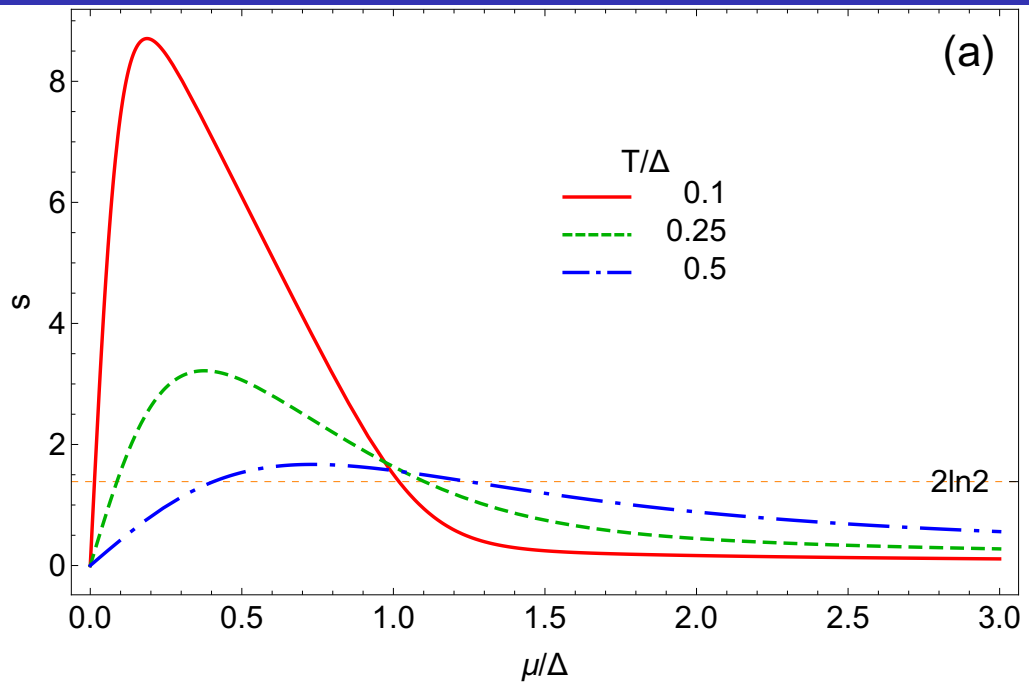
$$n(T,\mu,\Delta)=\frac{2T^2}{\pi\hbar^2 v_F^2}\left[\frac{\Delta}{T}\ln\frac{1+\exp\left(\frac{\mu-\Delta}{T}\right)}{1+\exp\left(-\frac{\mu+\Delta}{T}\right)}+\mathrm{Li}_2\left(-e^{-\frac{\mu+\Delta}{T}}\right)-\mathrm{Li}_2\left(-e^{\frac{\mu-\Delta}{T}}\right)\right]$$

where $\mathrm{Li}_2(x)$ is the dilogarithm function:
$\mathrm{Li}_s(x)=\sum_{k=1}^{\infty}\frac{z^k}{k^s}, \quad \mathrm{Li}_\nu(1)=\zeta(\nu)$.
E. Gorbar, V.G., V. Miransky, and I. Shovkovy, PRBB 66, 045108 (2002).
The Fermi-Dirac integral

$$F_\alpha(\mu)=\int_0^\infty d\epsilon\frac{\epsilon^\alpha}{e^{\epsilon-\mu}+1}=-\alpha\Gamma(\alpha)\mathrm{Li}_{\alpha+1}(-e^\mu).$$

One can consider silicene as a superposition of two gapped graphene layers characterized by different gaps:
$n(T,\mu,\Delta_1,\Delta_2)=1/2\left[n(T,\mu,\Delta_1)+n(T,\mu,\Delta_2)\right].$

Results: gapped graphene



The entropy per electron s vs the chemical potential $\mu > 0$, $s(-\mu) = -s(\mu)$.

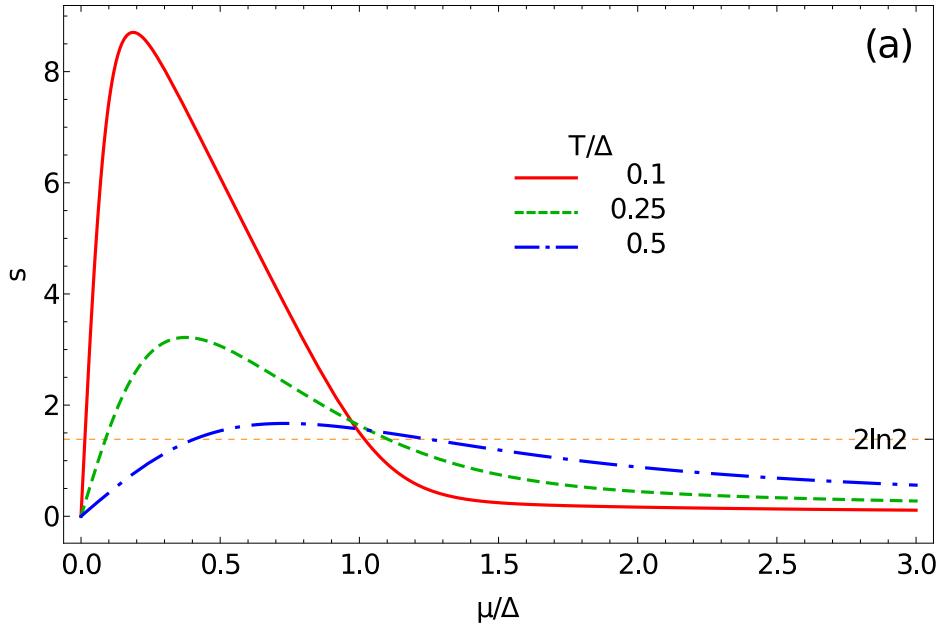
⊛ The most prominent feature is a sharp peak observed for the chemical potential in the temperature vicinity of the Dirac point, $|\mu| \sim T$.

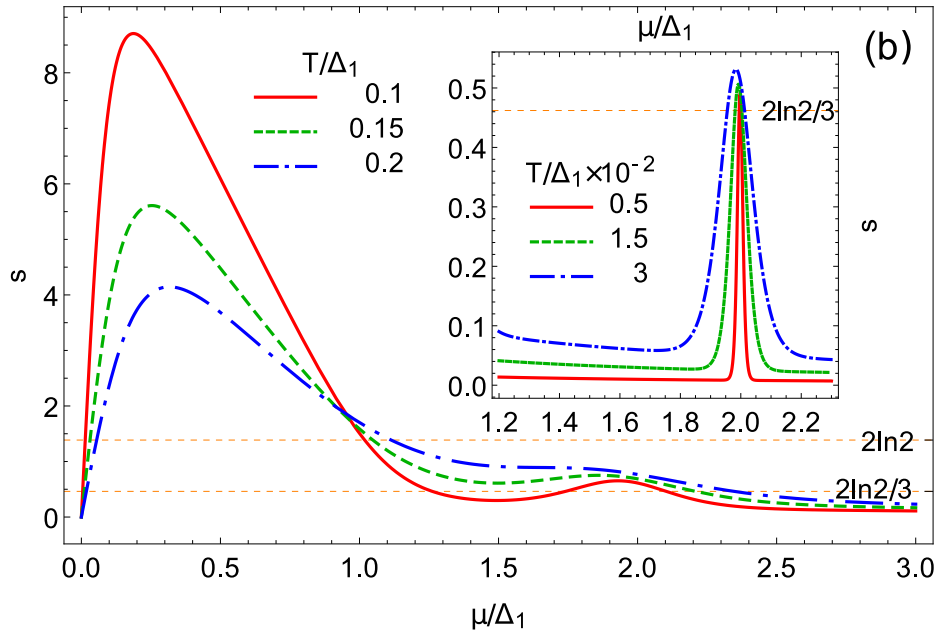
Near the Dirac point:

$$s(T, \mu, \Delta) \simeq \frac{\mu\Delta}{T^2}\left[1 + O(e^{-\Delta/T})\right], \qquad |\mu| \ll T \ll \Delta.$$

⊛ Near $\mu = \pm\Delta$, the dependence $s(\mu)$ is monotonic function, no spikes (the DOS has just one discontinuity).

Results: gapped graphene vs silicene





The entropy per electron $s(-\mu) = -s(\mu)$. Left: (a): Gapped graphene. Right: (b): Silicene. The vicinity of $\mu = \Delta_2 = 2\Delta_1$ is shown in the insert.

⊛ The presence of the second gap in silicene, germanene and similar materials, $\Delta_2 > \Delta_1$, results in the appearance of the peak in $s(\mu)$:

$$s(T, \mu = \pm\Delta_2) = \pm\left[\frac{2\ln 2}{3} + \frac{\pi^2 - 4\ln^2 2}{9}\frac{T}{\Delta_2}\right], \qquad T \ll \Delta_2.$$

Case of gapless graphene: $\Delta = 0$

$$s(T,\mu,0) = \begin{cases} \frac{\mu}{T}\left(1 - \frac{\mu^2}{T^2}\frac{1}{6\ln 2}\right), & |\mu| \ll T, \\ \frac{\pi^2}{3}\frac{T}{\mu}, & T \ll |\mu|. \end{cases}$$

The second line by the factor k_B/e yields the Seebeck coefficient for a free electron gas: $S = -\frac{\pi^2}{3}\frac{k_B}{|e|}\frac{k_B T}{\mu}$. This is not surprising, because

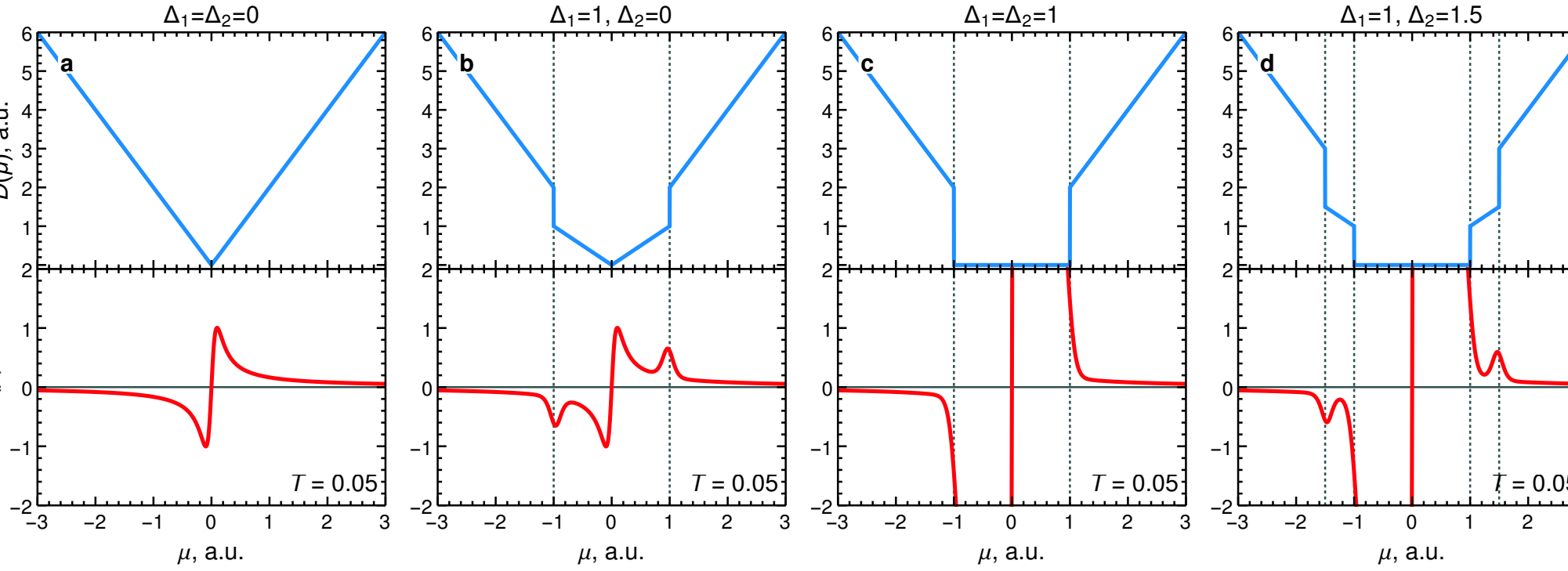
$$s(\mu,T) = \frac{1}{T}\frac{\int_{-\infty}^{\infty} d\varepsilon\, D(\varepsilon)(\varepsilon-\mu)\cosh^{-2}\left(\frac{\varepsilon-\mu}{2T}\right)}{\int_{-\infty}^{\infty} d\varepsilon D(\varepsilon)\,\cosh^{-2}\left(\frac{\varepsilon-\mu}{2T}\right)}$$

compared to the thermal power

$$S_{\mathrm{TP}} = -\frac{k_B}{|e|\,T}\frac{\int_{-\infty}^{\infty} d\varepsilon\,(\varepsilon-\mu)\sigma(\varepsilon)\cosh^{-2}\left(\frac{\varepsilon-\mu}{2k_B T}\right)}{\int_{-\infty}^{\infty} d\varepsilon\sigma(\varepsilon)\,\cosh^{-2}\left(\frac{\varepsilon-\mu}{2k_B T}\right)}, \sigma(\varepsilon) = v_F^2(\varepsilon)\tau(\varepsilon)D(\varepsilon).$$

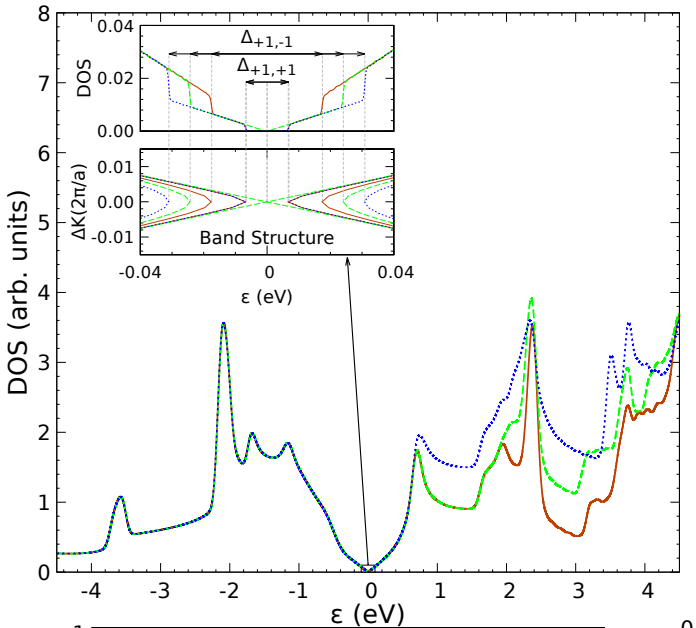
When one of the gaps turns to zero, the peak near the Dirac point becomes less sharp: compare $\sim 1/T$ vs $\sim 1/T^2$. Of course, thermodynamics does not allow to distinguish topological and band insulators.

How to detect topological transition?

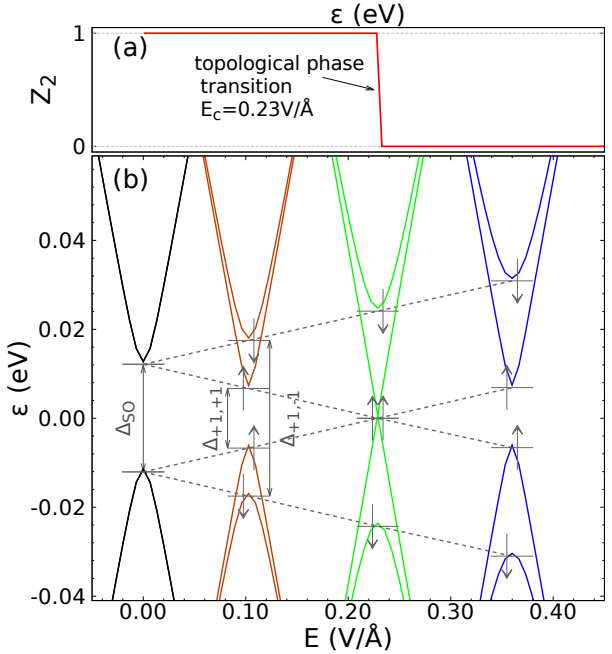


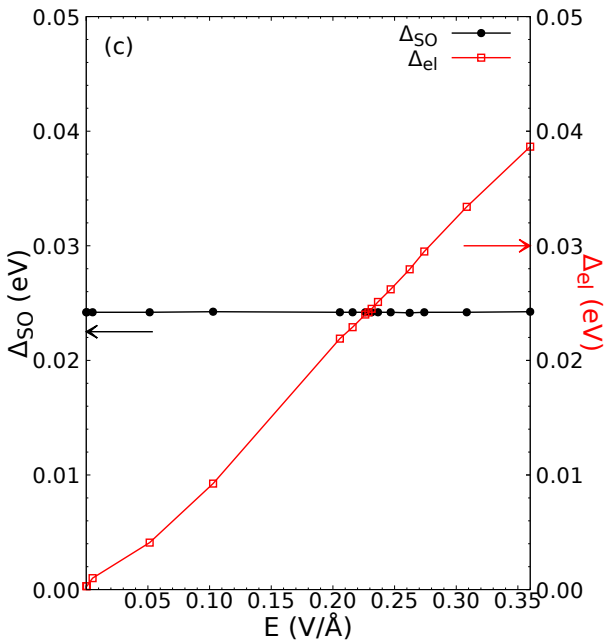
The correspondence between the shape of the DOS shown in the top and behavior of $s(\mu)$ shown underneath. (a) Massless Dirac fermions in graphene. (b) Silicene and others at the point of topological transition. (c) Two gaps are equal to each other. (d) Two different gaps.

Ab initio calculations of the DOS in germanene



DOS and band structure computed within the DFT for the external electric fields E_z below/at/above the critical value E_c: $E = 0.10 V/Å$ (orange solid line), $0.23 V/Å$ (green dashed line) and $0.36 V/Å$ (blue dotted line). The zero denotes the Fermi energy.

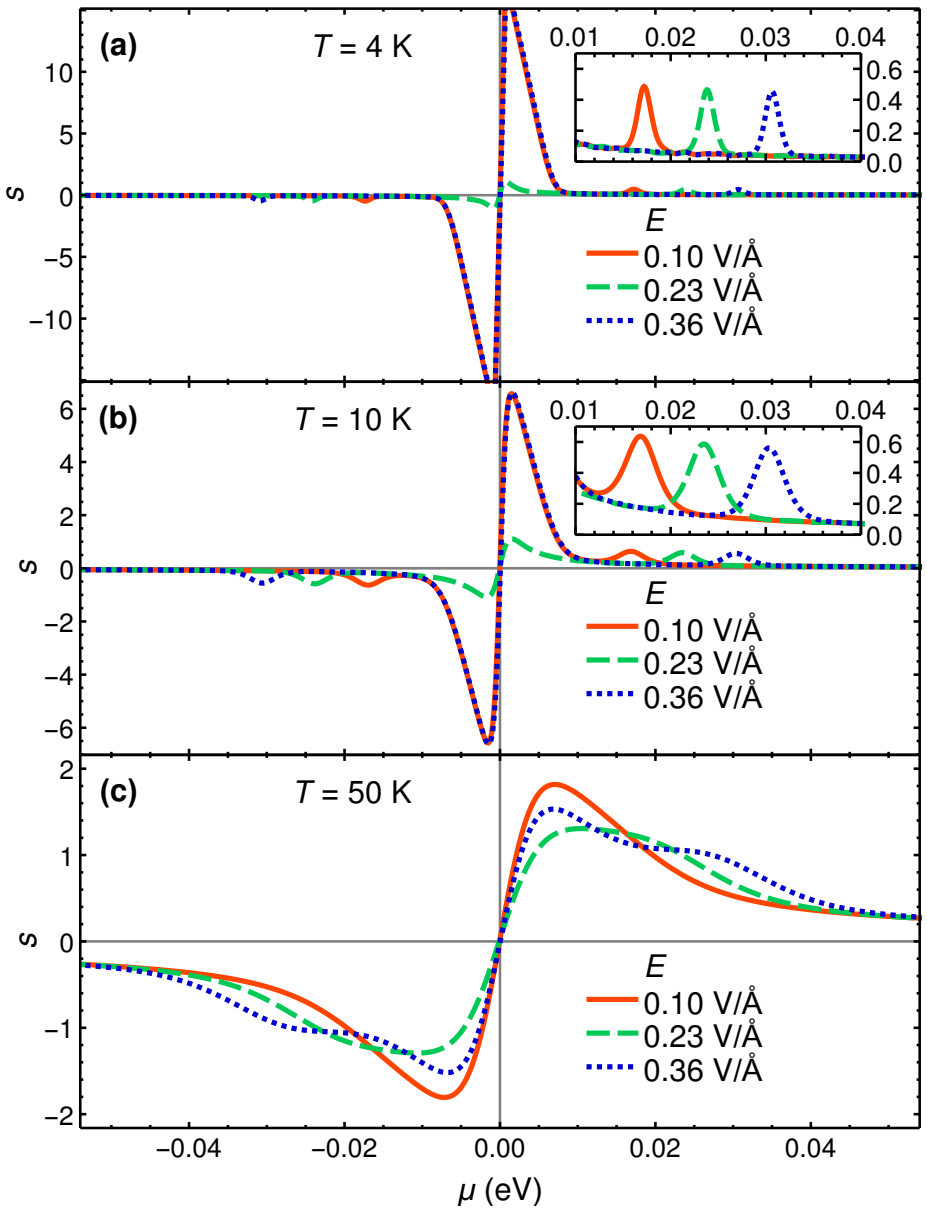




Topological invariant (Z_2), $2\Delta_{SO} \sim 24 meV$ and Δ_{el} as functions of E_z.

D. Grassano, O. Pulci, V. Shubnyi S. Sharapov, V.G., A. Kavokin, A. Varlamov, PRB 97, 205442 (18).

Numerical experiment



$s(\mu)$ in the vicinity of the Dirac point. Green line for the critical field, $E_c = 0.23 V/\AA$.

⊛ The most prominent is that the strong resonant feature of s in the close vicinity of $\mu = 0$ is nearly fully suppressed at E_c.

Insets in (a) and (b) show the zoomed domains with the entropy spikes of the height $s = 2 \ln 2/3$ at low temperatures.

Transition-metal dichalcogenides

The effective Hamiltonian for monolayer compounds MX_2 (M = Mo, W is a transition metal, and X = S, Se, Te is a chalcogen atom):

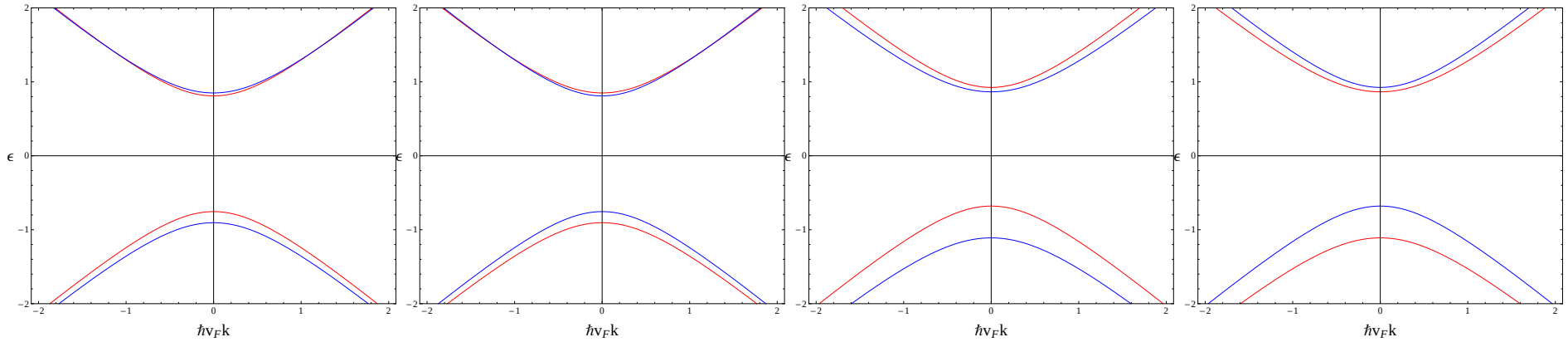
$$H = \sum_{\tau=\pm 1} \left[\hbar v_F (\tau k_x \sigma_x + k_y \sigma_y) + \frac{\Delta}{2}\sigma_z + \lambda_v \tau \frac{\sigma_0 + \sigma_z}{2} s_z + \lambda_c \tau \frac{\sigma_0 - \sigma_z}{2} s_z \right],$$

s_z is the Pauli matrix for the spin, $\Delta \sim 1 - 2\text{eV}$, $v_F \sim 0.5 \times 10^6 \text{m/s}$ $2\lambda_v \sim 150 - 500\text{eV}$ is the spin splitting at the valence-band top caused by the spin-orbit coupling, $2\lambda_c$ is the spin splitting at the conduction-band bottom. DFT calculations show that $2\lambda_v \gg |2\lambda_c| \sim 3 - 50\text{meV}$ and $\lambda_c > 0$ for MoX_2 and $\lambda_c < 0$ for WeX_2 compounds.

$$\epsilon_{c,v} = \frac{\lambda_v + \lambda_c}{2}\tau\sigma \pm \sqrt{\hbar^2 v_F^2 \mathbf{k}^2 + [\Delta - (\lambda_v - \lambda_c)\tau\sigma]^2/4}.$$

Transition-metal dichalcogenides

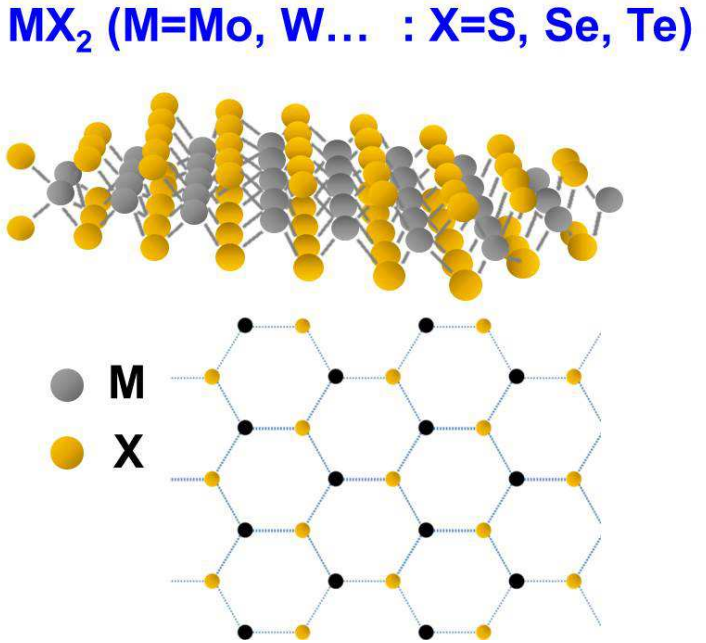
Energy spectra of MoS_2 and WS_2:



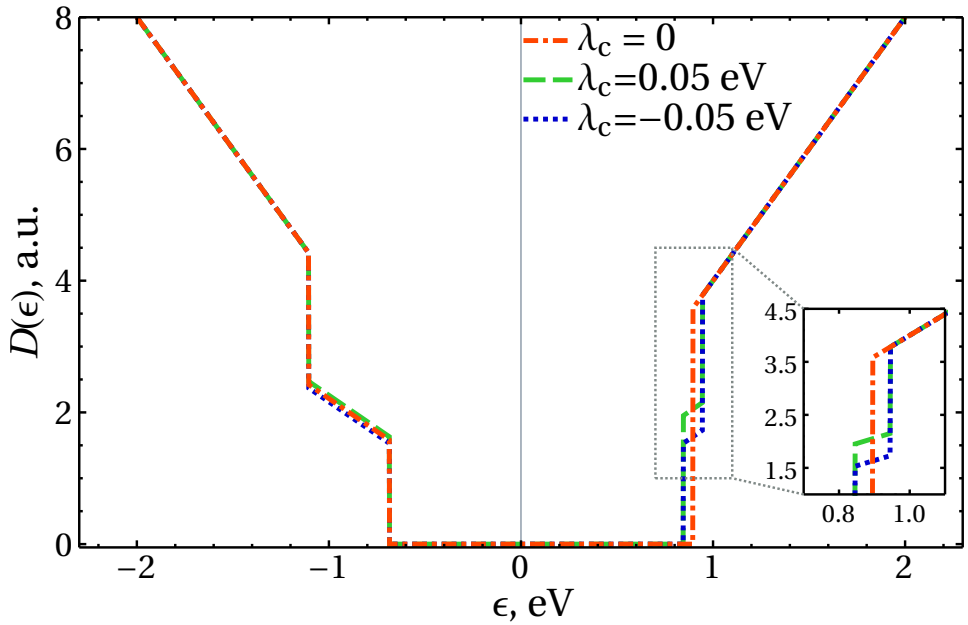
The energy spectrum of the Hamiltonian for the valley $\tau = 1$ and $\tau = -1$ in case of MoS_2 ($\Delta = 1.66$eV, $2\lambda_v = 0.15$eV and $\lambda_c = -0.02$eV) (two left panels) and WS_2 ($\Delta = 1.79$eV, $2\lambda_v = 0.43$eV and $\lambda_c = 0.03$eV) (two right panels). Red and blue lines correspond to spin-up and spin-down, respectively.

Transition-metal dichalcogenides

M = Mo, W is a transition metal, and X = S, Se, Te is a chalcogen atom



More chances to succeed with experiment.



The DOS as the function of energy. The parameters are $\Delta = 1.79\text{eV}$, $2\lambda_v = 0.43\text{eV}$.

$$D(\varepsilon) = \frac{1}{\pi(\hbar v_F)^2}\sum_{i=\pm 1}|\varepsilon - E_i|\,\theta\left[(\varepsilon - E_i)^2 - \Delta_i^2\right]$$

Peaks in s can be observed for higher T due to large band gap, 1eV to 2eV, but there is no quantization of s. V. Shubnyi, V.G., S. Sharapov, and A. Varlamov, Low Temp. Physics (Kharkov) 44, 721 (18).

Concluding remarks

- Entropy per particle is expected to be approximately quantized at $T \to 0$.
- The strong resonant feature of s in the close vicinity of $\mu = 0$ is nearly fully suppressed at the topological transition.
- The interaction effects were neglected. The motion of electrons in graphene can become hydrodynamic when the frequency of electron-electron collisions is much larger than the rates of both electron-phonon and electron-impurity scattering.

Review: Y. Galperin, D. Grassano, V.G, A. Kavokin, O. Pulci, S. Sharapov, V. Shubnyi, A. Varlamov, JETP 127, 958-983 (2018).

THANK YOU FOR ATTENTION!