Chair of Experimental Solid State Physics, LMU Munich

"Introduction to Graphene and 2D Materials"

Outline of lecture 5

→ Everything needed to understand transport experiments on 2D samples

- Cryogenic low-temperature techniques.

- Electronic transport theory – Drude, Hall, Sommerfeld, Boltzmann

- Measurement techniques - 2-terminal vs. 4-terminal measurements, van der Pauw technique, I/V and dI/dV, electric field effect.

- Measurements of graphene devices – resistance and conductivity vs. gate voltage, Hall effect and carrier density, effect of disorder and substrate effects, extraction of electron mobility, mean free path, contact resistance.

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Atomic force image of final graphene device
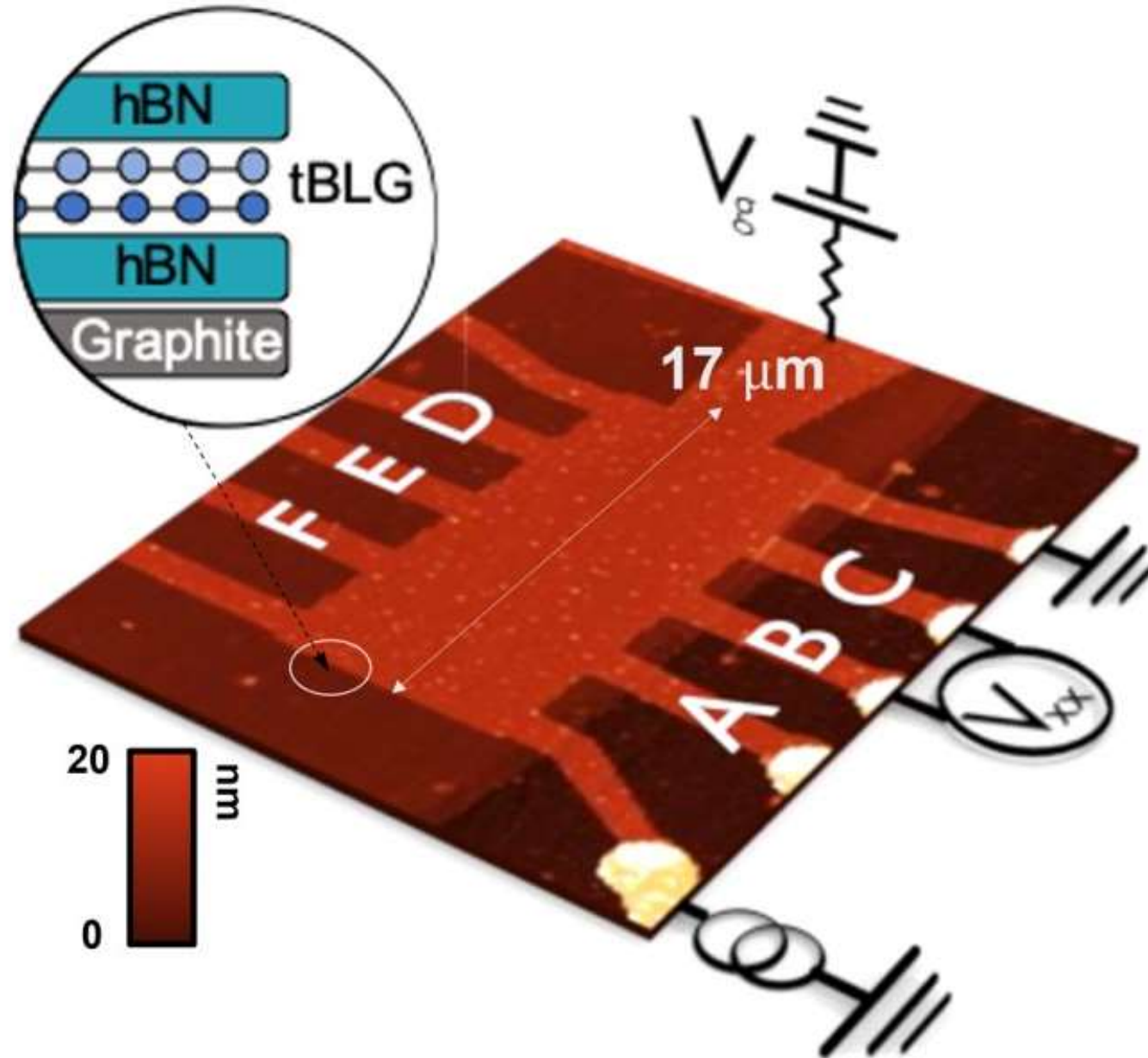
Cooling with cryogenic liquids

Cryogenic fluids:

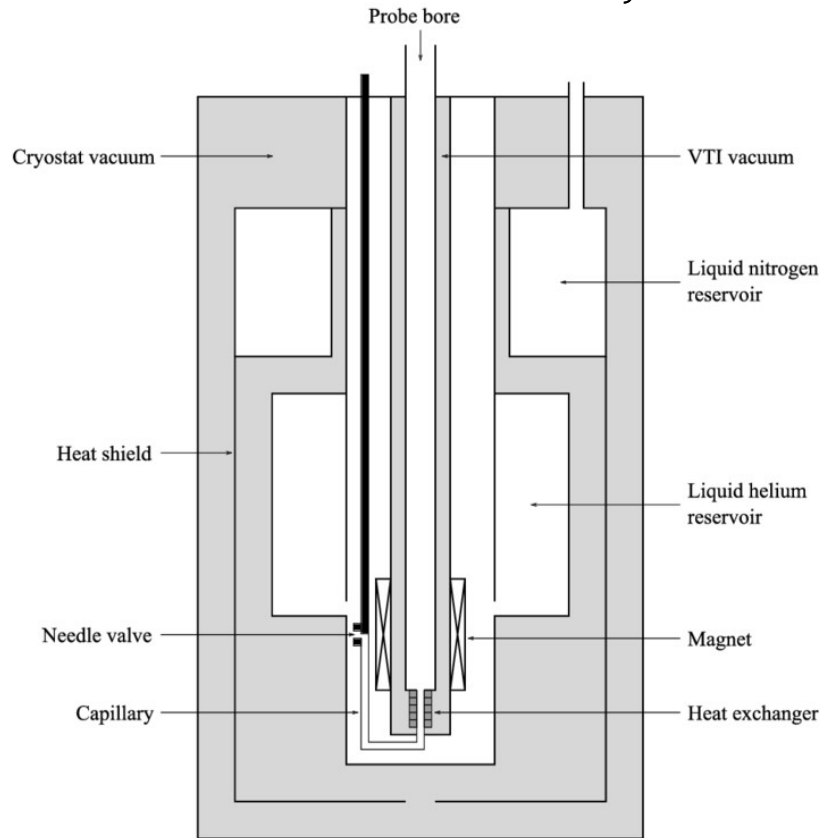| Fluid	Boiling point (K)	Boiling point (°C)
Helium-3	3.19	-269.96
Helium-4	4.214	-268.936
Hydrogen	20.27	-252.88
Neon	27.09	-246.06
Nitrogen	77.09	-196.06
Air	78.8	-194.35
Fluorine	85.24	-187.91
Argon	87.24	-185.91
Oxygen	90.18	-182.97
Methane	111.7	-161.45

Helium 4 phase diagram:
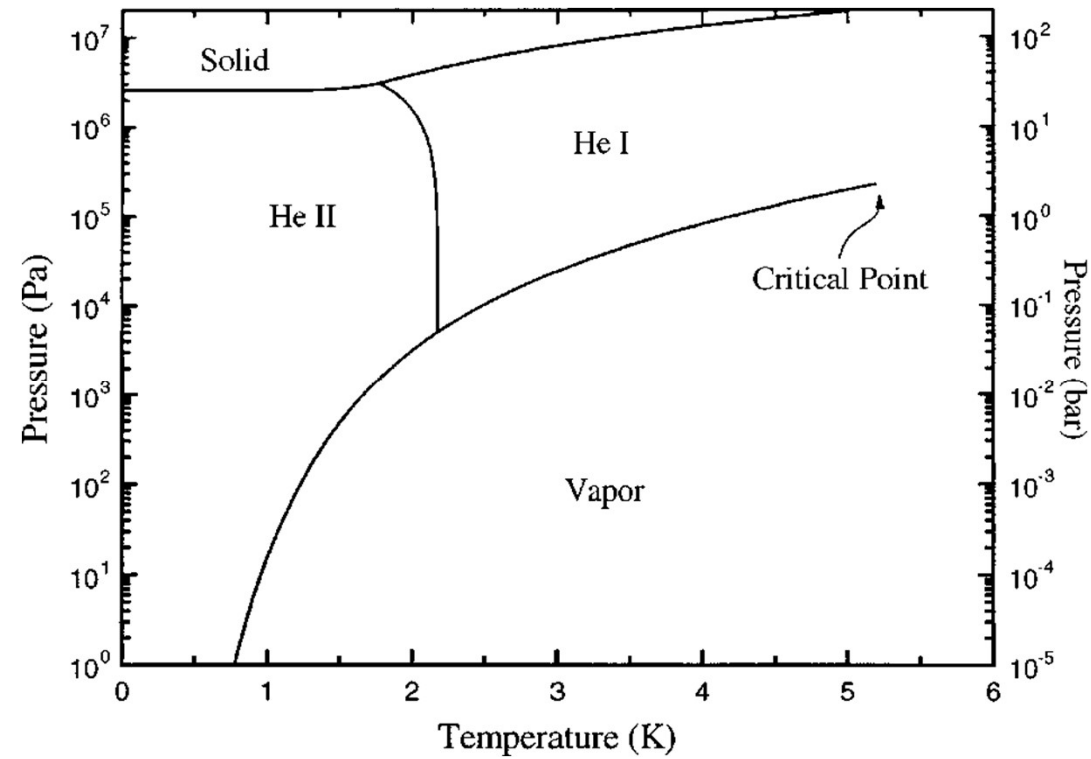
→ Cryogenics is the production and behavior of materials at very low temperatures.

- Evaporative cooling, otherwise known as adiabatic cooling, works on the principle of liquid evaporation, through which the liquid undergoes a phase transition into the gas phase, and in the process loses energy.
- One can use other phase transitions for cooling, such as the He3/He4 phase separation and magnetic phase transitions.

Typical VTI cryostat for ~ T > 1.5K

Crosssection of a VTI cryostat:

Probe bore

Cryostat vacuum — VTI vacuum

Liquid nitrogen reservoir

Heat shield

Liquid helium reservoir

Needle valve — Magnet
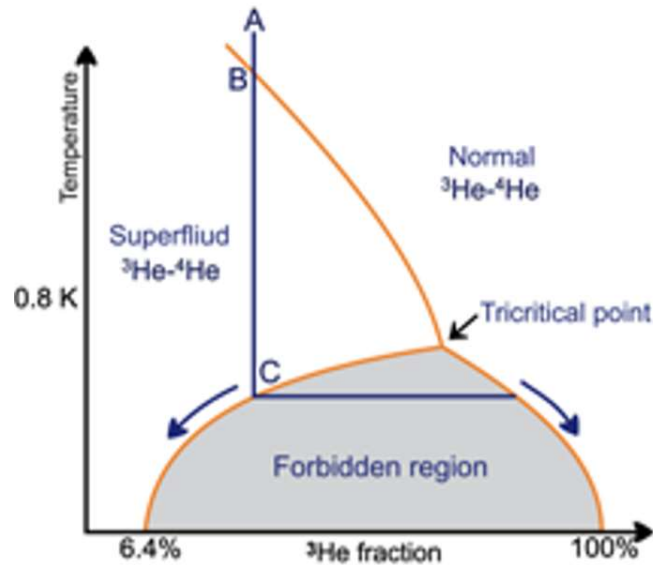
Capillary — Heat exchanger
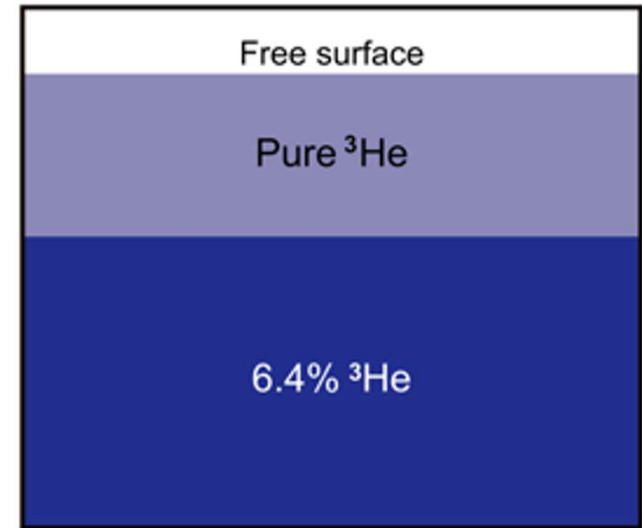
Insert with sample holder and electrical lines:

- A typical variable temperature insert (VTI) is inserted to a cryostat containing liquid helium to cool a superconducting magnet and controls the temperature of the sample.

- The VTI operates by drawing liquid helium through a needle valve. The liquid He-4 passes through a heat exchanger into the sample space and is then pumped away by a room temperature vacuum pump. An integral heater and sensor on the heat exchanger allows the temperature to be set to any value from 1.6 to 320K.

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3He - 4He mixtures

## 3He - 4He phase diagram:

Phase separation of 3He - 4He :

- Pure 4He, with a nuclear spin of I = 0, obeys Boson statistics and forms a superfluid at 2.17 K.

- Pure 3He, with a nuclear spin of I =1/2, obeys Fermi statistics and undergoes a superfluid transition until much lower temperatures at which the spins pair up and then they also obey Boson statistics.

- The superfluid transition temperature of a 3He - 4He mixture depends on the 3He concentration.

- When this is cooled down from point A to the temperature at point B, it undergoes a superfluid transition. If we cool the mixture further to point C, it separates into two phases with the 3He-rich phase floating on top of the heavier 4He-rich phase.

- The 4He-rich phase (the 'dilute' phase) contains 6.4% 3He all the way down to 0 K. This finite solubility of 3He in 4He is the key to dilution refrigeration.

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Dilution refrigerator for ~ T < 10mK

Cooling stages of a dilution refrigerator:
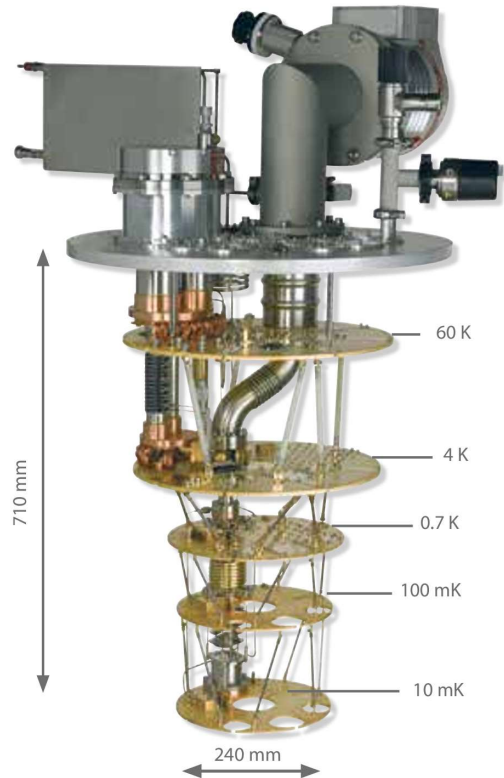
3He - 4He circulation cycle:
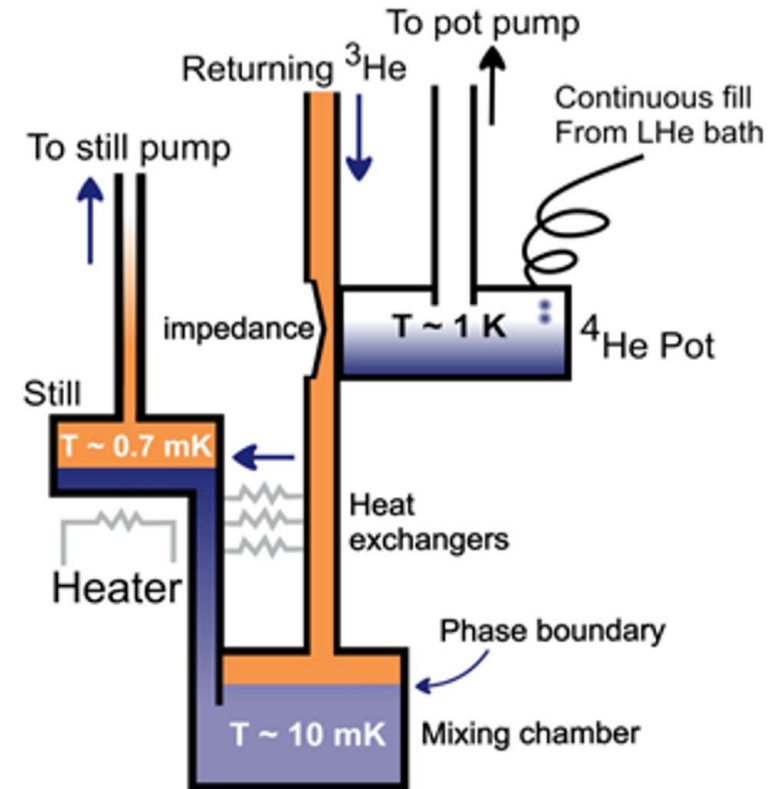

→ A 3He/4He dilution refrigerator is a cryogenic device that provides continuous cooling to temperatures as low as 2 mK, where the cooling power is provided by the heat of mixing of the helium-3 and helium-4 isotopes.

- As we pump 3He vapour from the liquid inside the still, the 3He concentration in the liquid will decrease.

- The difference in 3He concentration between the still and the mixing chamber results in an osmotic pressure gradient along the connecting tube, this pulls 3He from the mixing chamber.

- The 'dilution process' of 3He moving across the phase boundary is equivalent to an upside-down evaporator.

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Electronic transport in graphene

Band-structure:
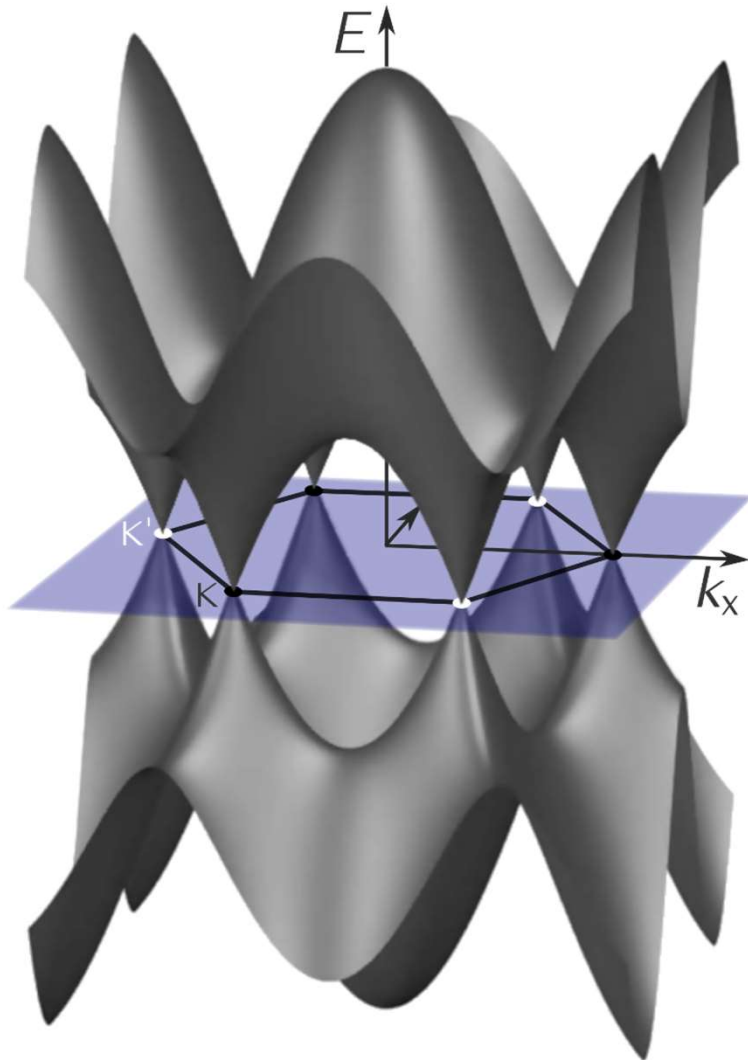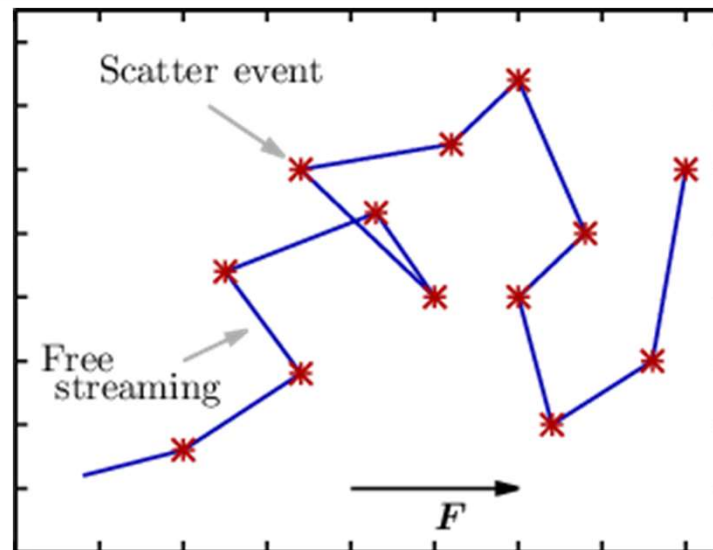

R_{xx} and R_{xy} vs. gate voltage:
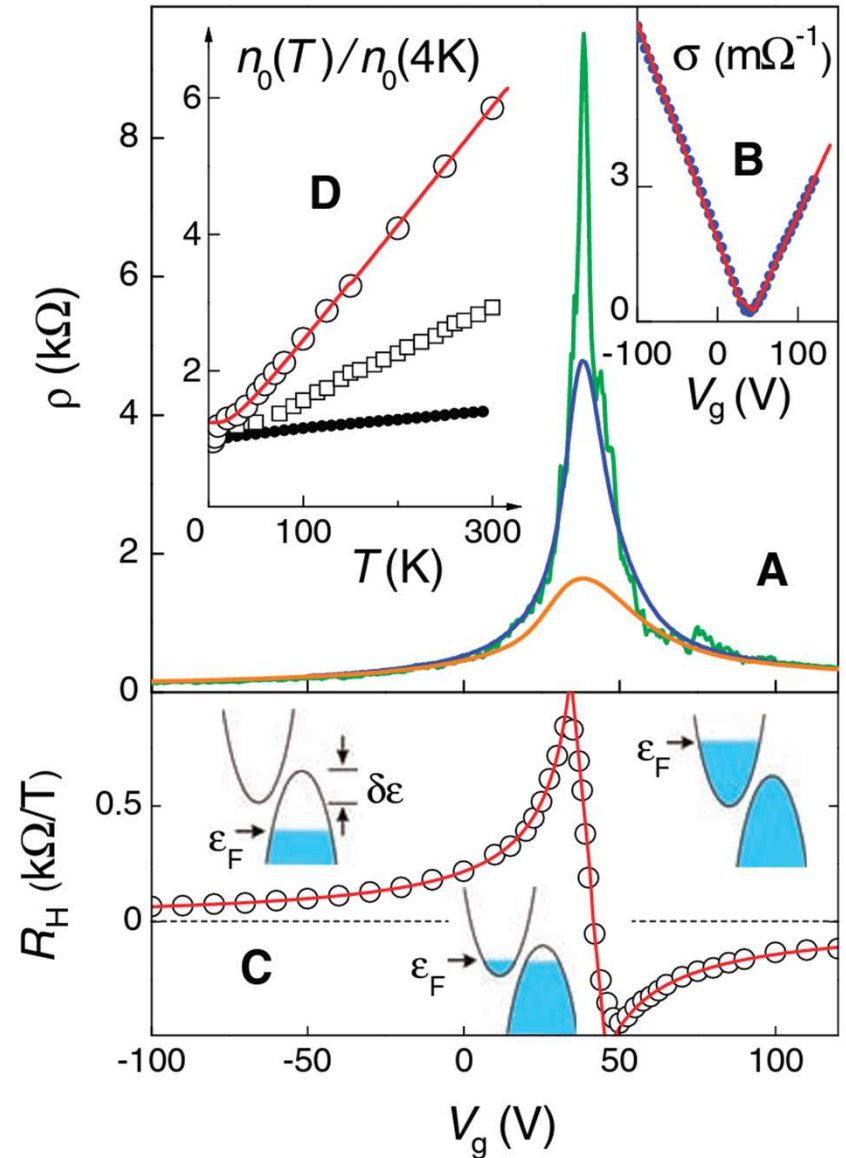
Bloch oscillations

- These oscillations are known as Bloch oscillations.

- The electron position oscillates between 0 and x = $-2x_0$, where $x_0 = 2t/eE$.

- In the absence of scattering no net macroscopic current can flow.

- The oscillations are due to the fact that with increasing k, the electron moves up in the band, where ist effective mass increases. Therefore the electrons acceleration decreases over time.

- The effective mass $m^* \to \infty$ and then flips sign. This is the origin of the Bloch oscillations, as the electron moves up and down the band E(k) over time.

- → A substance which contains free band electrons is an insulator!
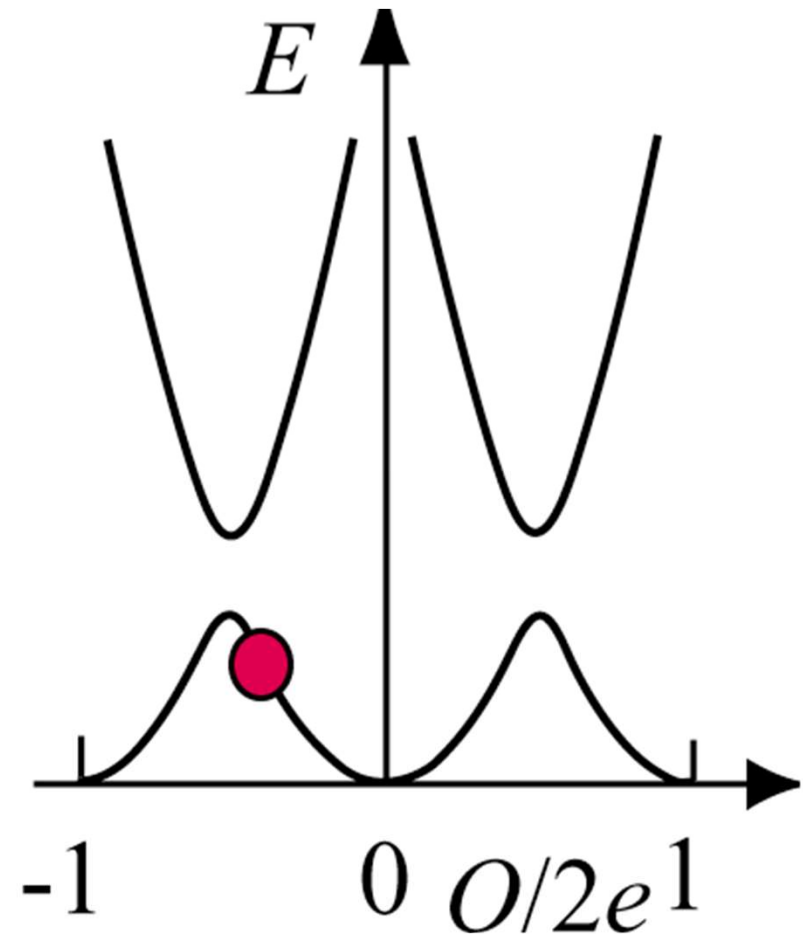
Drude theory – three assumptions

1. Electrons have an average scattering time τ. The probability of scattering within a time-interval dt is dt/τ.

2. After each scattering event the electron returns to a momentum p=0.

3. Between scattering events, the electrons are accelerated by applied electric and magnetic fields, E and B, and exhibit the Lorentz force – $F = -e(E + v \times B)$.

Scatter event

Free streaming

F

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Derivation of Drude formalism

- Consider an electron that at time t has a momentum p.

- At time t+dt it will, with probability dt/τ, scatter to p=0, and with probability (1-dt/τ) it will not scatter.

- If it does not scatter, it can accelerate based on an applied force F, with the usual equation of motion:

$$\vec{F} = \frac{d\vec{p}}{dt} \qquad\qquad \vec{p}(t+dt) = \vec{p}(t) + \vec{F}dt$$

- Combining these two terms, and weighting them with the probabilities to give the average:

$$\langle \vec{p}(t+dt) \rangle = \left(1 - \frac{dt}{\tau}\right)\left(\vec{p}(t) + \vec{F}dt\right) + \frac{dt}{\tau}0 = \vec{p}(t) + \vec{F}dt - \frac{\vec{p}(t)}{\tau}dt + O(dt^2)$$

- In steady state (to first order in dt):

- With F=0 current decays to zero:

$$\frac{d\vec{p}(t)}{dt} = \vec{F} - \frac{\vec{p}(t)}{\tau} \qquad\qquad \vec{p}(t) = \vec{p}(0)e^{-t/\tau}$$

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Drude model in electric field E

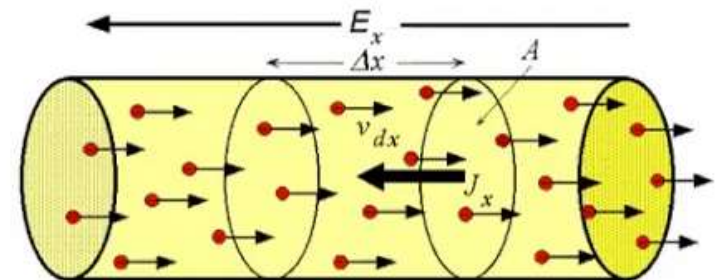- In the presence of an electric field E (but no magnetic field B), we have:

$$\frac{d\vec{p}(t)}{dt} = -e\vec{E} - \frac{\vec{p}(t)}{\tau}$$

- In the steady state we then get dp/dt=0 (m is mass and v is velocity):

$$\frac{\vec{p}(t)}{\tau} = -e\vec{E} \qquad \vec{p}(t) = m\vec{v}(t) = -e\tau\vec{E}$$

- If we have a density of electrons n=N/V (N is total number of electrons and V is volume) and each electron moves with an average velocity of v, then the total current density j is:

$$\vec{j} = -en\vec{v} = \frac{ne^2\tau}{m}\vec{E}$$

Drude model in electric field E

- We can now define the conductivity σ, of a metal by j= σ E, so that:

$$\sigma = \frac{ne^2\tau}{m}$$

- We can similarly define the resisitiviy ρ, so that E= ρj:

$$\rho = \frac{m}{ne^2\tau}$$

- The mean free path of the electron is then:

$$l_{mfp} = v\tau$$

- Electron mobility characterizes how quickly an electron can move through a metal, while scattering events are pulling it back. The higher the mobility, the purer the material:

$$\mu = v/E = e\tau/m = \sigma/en$$

Drude model in a magnetic field

- In the presence of an electric field E and magnetic field B, we have:

$$\frac{d\vec{p}(t)}{dt} = -e(\vec{E} + \vec{v} \times \vec{B}) - \frac{\vec{p}(t)}{\tau}$$

- In the steady state we then get dp/dt=0 (m is mass and v is velocity):

$$\frac{\vec{p}(t)}{\tau} = -e(\vec{E} + \vec{v} \times \vec{B}) \qquad\qquad \vec{E} = -\frac{\vec{p}(t)}{e\tau} - \vec{v} \times \vec{B}$$

- Using j=-nev:

$$\vec{E} = \frac{m\vec{j}(t)}{ne^2\tau} + \frac{1}{ne}\vec{j} \times \vec{B}$$

- So ρ is now a matrix that relates E and j:

$$\vec{E} = \rho\vec{j}$$

Drude model in a magnetic field

- If the magnetic field is oriented along the z-direction we get:

$$\rho = \begin{pmatrix} \rho_{xx} & \rho_{xy} & \rho_{xz} \\ \rho_{yx} & \rho_{yy} & \rho_{yz} \\ \rho_{zx} & \rho_{zy} & \rho_{zz} \end{pmatrix} = \begin{pmatrix} \dfrac{m}{ne^2\tau} & \dfrac{B}{ne} & 0 \\ \dfrac{B}{ne} & \dfrac{m}{ne^2\tau} & 0 \\ 0 & 0 & \dfrac{m}{ne^2\tau} \end{pmatrix}$$

- The off-diagonal term in the resisitivity are known as Hall resistivity, and correspond to the formation of a voltage perpendicular to the current and to the applied magnetic field:

Hall effect circuit:
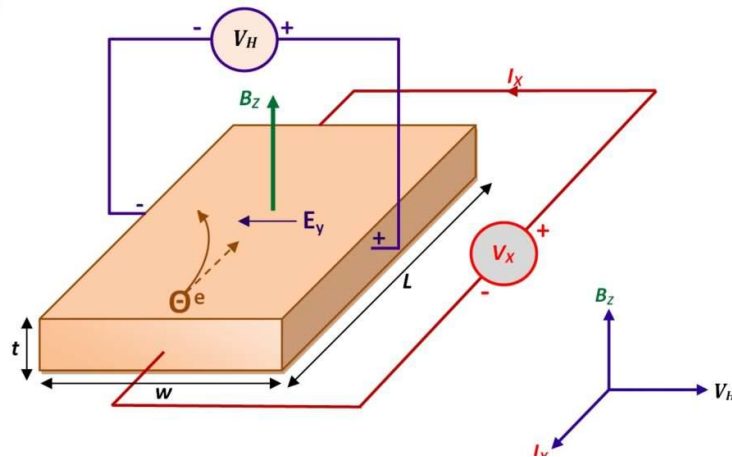
Hall effect measurement:
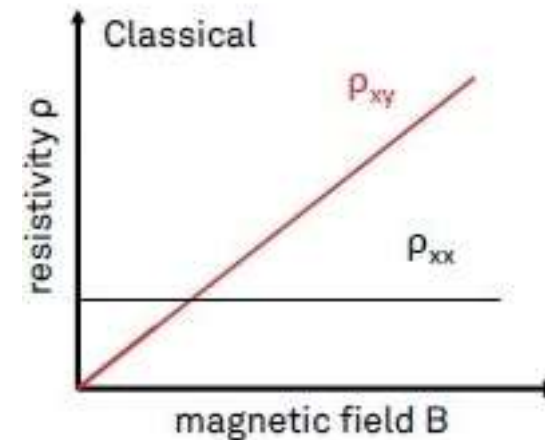
Drude model in a magnetic field

Hall coefficient materials:

- We define the Hall coefficient as:

$$R_H = \frac{\rho_{xy}}{B} = -\frac{1}{ne}$$

Material	$\dfrac{1}{-e\,R_H\,n_{atomic}}$	Valence
Li	.8	1
Na	1.2	1
K	1.1	1
Cu	1.5	1
Be	-0.2*	2
Mg	-0.4	2
Ca	1.5	2

- In Drude theory this allows us to determine the density of electrons in metals n – or by knowing the density of the elctrons in the matal, we could use this effect to probe magnetic fields (Hall probe):

- If we consider this for many metals, it is not difficult to estimate the number of the electrons, and see whether this result is reasonable.

Drude model in electric field E, with band-structure

- We can now define the conductivity σ, of a metal by j= σ E, so that:

$$\sigma = \frac{ne^2\tau}{m^*}$$

- We can similarly define the resisitiviy ρ, so that E= ρj:

$$\rho = \frac{m^*}{ne^2\tau}$$

- For a typical metal we have:

$$\rho \sim 1 - 10 \ \mu\Omega cm$$

$$n \sim 10^{23} \ cm^{-3}$$

$$\tau \sim 1 - 10 \ fs$$
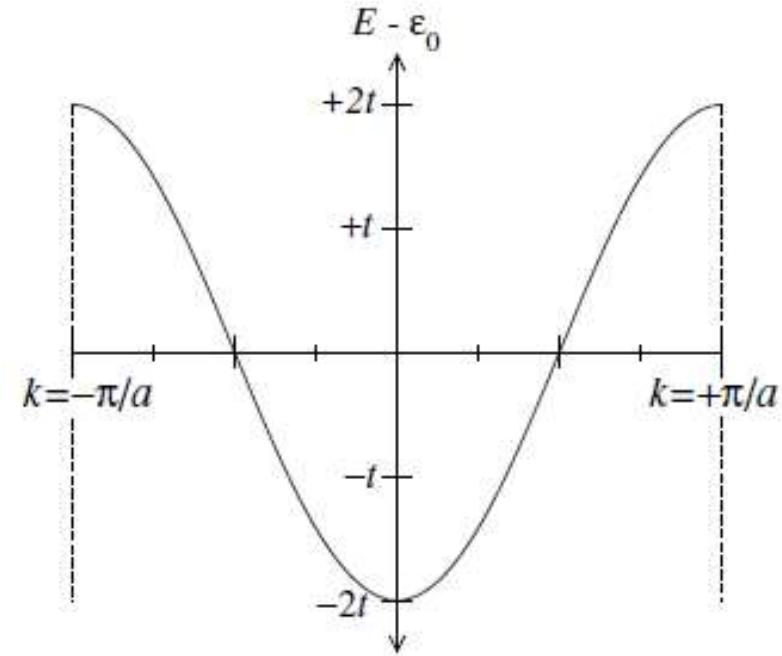
$$E = \epsilon_0 - 2t\cos(ka)$$

$$m^* = \frac{\hbar^2}{2ta^2} \frac{1}{\cos(ka)}$$

Shortcomings of the Drude formulas

- At this point of the calculation, Drude made two assumptions now known to be errors.

- 1. He used the classical result for the specific heat capacity of the conduction electrons. This overestimates the electronic contribution to the specific heat capacity by a factor of roughly 100.

$$c_v = \frac{3}{2} n k_{\mathrm{B}}$$

- 2. Drude used the classical mean square velocity for electrons. This underestimates the energy of the electrons by a factor of roughly 100.

$$\frac{1}{2} m v^2 = \frac{3}{2} k_{\mathrm{B}} T$$

- Thermal conductivity - The cancellation of these two errors results in a good approximation to the conductivity of metals.

- Thermopower - the typical thermopowers at room temperature are 100 times smaller than experimentally found of the order of micro-Volts.

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Fermi-Dirac distribution + Boltzmann transport

- The Fermi energy - at T=0 all energy levels are filled up to this energy:

$$E_F(T = 0, V, N) = \frac{\hbar^2}{2m}\left(3\pi^2 \frac{N}{V}\right)^{2/3}$$

- We can define the Fermi velocity corresponding to the velocity of the highest filled level:

$$v_F = \frac{p_F}{m}$$

- When an E-field is applied, the Fermi surface is displaced by a small amount:

$$\frac{e\tau_m \mathcal{E}_x}{\hbar}$$

- The average velocity is now defined by the Fermi velocity:

$$< v^2 > = v_F^2 = \frac{2E_F}{m^*}$$
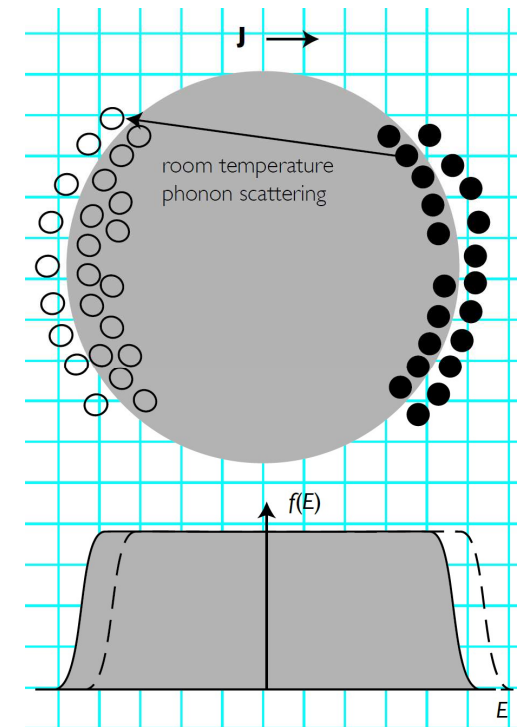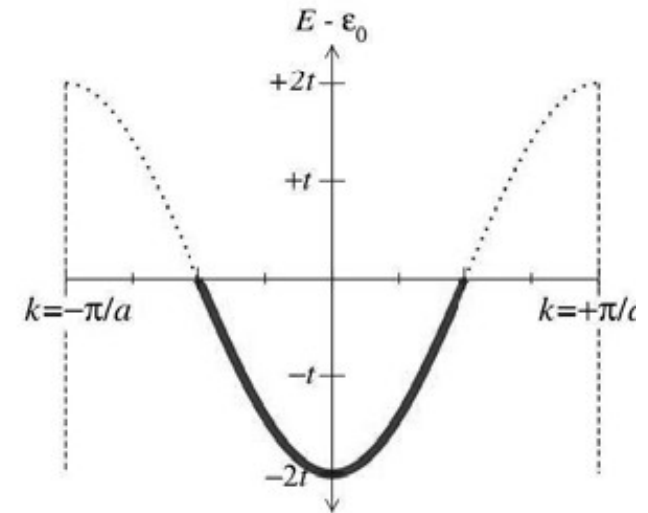
2-terminal and 4-terminal measurements

- 4-terminal measurement schemes allow to eliminate unwanted contact resistance.

- Current injection and voltage measurement contacts are separated.

- Current flowing through Voltmeter contacts are negligible (orders of magnitude lower).

Typical gated 4-terminal graphene hall bar device:
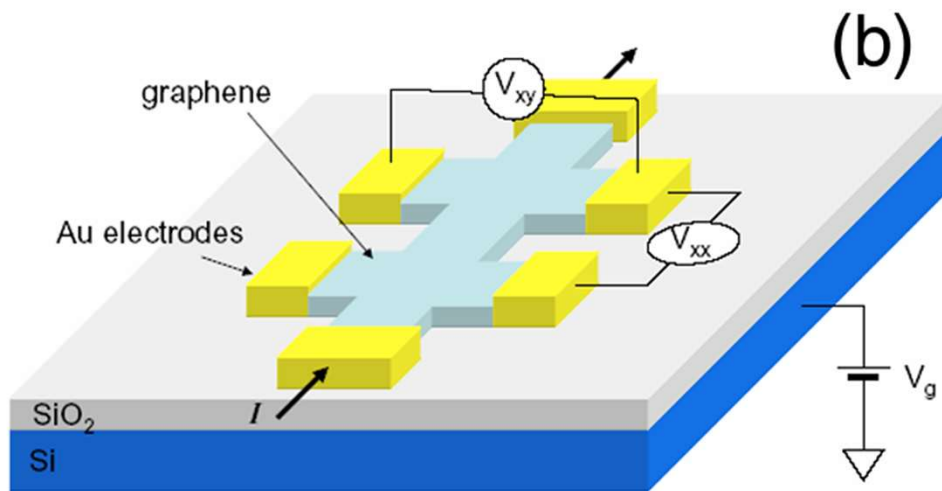
Longitudinal resistance: $R_{xx} = V_{xx}/I$

Hall resistance: $R_{xy} = V_{xy}/I$

2 terminal measurement:

4 terminal measurement:

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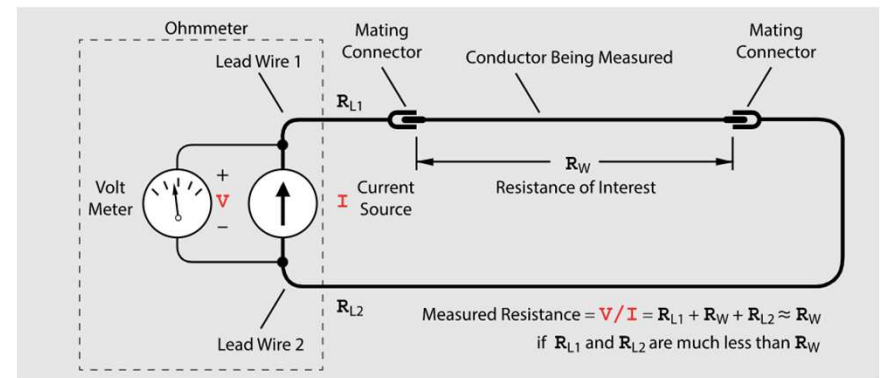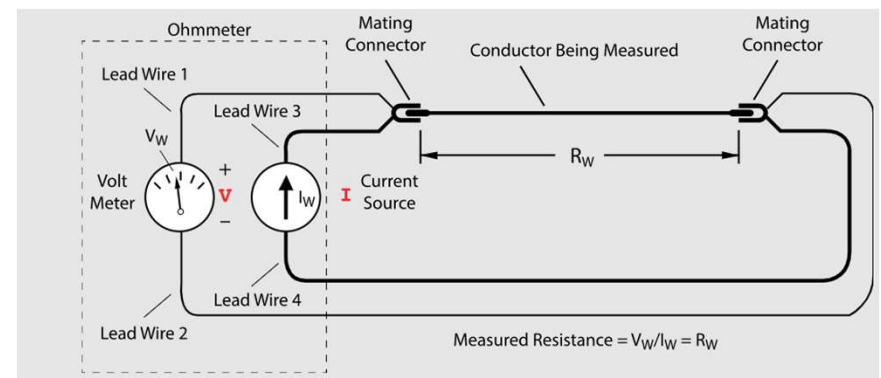
Electric field effect

- The field effect is the modulation of the electrical conductivity of a material by the application of an external electric field.

Typical gated 4-terminal graphene hall bar device:
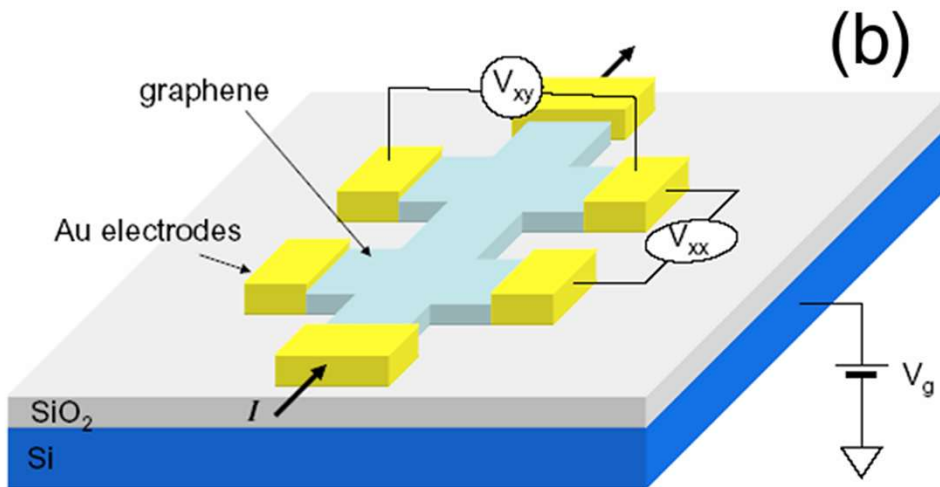
Field effect transistor (FET):
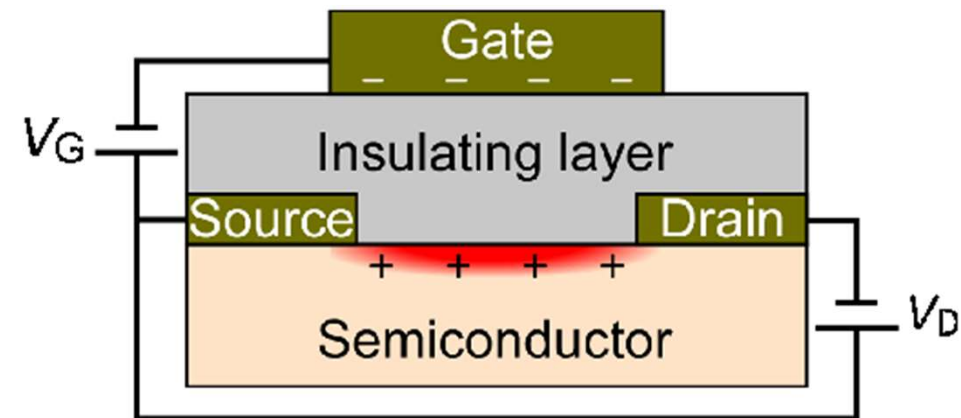
Gate capacitance : $C_g = \varepsilon_r \varepsilon_0 A/d$

Applied gate voltage: V_g

Carrier density: $n = C_g * V_g /e = 115aF/\mu m^2 * Vg$

Electric field effect in graphene

- The field effect is the modulation of the electrical conductivity of a material by the application of an external electric field.

Typical gated 4-terminal graphene hall bar device:

R$_{xx}$ vs. V$_g$ measurement:

Gate capacitance : $C_g = \varepsilon_r\varepsilon_0 A/d$

Applied gate voltage: V_g

Carrier density: $n = C_g * V_g /e = 115 aF/\mu m^2 * Vg$

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Hall effect measurements and carrier density

Hall effect:

R_{xx} vs. Hall vs. V_g measurements:

Lorentz force is balanced by electric force: $e(v \times B) = eE$

Current: $I = neAv$ (n – carrier density, A - area, v – drift velocity)

Hall voltage: $V_H = Ew = IB/net$

Hall resistance: $R_{xy} = Ew = IB/net$ (t = 1 in 2D)

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Hall effect measurements and carrier density

Hall effect:

R_{xx} vs. Hall vs. V_g measurements:

Lorentz force is balanced by electric force: $e(v \times B) = eE$

Current: $I = neAv$ (n – carrier density, A - area, v – drift velocity)

Hall voltage: $V_H = Ew = IB/net$

Hall resistance: $R_{xy} = Ew = IB/net$ (t = 1 in 2D)

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Extraction of device mobility and mean free path

Electron mass (cyclotron resonance):
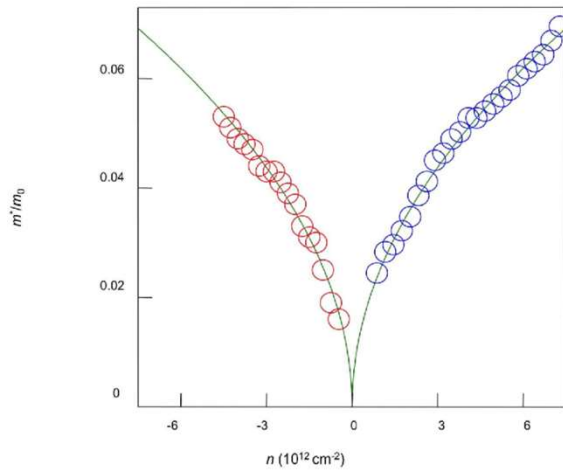
Mean free path:

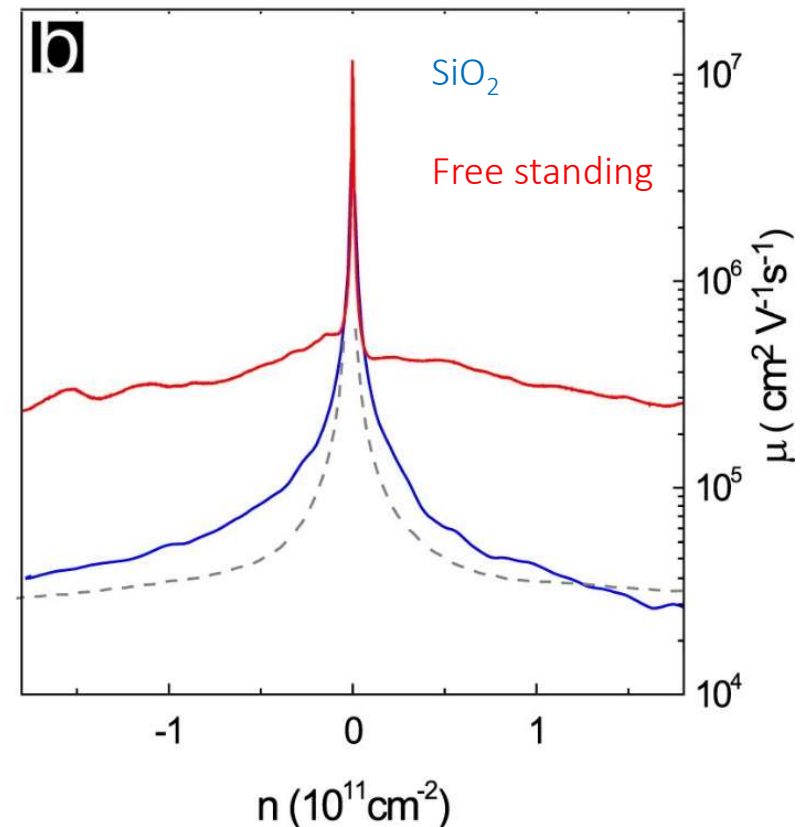Free standing and hBN encapsulated graphene mean free path exceeds $l_{mfp} > 100\ \mu m$
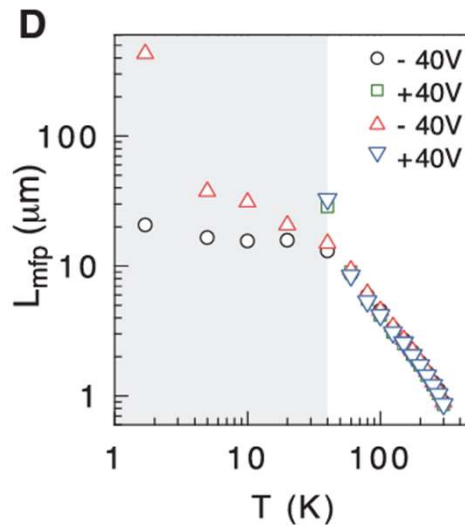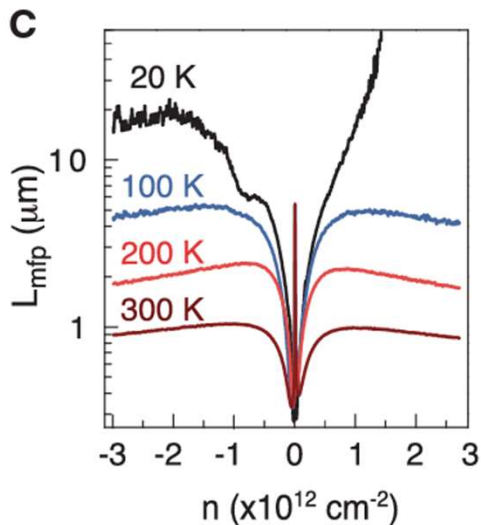
Mobility vs. n measurements:

Graphene on SiO_2 mobility exceeds >10.000 cm²/Vs

Free standing graphene mobility exceeds > 100.000 cm²/Vs

Free standing and hBN encapsulated graphene mobility at low temperatures exceeds > 1.000.000 cm²/Vs

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Different scattering processes and Matthiessen's rule

In a real solid, there are a variety of sources for electronic scattering, most prominently:

- collisions with electrons

- absorption and emission of phonons

- impurities, defects etc.

One usually assumes that the associated electronic scattering rates are additive (Matthiessen's rule): Implicit is the assumption that all scattering processes are independent and that τ_j is not a function of k.

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2} + \frac{1}{\tau_3} + etc. \qquad \rho = \rho_1 + \rho_2 + \rho_3 + etc.$$

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Different scattering processes and Matthiessen's rule

- <u>Impurity Scattering ρ_0(T=0)</u>

  const.

  - Charged Impurities
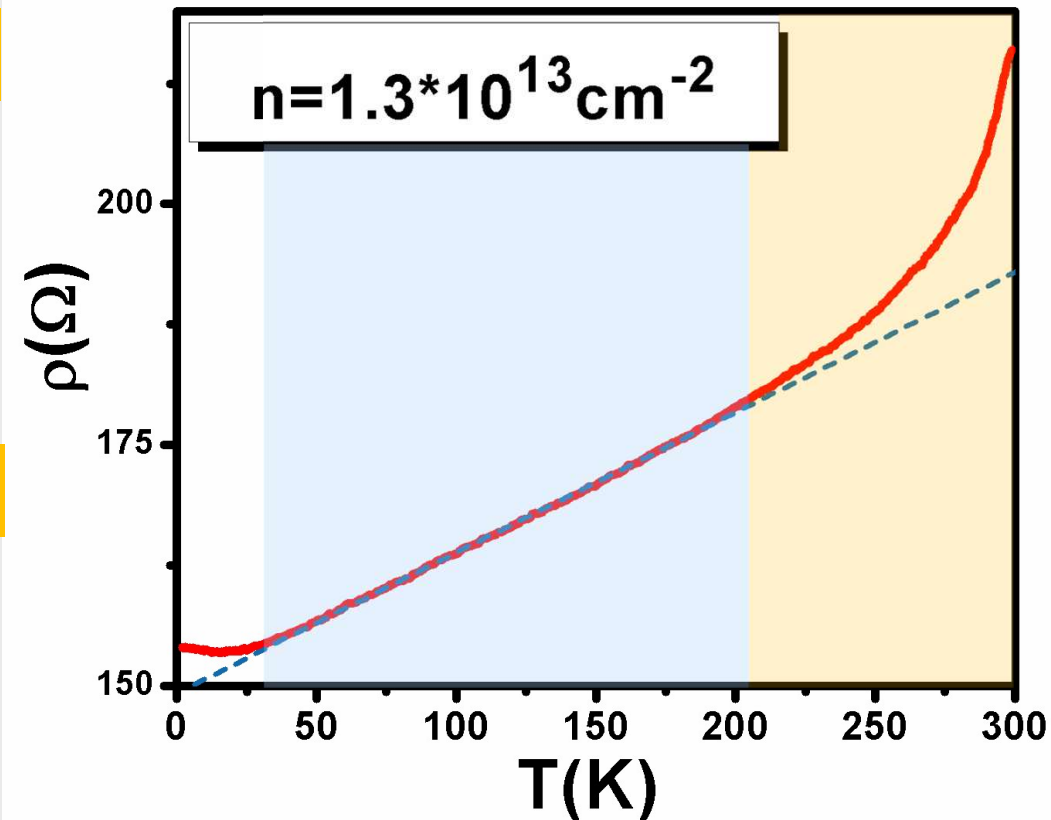
  - Lattice defects

  - Substrate etc.

- <u>Substrate ρ_r(n,T)</u>
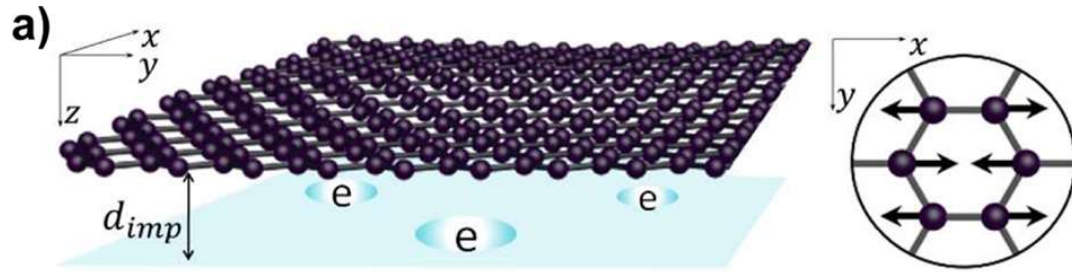
  ~ exp(T)

  - Polar Optical Phonons

  - Trapped Charges

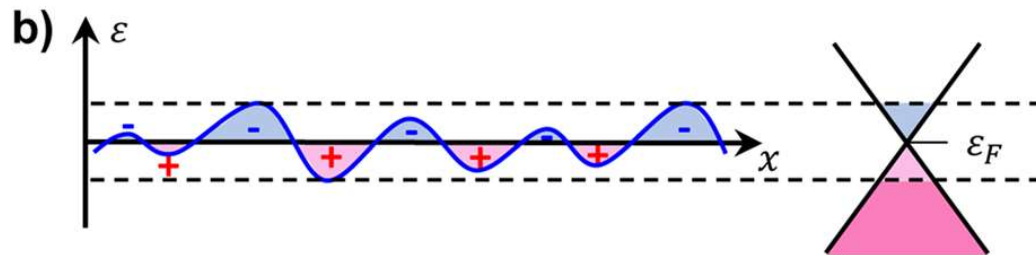- <u>Intrinsic Graphene Phonons ρ_A(T)</u>

  ~ βT

$n = 1.3 \times 10^{13} cm^{-2}$

$\rho(\Omega)$

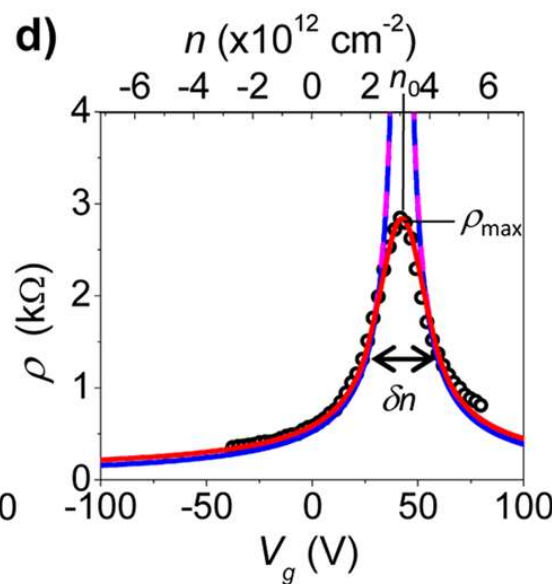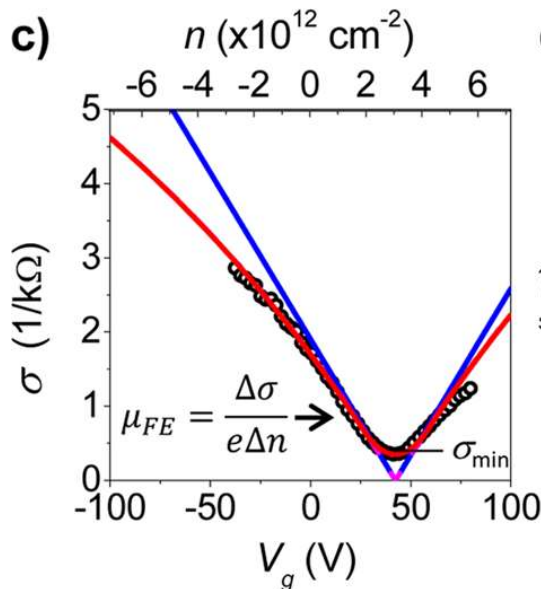T(K)

$$\rho = \rho_1 + \rho_2 + \rho_3 + etc.$$

What limits mobility in graphene?

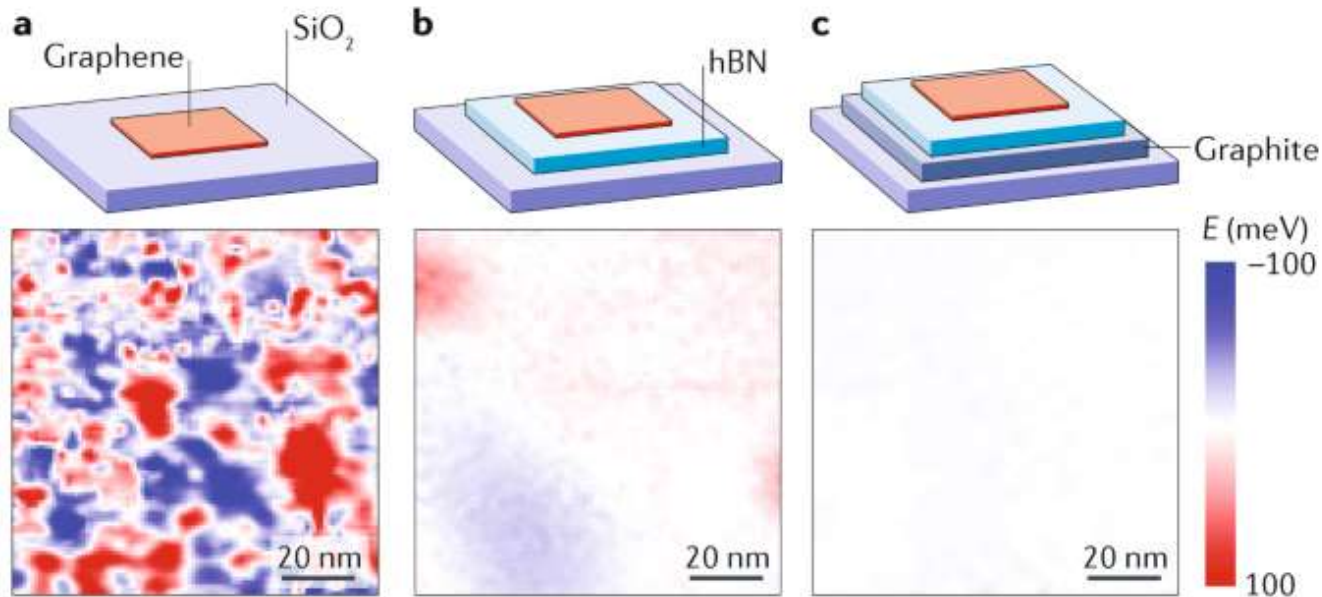- Impurity and phonon scattering.

- Potential variations broaden the Fermi energy – puddles.

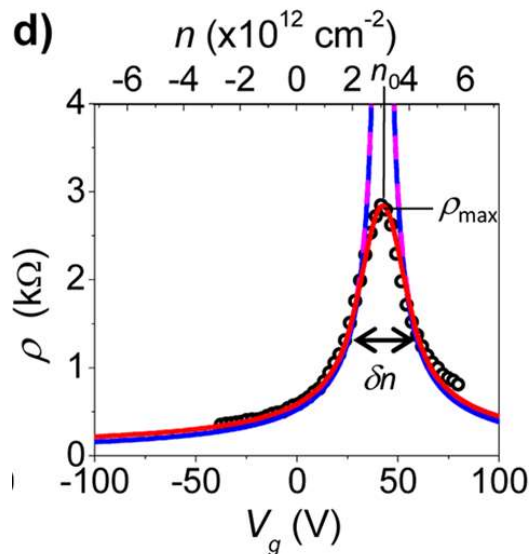- Results in increased resistivity and decreased mobility.
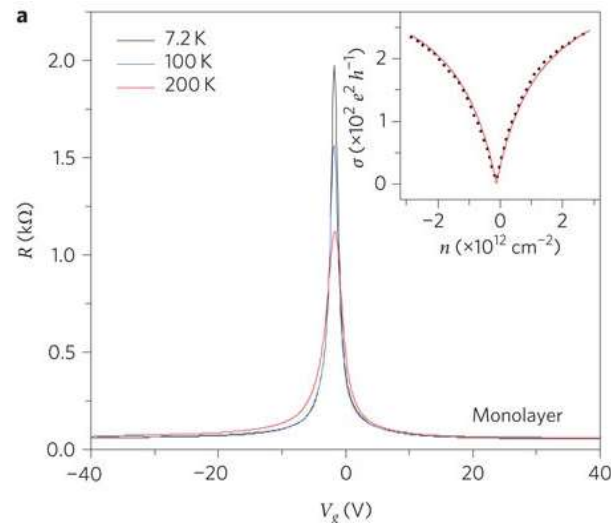
- Results in broadening of the Dirac point.

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Different substrates for graphene

Potential variations on different substrates (STM measurements):

SiO₂ :

hBN:

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Graphene/hBN - record mobility at room temperature